A comparison of Eulerian and Lagrangian transport and non-linear reaction algorithms

David A. Benson

Hydrological Science and Engineering, Colorado School of Mines, Golden, CO, 80401, USA. (dbenson@mines.edu)

Tomás Aquino and Diogo Bolster

Civil and Environmental Engineering, University of Notre Dame, Notre Dame, IN, 46556, USA. (tomas.c.aquino@gmail.com, dbolster@nd.edu)

Nicholas Engdahl

Civil and Environmental Engineering, Washington State University, Pullman WA 99164, USA. (nick.engdahl@wsu.edu)

Christopher V. Henri and Daniel Fernández-García

Department of Geotechnical Engineering and Geosciences, Universitat Politècnica de Catalunya, Barcelona, Spain (christopher.henri@upc.edu, daniel.fernandez.g@upc.edu)

Abstract

When laboratory-measured chemical reaction rates are used in simulations at the field-scale, the models typically overpredict the apparent reaction rates. The discrepancy is primarily due to poorer mixing of chemically distinct waters at the larger scale. As a result, realistic field-scale predictions require accurate simulation of the degree of mixing between fluids. The Lagrangian particle-tracking (PT) method is a now-standard way to simulate the transport of conservative or sorbing solutes. The method's main advantage is the absence of numerical dispersion (and its artificial mixing) when simulating advection. New algorithms allow particles of different species to interact in nonlinear (e.g., bimolecular) reactions. Therefore, the PT methods hold a promise of more accurate field-scale simulation of reactive transport because they eliminate the masking effects of spurious mixing due to advection errors inherent in grid-based methods. A hypothetical field-scale reaction scenario is constructed and run in PT and Eulerian (finite-volume/finite-difference)

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30 simulators. Grid-based advection schemes considered here include 1st- to
 31 3rd-order spatially accurate total-variation-diminishing flux-limiting schemes,
 32 both of which are widely used in current transport/reaction codes. A homo-
 33 geneous velocity field in which the Courant number is everywhere unity, so
 34 that the chosen Eulerian methods incur no error when simulating advection,
 35 shows that both the Eulerian and PT methods can achieve convergence in
 36 the L^1 (integrated concentration) norm, but neither shows stricter pointwise
 37 convergence. In this specific case with a constant dispersion coefficient and
 38 bimolecular reaction $A + B \rightarrow P$, the correct total amount of product is
 39 $0.221M_{A0}$, where M_{A0} is the original mass of reactant A . When the Courant
 40 number drops, the grid-based simulations can show remarkable errors due
 41 to spurious over- and under-mixing. In a heterogeneous velocity field (keep-
 42 ing the same constant and isotropic dispersion), the PT simulations show
 43 an increased reaction total from $0.221M_{A0}$ to $0.372M_{A0}$ due to fluid deform-
 44 ation, while the 1st-order Eulerian simulations using $\approx 10^6$ cells (with a
 45 classical grid Peclet number $\Delta x/\alpha_L$ of 10) have total product of $0.53M_{A0}$,
 46 or approximately twice as much additional reaction due to advection error.
 47 The 3rd-order TVD algorithm fares better, with total product of $0.394M_{A0}$,
 48 or about 1.14 times the increased reaction total. A very strict requirement
 49 on grid Peclet numbers for Eulerian simulations will be required for real-
 50 istic reactions because of their nonlinear nature. We analytically estimate
 51 the magnitude of the effect for the end-member cases of very fast and very
 52 slow reactions and show that in either case, the mass produced is propor-
 53 tional to $1/\sqrt{Pe}$, where Pe is the Peclet number. Therefore, extra mass is
 54 produced according to $\sqrt{D}$, where the dispersion includes any numerical dis-
 55 persion error. We test two PT methods, one that kills particles upon reaction
 56 and another that decrements a particle's mass. For the bimolecular reaction
 57 studied here, the computational demands of the particle-killing methods are
 58 much smaller than, and the particle-number-preserving algorithm are on par
 59 with, the fastest Eulerian methods.

60 *Keywords:* Particle tracking, Chemical reaction, Numerical dispersion,
 61 Nonlinear amplification

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63 1. Introduction

64 Chemical reactions occur ubiquitously at a multitude of scales in hy-
65 drologic and hydrogeologic environments. A common observation is that
66 reactions progress at lower rates at larger scales. Imperfect mixing is an im-
67 portant contributor to the various processes that contribute to the scaling
68 of reaction rates [38]. Mixing is the fundamental process that brings reac-
69 tants into contact with one another and accurate simulations of mixing are
70 key to correctly predicting reactions [36, 37, 47]. Recent studies of mixing
71 in heterogeneous hydrologic systems demonstrate that complex rate changes
72 can emerge, and simple assumptions about upscaled rates have been shown
73 to lack realism [62, 61, 63, 24, 19, 21]. While most of these studies have
74 focused on mixing of conservative solutes (and/or instantaneous reactions),
75 the results have broad implications for all mixing-driven and rate-limited re-
76 actions [36, 37, 24]. Many numerical and experimental studies have shown
77 that governing equations or numerical models that do not adequately simu-
78 late mixing will also suffer error in ultimately predicting chemical reactions
79 [47, 33, 32, 39, 87, 80].

80 Many numerical approaches exist for modeling transport of *non-reactive*
81 solutes through heterogeneous porous media. A recent paper [20] focuses
82 on five currently popular schemes. Broadly speaking, these authors con-
83 clude that, because of spurious numerical dispersion, the grid-based Eulerian
84 schemes overestimate dilution/mixing, while Lagrangian approaches, includ-
85 ing both random walk particle tracking (RWPT) and Smoothed Particle
86 Hydrodynamics (SPH) approaches, given a sufficiently resolved and smooth
87 velocity field, are free of numerical dispersion. The authors report that
88 SPH is relatively computationally demanding and does not readily han-
89 dle anisotropic dispersion [3]. Furthermore, the discrete nature of RWPT
90 can lead to discontinuous concentrations, although a variety of novel algo-
91 rithms have evolved in recent years to remove such spurious fluctuations
92 [44, 78]. While the errors associated with these methods for non-reactive
93 solutes are well known, the complicating factor of nonlinear reactions (which
94 may amplify these errors), has been recognized but only qualitatively re-
95 ported [27]. In this paper, we take a more quantitative look at the difference
96 between several widely-used Eulerian (grid-based) and Lagrangian reactive
97 transport algorithms. For reactive transport, grid-based methods—including
98 finite-element, finite-volume, and finite-difference—continue to largely be the
99 norm, although there have been significant recent advances in Lagrangian ap-

100 proaches [11, 94, 95, 42, 18]. Here we will focus on classical finite-volume/finite-
 101 difference Eulerian methods and the purely Lagrangian PT advection-dispersion-
 102 reaction schemes.

103 Regarding the widespread use of grid-based codes, we highlight a few ap-
 104 proaches and recent studies. More detailed descriptions are given by Steefel
 105 et al. [91]. While different in their underlying numerical method (finite-
 106 volume, finite-element, integrated finite-difference, etc.), PFLOTRAN [69],
 107 TOUGHREACT [106], HYDROGEOCHEM [107], FEHM [110] and NUFT
 108 [74] use a 1st-order spatially accurate ($\mathcal{O}(\Delta x)$) upwind advection scheme (al-
 109 though NUFT allows an iterative scheme to improve accuracy [89]). The
 110 TOUGH and TOUGHREACT family of codes is routinely used to simulate
 111 CO₂ injection and reaction [e.g., 75, 2]. Hammond and Lichtner [48] use
 112 PFLOTRAN to simulate Uranium transport and speciation on the several-
 113 kilometer scale. Navarre-Sitchler et al. [73] use PFLOTRAN, and Keating
 114 et al. [56] use FEHM to simulate the release of metals and Uranium, respec-
 115 tively, from CO₂-acidified aquifers. None of these studies specify values for
 116 dispersivity or diffusivity, so it is likely that the authors rely on numerical
 117 error, which is a function of discretization and local velocity, to emulate real
 118 dispersion. Regardless of which code is selected, the effects of realistic disper-
 119 sion on reaction are often ignored and the fastest and least accurate transport
 120 algorithm is used [55]. Steefel [90] and White and Oostrom [104] recognize
 121 the importance of spurious dispersion and mixing (particularly transverse to
 122 flow) on reactions and implement a 2nd-order accurate variant of Leonard’s
 123 [65, 31] 3rd-order total-variation-diminishing (TVD) scheme. However, these
 124 codes use a 1st-order upwind scheme when the simultaneous implicit reaction
 125 and transport option is chosen. Finally, reaction algorithms (i.e., PHT3D
 126 [6, 82]) based on transport in the MT3DMS code [109] may choose among
 127 several advection schemes including 1st and 3rd-order ($\mathcal{O}(\Delta x^3)$) TVD algo-
 128 rithms. One may also choose a mixed Lagrangian/Eulerian scheme in which
 129 advection is performed by particles and dispersion/reaction are performed
 130 on a grid after mapping particle masses back into gridded concentrations
 131 similar to the scheme by Tompson and Dougherty [97]. It is notable that
 132 Prommer et al. [82] compare the strictly Eulerian methods to the hybrid La-
 133 grangian/Eulerian advection/dispersion scheme in MT3DMS and find that
 134 this Lagrangian/Eulerian scheme is superior to the 3rd-order Eulerian scheme
 135 in MT3DMS. Those authors recommend the use of particle-tracking for ad-
 136 vection as a general rule, and a similar conclusion was reached by Herrera
 137 et al. [51] with their SPH model.

138 While more accurate (higher order) grid-based advection schemes have
 139 been developed (see, e.g., [98]), including the weighted essentially non-oscillatory
 140 (WENO) and advection-diffusion-reaction (ADER) families of methods, they
 141 have not been widely adopted in studies of aquifer geochemical reactions.
 142 One possible reason is the relatively complex nature of these methods, which
 143 reconstruct (interpolate) the profiles of the advected quantities using n^{th} -
 144 order polynomials. The polynomials can be analytically advected with $(n +$
 145 $1)^{th}$ -order accuracy in 1- d , but the construction process is somewhat compli-
 146 cated and a matter of choice. Moving the methods to multi-dimensions is also
 147 tricky, because maintaining high-order accuracy requires an algorithm that
 148 looks in all directions (not simply a combination of 1-D sweeps) [98, 68, 67].
 149 The higher-order polynomial reconstruction can be extended to arbitrary-
 150 order polynomial basis functions in finite-element implementations [28, 70, 4]
 151 with analogous results to the WENO finite volume algorithms [e.g., 59]. A
 152 further complication to many higher-order methods is the potential for neg-
 153 ative concentration oscillations and/or mass balance errors when spurious
 154 negative masses are quashed. Another method used to increase accuracy
 155 uses adaptive grid refinement to decrease grid size in areas of large concen-
 156 tration gradients (e.g., [105, 30, 72]). These and other efforts to improve
 157 the efficiency, accuracy, and parallel implementation of Eulerian methods for
 158 advective flux continue [e.g., 57, 53]. But the situation remains that 1st-
 159 through 3rd- order accurate, directionally split, upstream weighting is the
 160 prevailing solution method in aquifer transport and reaction studies; there-
 161 fore, we investigate these schemes.

162 One issue with the various Eulerian implementations in that artificial mix-
 163 ing is exacerbated by low Courant numbers (low velocities). As a result, the
 164 artificial dispersion in the transverse, low-velocity direction can be as great as
 165 either the spurious or real dispersion in the longitudinal direction. This spu-
 166 rious transverse mixing is responsible for overestimating reactions for many
 167 boundary value problems [27]. To address this problem, *Cirpka et al.* [27]
 168 developed a gridding-along-streamlines approach. In 2- d the streamlines can
 169 be solved analytically, but in 3- d , particles must be used to trace streamlines
 170 or streamtubes in the areas of interest. The domain is re-discretized along
 171 streamlines so that advective fluxes do not cross cells in the transverse direc-
 172 tion. Solving dispersion and reaction is then either done on the Eulerian grid,
 173 or the particles used to trace streamlines can be treated via SPH kernels, and
 174 the problem is reduced to minimizing error in the longitudinal direction. In
 175 complex flows, however, excess longitudinal dispersion can deplete reactants

176 that are rotated and placed into lateral contact, so depending on the configu-
177 ration of reactants, longitudinal errors in one location can influence reaction
178 errors in another (see, e.g., [35, 64, 43]).

179 The various issues with purely Eulerian and mixed Lagrangian/Eulerian
180 methods motivated the development of purely Lagrangian transport and re-
181 action algorithms. The Lagrangian particle-tracking (PT) method for sim-
182 ulating *passive scalar* transport has several features that have justified their
183 continued development and implementation [60, 85, 9]. These include 1)
184 independence of the simulation speed from the underlying velocity (and hy-
185 draulic conductivity) discretization, 2) computationally simple representa-
186 tion of temporal [12, 84] and/or spatial nonlocality [108], and 3) the lack of
187 artificial mixing and negative concentrations. The PT method was extended
188 to simulate chemical reactions by calculating the physically-based probabil-
189 ity of particle collision and subsequent conditional probability of reaction
190 [11, 18]. In this framework, the chemical reactions occur without an explicit
191 calculation of concentrations, thus removing the need for interpolation onto
192 an Eulerian grid or using SPH kernels for dispersion and reaction calculation
193 [e.g. 97, 81, 3], which can reintroduce numerical dispersion and other inter-
194 polation errors. Instead, the proximity of particles in the flow field dictate
195 the occurrence of reactions. This point highlights a potential advantage of
196 the PT method over Eulerian reactive transport models because imperfect
197 mixing and chemical spatial heterogeneity are represented by particle num-
198 bers and proximities at all scales [76, 77], whereas perfect mixing is assumed
199 at some scale in grid-based models. Furthermore, this PT reaction algorithm
200 can be derived and applied to experimental data without the need for em-
201 pirical parameters such as effective reaction radii or rates, providing a direct
202 link to the physical mechanics of chemical reactions [39].

203 One of the goals of the work on PT methods is to provide a theoret-
204 ical basis for upscaling effective reaction rates in heterogeneous flow fields
205 within larger-scale Eulerian codes, based on subgrid fluid deformation met-
206 rics [35, 43]. When an incompressible fluid moves through porous media, the
207 velocity field influences reactions by deforming a hypothetical fluid parcel.
208 Gradients in the velocity field will cause stretching of the fluid parcel in one
209 dimension which is accompanied by compression in others. Compression can
210 bring fluids of different composition into closer proximity, facilitating mix-
211 ing and immediate (or future) reactions. In 3-D, twisting flow and eddy-like
212 whirls can significantly add to enhanced mixing by fluid deformation [5, 25].
213 Fluid deformation enhances mixing, which cannot be undone [103, 26]. This

214 mixing is poorly constrained in many grid-based models, leading to incorrect
 215 effective reaction rates. The PT reaction theory has been used to estimate the
 216 increased reaction rates that may accompany any sort of fluid deformation
 217 [43]. This work parallels similar work that examines Eulerian deformation
 218 metrics [35, 64] and the similarities may provide a connection between the
 219 Eulerian and Lagrangian methods for simulating deformation-enhanced re-
 220 actions. In other words, the PT methods provide a computationally simple
 221 way to inform larger upscaled grids about the increased reaction rates that
 222 are engendered by subgrid fluid deformations.

223 However, it remains to be shown the conditions under which the PT and
 224 Eulerian methods converge to the same solutions for a given boundary value
 225 problem (BVP). Because mixing-driven reactions can be highly non-linear,
 226 the simulated mass of the products and reactants may be highly sensitive
 227 to any transport errors. In this work we construct a few simple problems
 228 that isolate (and/or eliminate) potential sources of error to investigate the
 229 supposed similarity of the methods used to simulate a basic set of n coupled
 230 advection-diffusion-reaction equations (ADRE)

$$\frac{\partial C_i}{\partial t} = -\nabla \cdot (\mathbf{v}C_i - \mathbf{D}\nabla C_i) + R(C_1, C_2, \dots, C_n); \quad i = 1, \dots, n, \quad (1)$$

231 where C_i is the concentration of species i , $\mathbf{v}$ is the local mean velocity vector,
 232 $\mathbf{D}$ is a dispersion tensor, and $R()$ is a reaction function of all n species.
 233 We investigate simulation of dispersion using either a constant $D_{ij} = D_m\delta_{ij}$
 234 or a velocity-dependent $D_{ij} = (|\mathbf{v}|\alpha_T + D_m)\delta_{ij} + (\alpha_L - \alpha_T)v_iv_j/|\mathbf{v}|$, where
 235 D_m is a diffusion-like constant, $\alpha_L \geq \alpha_T$ are longitudinal and transverse
 236 dispersivities, and δ_{ij} is the Kronecker delta. The reaction rate is typically
 237 dictated by the law of mass action, and non-equilibrium rates must often be
 238 estimated empirically [1].

239 In general terms, any grid-based approximation of (1) will incur several
 240 types of error. Foremost is the difficulty in representing a sharp interface
 241 with points spaced some distance away from each other in the hyperbolic
 242 (advection) portion, along with lesser amounts in the parabolic (dispersive)
 243 portion. Additional error in the reaction term arises by representing the var-
 244 ious (subgrid) concentration values for each species in a cell by single values.
 245 Less obvious are errors incurred in the approximation of the velocity vectors
 246 [10], and error from sequentially solving several components of the equation
 247 by operator splitting [98]. In any realistic heterogeneous flow field simula-
 248 tion, the various errors will have different magnitudes in different regions of

the flow domain because of different velocity magnitudes, orientations relative to a grid, and different concentration, velocity, and dispersion coefficient gradient magnitudes and orientations.

On the other hand, the discrete and potentially stochastic nature of the PT simulations means that simulation of a deterministic BVP can be numerically taxing, as an ensemble of simulations is often needed to ascertain statistics of the solutions. Moreover, the reactions have been shown to depend on the number of particles used: we specify only the positions of particles, so that the initial concentration is approximated by a sum of Dirac delta functions. The initial concentration can only be everywhere equal when the number of particles goes to infinity. Conversely, smaller numbers of particles represent greater heterogeneity in the initial concentration field (in this case, greater correlation length of concentration fluctuations [77]). This heterogeneity may increase over the duration of the simulation. Finally, it is currently necessary to solve the transport and reactions sequentially, so that error is incurred in the operator splitting. Therefore, it is unclear if the PT simulations will converge to a “correct” solution for a realistic problem, or if a small number of realizations is sufficiently representative of the ensemble mean.

Our goal is to compare various aspects of Eulerian and PT simulations of (1). To do so we set up a series of simulations with increasing complexity. The first problem considered here is simple 1- d flow aligned along an x -axis in a 2- d domain. Diffusion is spatially uniform and isotropic. Reaction is limited to a simple (albeit non-linear) irreversible bimolecular system $A + B \rightarrow P$, as this system has been widely used to analyze reactive transport behavior and has been shown to be a fundamental building block of more complex reaction chains [45, 46]. The reaction term in Eq. (1) is $R(C_A, C_B) = -k_f C_A C_B$. For ease of visualization, the product P is made immobile. In uniform flow, all of the advection algorithms used here can be made free of error, so we can isolate diffusion/reaction errors. Following this comparison of PT and Eulerian convergence, a more complex heterogeneous velocity field is used to check the magnitude of errors introduced by Eulerian approximations of the heterogeneous advective fluxes.

2. Overview of Error in Eulerian Solutions

A common approach to solving the ADRE (1) on a grid is to use operator splitting and sequentially solve the advection, diffusion, and reaction

285 terms. The many algorithms [e.g., 92, 65, 67, 15] for the hyperbolic advection
 286 portion are well-known to produce varying degrees of numerical dispersion
 287 and/or oscillation and overshoot due to the truncation of higher-order space
 288 and time derivatives in the representation of the variability of the concen-
 289 tration. We investigate the family of TVD models (including the simplest
 290 and best known first-difference upwind weighted scheme) with a forward Eu-
 291 ler time approximation on uniform space-time grids of $(\Delta x, \Delta t)$. We choose
 292 these algorithms because for a Courant number defined in any direction i by
 293 $\lambda = v_i \Delta t / \Delta x_i$ of unity, the advection term is known to be free of numerical
 294 dispersion. The Courant number is a measure of how far solute is allowed
 295 to traverse any grid block, and most grid-based solutions require $\lambda \leq 1$. In
 296 a heterogeneous flow domain, the Courant number is never uniformly unity,
 297 and higher-order algorithms that use Courant-based flux limiters are more
 298 accurate; however, numerical error is never eliminated entirely from the so-
 299 lution, and these algorithms require more computation time. The benefit is
 300 a reduction in the number of nodes required to get “equivalent” solutions
 301 to the lower-order algorithms. As well, many other schemes can be adopted
 302 to manage the error and computational cost of Eulerian methods including
 303 adaptive refinement of grids where necessary (e.g., [50]) or more accurate
 304 timestep interpolation (e.g., [93]). However, there is no consensus on the
 305 most appropriate algorithm, and solutions based on 1st-, 2nd-, and 3rd-order
 306 accuracy in space on uniform grids are common.

307 Generally speaking, the discretized diffusion operator is thought to be
 308 sufficiently error-free, relative to any advective error. On the other hand,
 309 application of the law of mass action for the reaction term assumes perfect
 310 mixing within any Eulerian block. The effect of subgrid concentration per-
 311 turbations are not resolved by the numerical method. Recent studies have
 312 focused on this effect and shown that incomplete mixing effects can be strong,
 313 leading to significantly altered reaction rates [11, 77, 76, 23, 80] compared to
 314 those predicted by the assumption of perfect mixing. The non-linear nature
 315 of the reactions can make the simple act of concentration averaging highly
 316 variable [e.g., 7, 8, 88]. Newer formulations of the reaction term can account
 317 for subgrid concentration variability by assuming both a distribution of con-
 318 centration and a subgrid mixing rate, but this method requires calibration
 319 with measured reactions at the appropriate scale (e.g., [23]). In short, the
 320 “spikier” the unknown subgrid concentration heterogeneity and the more
 321 nonlinear the reaction, the greater the averaging error that will occur.

3. Overview of Error in Lagrangian Solutions

In the PT simulations at hand, the advection of individual particles can be made essentially free from error by using Pollock’s algorithm [79]. For the explicit Euler approximation we use here, the advection error is negligible as long as the velocity field is fairly smooth [10]. The diffusion operator can be made arbitrarily accurate in the mean by using motions that solve the correct Fokker-Planck equation [60, 9, 85]. For example, if a spatially heterogeneous dispersion equation is being solved, then the motions are generated according to an Itô implementation of the nonlinear Langevin equation for Gaussian random walks ([60, 85], and see Appendix C). If post-simulation reconstruction of the concentration field is required, errors arise with variance related to the particle numbers, binning size and smoothing kernels used [e.g., 22, 78]. A similar problem to the “subgrid” concentration fluctuation is present for PT methods, in that a sufficient number of particles must be used to resolve the small-scale correlation structure of the concentration fields [39].

There are several methods for calculating the chemical reactions among the particles. Many are based on an on-off (binary) type of reaction calculation based on the hard-shell particle “radius” model [102, 41]. If two particles are located within this radius, then a reaction takes place [42, 49]. Others are based on a calculation of the probability that two particles will be collocated based on dispersion motion [101, 11]. This method is readily extended to spatially nonlocal dispersion [e.g., 16]. The co-location probability is then multiplied by the conditional probability that two co-located particles will react. This latter probability is a simple statement of the thermodynamic reaction rate [46, 54] so the particles are not forced to react (i.e., slow reactions may require multiple co-locations, while fast ones may require very few before a reaction actually occurs). In these models, no lattice is used, so the separations are real-valued and the probability of collision is not binary. This approach can be made arbitrarily accurate without the need for empirical parameters [77]. Bolster et al. [18] extend the algorithm by replacing the probability of conversion with a particle mass-fraction loss. Their algorithm gains resolution of low concentrations but has not been rigorously tested for convergence to the original particle birth-death algorithm, so we partially address this issue here. In particular, the original bimolecular algorithm of *Benson and Meerschaert* [11] converts entire reactant A and B particles into entire product P particles, so that number of $A + P$ particles remains constant in these simulations. However, the lowest possible resolved

359 concentrations are $\mathcal{O}(1/N_A)$, where N_A is the original number of A particles.
 360 *Bolster et al.* [18] convert portions of each particle’s mass during a reaction,
 361 so that low concentrations are infinitely resolvable, but: 1) numerically, a
 362 nearby P particle must be located, or 2) the product mass must be mapped
 363 to a fixed grid of concentration, given some binning procedure. Here we
 364 choose the latter with product mass mapped to the nearest square grid.

365 4. Convergence of the Diffusion/Reaction Operations

366 Because we later investigate the solutions in heterogeneous 2- d velocity
 367 fields, we first choose identical 2- d solutions with homogeneous velocity to
 368 isolate the diffusion/reaction portion of the ADRE. A series of simulations
 369 was constructed using geologically-relevant parameters for transport and in-
 370 teraction of two fluids in a 1000 m $\times$ 1000 m aquifer domain. Two fluids
 371 are placed next to each other in 15.6 m strips, separated by an initially
 372 sharp interface (Fig. 1a). The aquifer has a mean hydraulic conductivity
 373 $K = 1$ m/d, a uniform head gradient in the x -direction of 0.01, and a poros-
 374 ity of 0.3. The fluid velocity is uniform at 1/30 m/d aligned with the x -axis.
 375 The dispersion is made uniform and isotropic at 0.001 m²/d, representing
 376 an isotropic local dispersivity of 0.03 m. It is made homogeneous to allow
 377 comparisons with 1- d analytic models (Appendix B). The fluids are placed at
 378 mean concentrations of 1 M (molar), and the reaction follows the law of mass
 379 action $R(C_A, C_B) = -k_f C_A C_B$ with rate coefficient $k_f = 0.01$ (M d)⁻¹. We
 380 assume unit activity coefficients for simplicity. This rate was chosen so that
 381 a significant fraction of the reactants (on the order of 20%) will be consumed
 382 after 10,000 days of transport in the simplest case. Approximate measures
 383 of the reaction versus transport rates are given by either the advective or
 384 diffusive Damköhler numbers $Da_v = k_f C_0 / (\mathbf{v} / L)$ and $Da_D = k_f C_0 / (D / L^2)$,
 385 where L is a characteristic scale of transport. For local-scale Da , we choose
 386 $L \approx 1$ m, so for the uniform velocity case, we have $Da_v \approx 0.3$ and $Da_D \approx 10$.
 387 Neither of these numbers point to particularly slow or fast reactions relative
 388 to transport.

389 To compare the grid-based and PT codes, we should choose similar initial
 390 conditions (ICs). It has been shown that the PT codes inherently represent
 391 spatial variability in the initial condition and also as the particles diffuse and
 392 react: the spatial autocovariance decreases with increased particle number.
 393 *Paster et al.* [77] show that, for the Dirac-delta function particles that we
 394 use here, the initial particle number N_0 is related to the auto-covariance

395 structure of the initial concentrations by $N_0 = C_0^2 A_{strip} / (\sigma_C^2 l^d)$, where A_{strip}
 396 is the area over which the particles are placed, and $\sigma_C^2 l^d$ is the d -dimensional
 397 integral of the covariance function (i.e., the concentration variance times the
 398 d -dimensional correlation length). The concentration IC becomes smoother
 399 as the number of particles gets larger. Therefore, for the grid-based codes
 400 we choose initial concentrations that are deterministically uniform. We also
 401 uniformly and randomly distribute the particles in the same size strips as in
 402 the Eulerian codes (Fig. 1) and vary the number of particles.

403 4.1. L^1 convergence

404 The Eulerian code was run at different discretizations while holding the
 405 Courant number $\lambda = 1$. The first check of convergence is the integrated mass
 406 of product after 10,000 days (i.e., the spatial L^1 convergence). The Eulerian
 407 solutions appear to converge in this sense at $\Delta x \leq 1$ m and a total reaction
 408 completion of 22.08% (Fig. 2). Because of the $2-d$ nature of the problem
 409 and a low-to-intermediate value of $Da_v \approx 0.3$, we only have an approximate
 410 analytic solution to this problem (Appendix B.1), so the check of convergence
 411 is relative stability of the solution at 22.08%.

412 Because the initial particle locations and the dispersion motions both have
 413 random components, the PT simulations are stochastic in nature: each solu-
 414 tion will give slightly different results. Here we show the mean and standard
 415 deviations of the integrated mass of product for an ensemble of 20 particle-
 416 killing simulations (Fig. 2). The non-deterministic nature implies that the
 417 initial conditions have some inherent randomness that should be constructed
 418 to represent the actual physical heterogeneity [39]. The number of particles
 419 encodes the spatial autocorrelation of initial concentrations, and simulations
 420 with different number of initial particles are supposed to give different re-
 421 sults. Therefore, our check of convergence follows two tacks: varying the
 422 number of particles and the time-step size. As the former becomes larger,
 423 the effective concentration correlation length becomes a smaller fraction of
 424 the size of the specified initial condition structure (i.e., a better-mixed I.C.)
 425 and should mimic the homogeneous deterministic initial condition and so-
 426 lution given by the Eulerian simulations. Indeed, increasing the number of
 427 particles shows this kind of convergence to a reaction completion of 22.10%
 428 in the particle-killing simulations (Fig. 2). The inter-simulation variability also
 429 decreases when the particle density increases, as expected. It appears that
 430 the converged Eulerian (with $\Delta x = 0.98$ m) and Lagrangian solutions are

Figure 1: a) Aquifer domain showing location of initial reactants A (red rectangle) and B (blue rectangle) for both PT and Eulerian simulations. Also shown are the single-realization locations of individual particles of product P (black) and reactants A (red) and B (blue) for initial particle numbers $N_A(t=0) = N_B(t=0) = 5,000$. b) Base-10 logarithm of binned product concentrations (colorbar shows $\log_{10}(\text{Molar})$) from an ensemble of 10 particle-number preserving [18] simulations, using bin size of $\Delta x = \Delta y = 4$ m. The colorbar is scaled to match later plots - it does not show all of the low-concentration detail.

431 very similar when the initial number of A and B particles is 20,000 (22.05%
 432 and 21.94% respectively).

433 We also checked the solutions when the timestep size was varied, and
 434 also checked the newer algorithm [18] that does not kill reactant particles
 435 (instead, the particle masses are allowed to decrease). These simulations are
 436 more accurate at lower concentrations with the tradeoff of longer simulation
 437 times. We checked the simulations for initial particle numbers of 10,000
 438 at different Δt over a very large range. The means of the particle-killing
 439 and particle-preserving algorithms are not statistically significantly different
 440 at the particle number and timestep resolutions duplicated here (Figure 2
 441 inset).

442 As explained by Paster et al. [77] (and reiterated by Hansen et al. [49]),
 443 there is a potential for multiple particle collisions during a single timestep
 444 that may be under-estimated by large Δt . The neglect of the diminishing
 445 survival probability should tend to over-estimate reactions for too large a
 446 Δt . On the other hand, too small a timestep reduces the area “probed”
 447 by a particle and reduces the number of potential reaction partners, until,
 448 as $\Delta t \rightarrow 0$, only the nearest neighbors are allowed to react. So too small
 449 a timestep should tend to underestimate reaction rates. The correct Δt
 450 lies between a lower value dictated by the average particle density and an
 451 upper number dictated by several stability criteria. We may bracket the
 452 timestep size by the ratio of the effective search radius for a particle pair
 453 undergoing diffusion to average particle spacing $0.25 < 2\sqrt{8D_m\Delta t}/\Delta x <$
 454 1.5 [77]. The factor 8 in the square root differs from pure diffusion and
 455 comes from the convolution of two Gaussians representing the co-location
 456 probability (Appendix C). The initial condition area A_{strip} over the particle
 457 number of one species $N_A(t)$ gives a first-order approximation of inter-particle
 458 spacing. In the simulations at hand, $D_m = 0.001m^2/d$, and average inter-
 459 particle distance $A_{strip}/N_A(t=0) \approx 0.78m$, so $1.2d < \Delta t < 340d$. Varying
 460 the timestep over a wide range shows that the solutions have an inflection
 461 point between too little and too much reaction at the point surrounding the
 462 smaller of the two values (Fig. 2 inset). From approximately $\Delta t \leq 10$, the
 463 mean product concentrations are not significantly different, so in general we
 464 recommend setting $\Delta t < 0.16\Delta x^2/D_m$.

465 4.2. Pointwise (L^∞) convergence

466 Because the Eulerian simulations are deterministic, we may also look
 467 at the shapes of the product distributions to assess qualitatively the point-

468 wise convergence (Fig. 3). The peak concentrations in the 1st-order upwind
 469 simulations continue to rise significantly over the range of discretizations
 470 tested (the finest discretization model comprised over 4 million cells), so
 471 that pointwise convergence was not seen in these simulations. Similar, but
 472 lower magnitude, issues were seen in simulations using 2nd- and 3rd-order
 473 TVD simulations (Appendix A). If maximum concentrations are a concern
 474 to the user, a finer discretization will be required than one derived (later in
 475 this paper) for accuracy in the L^1 norm.

476 In the PT simulations, the concentrations are only created by binning
 477 the particles, hence the concentrations will be functions of bin size and any
 478 kernels used to model the spatial influence of particles (see, e.g., Fig. 1b). In
 479 an effort to compare to the Eulerian results, the mean concentrations along
 480 the centerline of the product plume for ensembles of simulations are compared
 481 (Fig. 4). The concentrations are simple sums of particle masses in square
 482 cells of size $\Delta x = 4$ m. A similar effect in the PT relative to the Eulerian
 483 simulations is found when the number of initial particles increases: more
 484 particles tend to resolve higher peak mean concentrations. The effect is not
 485 enhanced a great deal by the choice of bin size; however, bigger bins will tend
 486 to smooth out the higher peak concentrations (Fig. 4). Furthermore, those
 487 PT simulations that have total masses of product similar to the Eulerian
 488 simulations (for example, 20,000 particles corresponding to $\Delta x = 0.98$ m)
 489 also have similar mean peak concentrations. It should be noted that there
 490 is considerable variability in the binned product concentrations from the
 491 particle-killing algorithm along the plume direction. For example, at the peak
 492 location in the 50,000 particle, 256 bin simulation, the product concentrations
 493 had a standard deviation of approximately 0.0065 M (compared to the mean
 494 concentration of 0.037 M).

495 5. Eulerian Velocity Error

496 The spatial approximation using 1st-order upwind advection scheme used
 497 here has a known numerical dispersion of magnitude $\frac{|v|\Delta x}{2}(1 - \lambda)$ [66]. A simi-
 498 lar magnitude error is incurred by the forward Euler time-stepping, so the the
 499 total error is of order $|v|\Delta x(1 - \lambda)$. Here we investigate 1) the combined effect
 500 of changing both Δx and λ in a simple homogeneous velocity field and 2) the
 501 effect of spatially variable λ in a more realistic heterogeneous field. We also
 502 implement a 3rd-order TVD and the particle-number-preserving Lagrangian
 503 algorithms on the same velocity fields.

Figure 2: Degree of reaction completion within Eulerian (solid squares) and PT simulations (whiskers denoting $\pm 1\sigma$). Red and blue denote $\Delta t = 10$ and 1 d, respectively. The top x-axis represents initial number of both A and B particles; the bottom x-axis is the number of finite-difference grids for 1,000 m domain (i.e., $\Delta x = 1,000/N_g$ m). All solutions appear to converge to a reaction completion of 22.1%. Based on similarity, convergence, and speed of solution, the “base-cases” of 40,000 particles and 1024 finite-difference grids (both highlighted) are chosen.

Figure 3: Product concentrations along horizontal slices of the aquifer for all upstream Eulerian schemes (because all have zero numerical dispersion for Courant number $\lambda = 1$) using different discretizations. Any deviations are due to different mixing at different discretizations.

Figure 4: Averaged product concentrations from particle-killing PT simulations along horizontal slices of the aquifer using different number of initial particles $N_A(0)$ and bin sizes (indicated by number of bins in x -direction). The vertical whisker bar denotes $\pm 1\sigma$ for the 50,000 particle peak concentration.

5.1. Homogeneous Velocity

For the homogeneous velocity case, the Courant number λ was varied between 0.1 and unity for three levels of discretization ($\Delta x = 0.49, 0.98$, and 1.95). The reacted masses at 10,000 days increased, in some cases dramatically, at all $\lambda < 1$ (Fig. 5) due to spurious numerical dispersion and erroneous mixing, particularly in the 1st-order upwind algorithm. The amount of product doubled or tripled at the lowest Courant numbers and highest Peclet numbers. In Appendix B we demonstrate semi-analytically how changes in dispersion coefficient might affect the total mass of product produced. The total mass of product produced, for either fast or slow bimolecular reactions, scales approximately as $\sqrt{D}$, meaning that any errors in D , arising from numerical dispersion, can result in significantly larger masses of product. For 1st-order, explicit forward Euler solutions, the numerical dispersion has a maximum on the order $|v|\Delta x$ so the the grid Peclet number ($P_g = v_{max}\Delta x/D$) is a measure of the ratio of spurious to real dispersion. For velocity-dependent dispersion this reduces to $P_g \approx \Delta x/\alpha_L$. A value of $P_g = 2$ means that real and spurious dispersion are of the same order, and excess product on the order of $\sqrt{2}$ times the correct amount is produced. In general, the maximum amount of error is approximately $\sqrt{1 + P_g/2} - 1$, so that obtaining 5% mass error from a 1st-order accurate algorithm would require $P_g \approx 0.2$.

The 3rd-order TVD scheme appears to give reasonable reaction totals (in the integrated L^1 sense) over a large range of λ for $\Delta x \leq 0.5m$, which corresponds to a classical $\Delta x/\alpha_L \leq 16$. Note that for the particle tracking schemes the results with advection are identical to those without advection presented in the previous section due to the principle of Galilean invariance (i.e., a uniform advection merely shifts all particle locations, but does not change their relative distance from one another, which is all that is required for reaction).

The peak concentrations in these Eulerian simulations were also tracked, and at all discretizations there were substantial errors introduced by the advection approximations (Fig. 6). Although not shown here, the 3rd-order advection algorithm converged to less than 5% error in this L^∞ sense at about $\Delta x = 0.1m$, while at this smallest discretization (representing $P_g = 4$) the 1st-order had peak concentrations approximately 50% too high. Also noticeable in these plots is the error due to the diffusion and reaction operators at a Courant number of unity. These numbers correspond to the different peak concentrations shown in Fig. 3.

Figure 5: Amount of product produced in Eulerian simulations at 10,000 days by the 1st-order upwind (filled symbols) and 3rd-order TVD schemes (open symbols) with different space and time discretizations. Lines added to aid visualization.

Figure 6: Maximum product concentration in Eulerian simulations at 10,000 days by the 1st-order upwind (filled symbols, solid connecting lines) and 3rd-order TVD schemes (open symbols, dashed connecting lines) with different space and time discretizations. Lines added to aid visualization.

542 5.2. Spatially Variable Velocity

543 A random fractal K field with anisotropic-, or operator-scaling, was gen-
 544 erated using Fourier filter methods [13]. Operator-scaling in this context
 545 means that transects of the K field are fractional Brownian motions with
 546 different Hurst coefficients in the x - and y -directions of 0.44 and 0.36 (with
 547 uniform weighting on the axes) so that there is greater correlation of the
 548 underlying Gaussian increments in the x -direction (Fig. 7). The geomet-
 549 ric mean K is 1 m/d to match the uniform velocity field in the previous
 550 section. The porosity is set to 0.3 and the mean hydraulic gradient to 0.01.
 551 The K and steady-state velocity fields were calculated using a block-centered
 552 scheme at a uniform discretization of $\Delta x = \Delta y = 0.98$ m. To illustrate the
 553 general features of the velocity field, a line of uniformly-spaced inert par-
 554 ticles was placed along a transect at the initial A/B reactant interface at
 555 $x = 256$ m (Fig. 8) and tracked at 1000-day intervals (with a blue line
 556 joining initially adjacent particles). The lines and particles allow a rough
 557 estimation of the local components of fluid deformation, including shear and
 558 dilation/compression transverse to the mean flow direction. Because of the
 559 divergence-free (incompressible) flow, any dilation in the flow direction must
 560 be accompanied by compression in the orthogonal direction and vice-versa
 561 [35, 43].

562 5.2.1. Isotropic, Spatially Constant Dispersion

563 Fluid deformation, including shear, can put reactants into closer prox-
 564 imity and increase reaction rates [43], as verified visually by the locations
 565 of generated product particles (mapped to $\log_{10}(\text{concentration})$ on a grid of
 566 0.98×0.98 m cells) in a 40,000-particle simulation (Fig. 9d). The regions of
 567 high deformation, as indicated by stretching and/or shearing flowlines, are
 568 expected to be regions of extremely high or hyper-mixing [17, 35]. Indeed
 569 they tend to be heavily populated with product particles (Fig. 9d). The to-
 570 tal amount of product, i.e., the completion of the reaction after 10,000 days,
 571 is 37.4% in this simulation, or roughly 70% greater than the total amount of
 572 product (22.1%) in the homogeneous domain, all other factors being equal.
 573 This increase is due entirely to fluid deformation. An ensemble mean of 10
 574 simulations shows the same features (Fig. 9c), demonstrating that the strong
 575 zonation of reaction intensity is not an artifact of random variations between
 576 realizations.

577 The 3^{rd} -order TVD solutions have unphysical negative concentrations
 578 spread throughout the lower-concentration regions, so only concentrations

Figure 7: Anisotropic, or matrix-scaling fractional Brownian motion K field. Color bar represents values of $\ln(K)$ in m/d.

Figure 8: Pure advection of a line of 500 particles (black dots) initially placed at the location of reactant interface $x = 256$ m. The blue line connects initially adjacent particles that were placed 1 m apart. The background colors are the logarithm of velocity magnitudes, with higher velocities represented by warmer colors. The colorbar shows the velocities converted to Courant (λ) and grid Peclet (P_g) numbers. Highlighted areas show regions of shear, compression, and dilation relative to local flow direction.

greater than 10^{-20} are shown here. A 1st-order Eulerian simulation with the same velocity field and parameters with $\Delta x = \Delta y = 0.98$ m (or a domain of $1024 \times 1024 \approx 10^6$ nodes) gives a total amount of product of 53%, or roughly double the increase seen in the PT simulations going from homogeneous to the heterogeneous velocity fields (Fig. 9a). This overestimation is consistent with the overestimations by the Eulerian simulators in a homogeneous domain for smaller Courant numbers (Fig. 5). Calculated velocities in the heterogeneous domain spanned over three orders-of-magnitude; therefore, the local Courant numbers go from essentially zero to unity across the entire domain (Fig. 8). The numerical dispersion in both the longitudinal and transverse directions (because flow is seldom exactly parallel to the x -axis in the heterogeneous flow field) leads to substantial overestimation of the spatial extent of reaction in both high and low velocity zones (Fig. 9a). The 1st-order Eulerian method does not resolve the fine “threading” of reaction that takes place in areas of high fluid deformation.

The 3rd-order TVD method is visually better at restricting spurious lateral dispersion and preserving structure within the plume (Fig. 9b), and has an integrated product concentration closer to the PT simulations (at 39.4%). For this algorithm, another level of grid refinement (at a cost of 8 times the computation time, addressed in a subsequent section) would be necessary for the simulation to adequately match the PT results. For the first-order algorithm, the values of Δx and Δt would need to be reduced to bring the grid Peclet numbers substantially below unity to reduce numerical mixing to less than the real mixing (see Appendix B). In the example used here, on the order of 1 to 100 billion cells would be required, which is far outside the computational resources available to us.

5.2.2. *Anisotropic, Velocity-Dependent Dispersion*

All of the transport and reaction algorithms are straightforward to extend to velocity-dependent and anisotropic dispersion (Appendix C, [85, 109]). The dispersion coefficient (and local dispersivity) at this scale represent sub-grid velocities that are not resolved and are a function of flow field variability. Because we are not following the assumptions of low velocity variability and finite and fixed correlation lengths, there are no analytic expressions for effective block dispersivity [34]. Instead we use a common assumption that sub-grid dispersion is some fraction of the size of the block (the size at which velocity is resolved). Here we chose $\alpha_L = 0.1\Delta x$, where Δx was held at 0.98 m based on the resolution of the velocities. The transverse dispersivity is

Figure 9: Base-10 logarithms of simulated product concentrations at 10,000 days using constant $D = 0.001 \text{ m}^2/\text{d}$: a) (Eulerian) first-order upwind, b) (Eulerian) third-order TVD, c) Ensemble average of particle-preserving PT, and d) Single realization from (c). Colorbars denotes Molar product concentration. TVD simulations have large areas of negative concentrations, so plots only show concentrations above 10^{-20} M.

Figure 10: Overlay of advection-only particle traces (Fig. 8) above base-10 logarithms of simulated product concentrations at 10,000 days from an ensemble average of particle-preserving PT (reproduced from Fig. 9d). Higher reaction rates are consistently found in places where the fluid deformation shows folding and compression lateral to mean flow. Colorbars denotes Molar product concentration.

616 set to one-tenth the longitudinal. The timestep size was chosen to maintain
 617 $\lambda = 1$ at the highest velocity (which is constant for the Eulerian simulations
 618 but may change based on the highest velocity experienced at any time by
 619 the particles).

620 Due to the lower values of dispersion in low-velocity areas (compared to
 621 the previous example with $\mathbf{D} = 0.001 \frac{m^2}{d} \mathbf{I}$), the particle-number-preserving
 622 PT simulations have lower integrated reaction product of 29.4% relative to
 623 the 37.4% in the isotropic $\mathbf{D}$ case (Figs. 11 c and d).

624 For the 1st-order upwind simulations, the common block-size based dis-
 625 persivity choice gives $P_g = 10$. This simulation is very similar, both vi-
 626 sually and quantitatively, to the previous isotropic $\mathbf{D}$ simulation (compare
 627 Figs. 9a and 11a). Each 1st-order simulation indicates reaction completion
 628 at about 50% — neither can resolve the subtle differences in the formulation
 629 of dispersion. The mixing is dominated by error. The 3rd-order simulation
 630 over-estimates the reactions by several percent (at 33.8%), consistent with
 631 the isotropic dispersion and homogeneous velocity cases. However, for both
 632 Eulerian simulations, spurious over-mixing in the source area, combined with
 633 excess transverse dispersion, depletes the reactants far downstream so that
 634 the peak concentrations modeled at the exit area of the aquifer are roughly
 635 3 to 10 times lower than in the PT simulations (compare exit zones in Figs.
 636 11a-d).

637 A clear feature of the more accurate PT and 3rd-order simulations is the
 638 high degree of variability and structure of the product distribution in space
 639 (Figs. 11b-d). There is more structure in this simulation than the isotropic
 640 $\mathbf{D}$ case because of the lower values of transverse dispersion, which limits mix-
 641 ing where the reactant interface has been sheared or folded. A comparison of
 642 cross-sections of the product concentrations in the middle of the plume (Figs.
 643 12 a-b) shows that the ensemble mean PT and 3rd-order simulations are in
 644 agreement, but that a single realization, which represents a potential path-
 645 way of an initially heterogeneous plume, has substantially greater variability.
 646 Even at a mean transport distance of ≈ 250 , some product concentrations
 647 are 100 times different within ≈ 5 meters of each other. The peaks and
 648 valleys are co-located in the single realization and ensemble plumes, but the
 649 combination of fluid deformation and perturbed concentrations in the initial
 650 conditions are amplified by the nonlinear reaction. The first-order Eulerian
 651 simulation is a poor indicator of reaction heterogeneity.

Figure 11: Base-10 logarithms of simulated product concentrations at 10,000 days using velocity-dependent D with $\alpha_L = 0.1m$: a) (Eulerian) first-order upwind, b) (Eulerian) third-order TVD, c) Ensemble average of particle-preserving PT, and d) Single realization from (c). Colorbars denotes Molar product concentration. TVD simulation has negative concentrations, so plots only show concentrations above 10^{-20} M.

Figure 12: Vertical cross sections $A—A'$ (see Fig. 11) of product concentrations: a) Eulerian simulations, and b) PT simulations—single and ensemble mean of 10 realizations, each with 40,000 particles.

5.3. Computation time

For a consistent means of comparing computation times, all of the codes were implemented in Matlab on a laptop machine with a 2.7 GHz Intel Core i7 processor and 8GB of 1333 MHz DDR3 RAM (and OSX 10.9.5 operating system). As long as there is enough RAM space, a table of execution times (Fig. 1) verifies that the Eulerian codes require a minimum time $T \approx K_1 \Delta x^{d+1} + K_2$, where T is execution time [s], d is the number of dimensions ($d = 2$ here), K_1 is a constant that depends on the number of executions per node, and K_2 [s] is a small overhead term that accounts for one-time processes such as initialization of arrays. For the homogeneous velocity case, the maximum Courant number of unity forces a minimum execution time with $K_1 \approx 175$ and 285 for 1st- and 3rd-order algorithms. The latter takes about 60% longer to run, all things held constant. The PT simulations are somewhat harder to quantify in the homogeneous velocity case, because there is no Courant number stability restriction. The particle-killing algorithm is more efficient in general, and for a range of values of Δt , it is clear that the computation time increases linearly with $1/\Delta t$ (Fig. 13). The particle-killing algorithm also scales approximately linearly with the initial number of particles (N), while the particle-number-preserving algorithm scales about linearly with small N but appears to scale with the (constant-in-time) number of particles to the 1.2 to 1.6th power for larger numbers (Fig. 13). This is due to the larger number of particles within some constant search radius given as a multiple of $\sqrt{8D\Delta t}$. For the same reason, for large particle numbers, decreasing Δt does not cause a linear slowdown of the particle-preserving method (see the converging computation times for $\Delta t = 50$ and 10 s in Fig. 13). In other words, because the search becomes more efficient when the search radius decreases, the cost is lessened when the timestep is made smaller. Comparing the PT methods to Eulerian, it is clear that single realizations of either PT method takes less time than the stable Eulerian methods. Also, achieving better results in the Eulerian methods by grid refinement is much more taxing than adding particles or changing timestep size in the PT methods.

In the heterogeneous velocity fields, the Eulerian methods still scale with $T \propto \Delta x^3$ in 2- d , but there is an additional penalty of about 20 $\times$ due to the higher maximum velocity in the field. The PT methods also run slower in the heterogeneous fields, but the penalty is only about 1.3 $\times$ to 5 $\times$ because the Courant number of unity applies to the fastest particle, not the fastest velocity anywhere in the domain. Because the velocity distribution is highly

690 skewed (Fig B.3), the maximum particle velocity is far less than the maxi-
691 mum domain velocity most of the time. Additionally, the number of particles
692 is a modeler’s choice dictated by the heterogeneity of the initial conditions.
693 Similarly, the choice of Δt is not as restrictive as in the grid-based methods,
694 so that simulation times for the PT method can be reduced without caus-
695 ing numerically unstable conditions (unlike the Courant requirement of the
696 Eulerian models). In theory, *Pollock’s* method can be used analytically in
697 steady flow and semi-analytically in transient flow to determine a particle’s
698 advected position over any time interval [79, 71], so the chosen timestep is
699 limited by the diffusion and reaction steps.

700 The reaction step also leads to a particle number stability constraint that
701 arises when dispersion is small: For the particle-number preserving method,
702 the relative change of a particle’s mass when reacting with another particle
703 is maximized when two particles (subscripts 1 and 2) are coincident, and
704 then in 2-d, $dm_1/m_1 = k_f m_2 / (4\pi \sqrt{\det(\mathbf{D})})$ (see [18]). The values dm_1/m_1
705 should be less than unity, so this can be checked at the start of a simulation
706 when m_2 is largest, and $\det(\mathbf{D})$ is checked at its smallest location. Then the
707 number of particles is increased until m_2 is a small enough number.

708 6. Conclusions

709 The ADRE (1) can be approximated by grid-based or PT algorithms.
710 When the advection error is completely eliminated in homogeneous flow con-
711 ditions, the diffusion and reaction portion of both Eulerian and PT methods
712 converge in an L^1 sense to a “correct” solution. Neither method shows a ten-
713 dency to converge in a pointwise sense given the limitations of desktop-scale
714 computational resources: as Δx is made smaller or the number of particles
715 made larger, the peak concentrations in the domain tend to rise. This point
716 was not exhaustively investigated but has implications for studies concerned
717 with maximum concentrations within a domain.

718 As expected, the errors associated with the approximation of advection
719 dominate the behavior of the grid-based simulations. For displacement of
720 one reactant with another starting with square pulse initial conditions, the
721 errors in a classical 1st-order upwind method are remarkably large. The
722 nonlinear interaction of reactants means that this algorithm would need grid
723 Peclet numbers far less than unity to achieve reasonable solutions in terms of
724 integrated product (i.e., total effective reaction rate). Higher-order methods
725 can have spurious over- or under-mixing, depending on the algorithm and

Homogeneous velocity, $D = 0.001I$							
Eulerian				Lagrangian (per realization)			
Δx	Δt	<i>1st-order upwind</i>	<i>3rd-order TVD</i>	N	Δt	<i>Particle- killing</i>	<i>Particle- preserving</i>
0.49	15	1500	2390	40000	50	170	560
0.98	30	190	332	20000	50	83	187
1.96	60	27	48	10000	50	43	74
				5000	50	23	32
				40000	10	780	1207
				20000	10	387	498
				10000	10	195	209
				5000	10	104	105
Heterogeneous velocity, $\alpha_L = 0.098m; \alpha_T = 0.0098m$							
Eulerian				Lagrangian (per realization)			
Δx	Δt	<i>1st-order upwind</i>	<i>3rd-order TVD</i>	N	Δt	<i>Particle- killing</i>	<i>Particle- preserving</i>
0.98	1.33	4106	6669	40000	varies	935	1650
				20000	O(5-10)	472	684
				10000		245	320
				5000		140	173

Table 1: Execution times (seconds) for Eulerian and PT simulations using uniform, isotropic and heterogeneous, anisotropic dispersion. All Eulerian simulations and PT simulations in heterogeneous velocity use a maximum Courant number of unity. Shaded rows highlight approximately similar solutions in the $\lambda = 1$ homogeneous velocity case.

Figure 13: Execution times for PT simulations for different particle numbers and timestep sizes (symbols) and best-fit lines. Particle-killing simulations (open symbols) scale linearly with initial particle numbers; Particle-preserving algorithm scales with $N^{1.7}$. Both scale with $1/\Delta t$.

726 shapes of reactant plumes (Appendix A). The 3^{rd} -order algorithm offers
 727 potentially the best balance for current Eulerian methods in use, and appears
 728 to require classical grid Peclet numbers $\Delta x/\alpha_L \lesssim 10$ for visually acceptable
 729 results in heterogeneous velocity fields. The additional computational cost
 730 of the 3^{rd} -order method over simple upwind weighting is about 60%, which is
 731 certainly justified for the additional accuracy. Quantitatively, when moving
 732 from homogeneous to heterogeneous velocities (all other things held equal
 733 with a constant $\mathbf{D}$) the 3^{rd} -order algorithm produced too much product by
 734 about 2% percent (going from 22.1% to 39.4%) relative to PT methods (from
 735 22.1% to 37.3%). This increased reaction due to fluid deformation (17.3%
 736 versus 15.2%) is too great by a factor of 1.14. The grid-based advection error
 737 has several interesting effects, including increased volume of reaction, large
 738 areas of negative concentrations, and depletion of reactants so that product
 739 cannot be formed farther downstream.

740 The PT methods, whether particle-killing or preserving, have very sim-
 741 ilar amounts of product produced realization to realization, although the
 742 peaks and valleys within single realizations are more pronounced due to the
 743 interplay of fluid deformation and concentration fluctuations. Computationally,
 744 the particle-killing PT method is, in general, much faster than the grid-
 745 based methods for comparable conditions. The particle-preserving algorithm
 746 is also faster, but not drastically so, compared to the Eulerian methods. The
 747 particle-preserving method is more accurate than any of the studied algo-
 748 rithms, particularly at lower concentrations, and requires fewer realizations
 749 to get an estimate of the ensemble average. If initial conditions are known ex-
 750 actly and deterministically, only one Eulerian run is required, so an advantage
 751 is found there. It is impossible to directly compare computation times for Eu-
 752 lerian and PT methods, but the former scales with Δx^{d+1} , and the latter with
 753 $N/\Delta t$ (particle-killing) to $N^1/\Delta t$ to $N^{1.7}/\Delta t$ (particle-preserving). A new
 754 criterion for timestep size $0.25 < 2\sqrt{(8D_m\Delta t)(N(t)/A)} < 3/2$ is proposed
 755 (for 2- d), assuming isotropic diffusion. Time steps falling within this range
 756 permit enough diffusion to allow sufficiently high collision probabilities while
 757 limiting long range, diffusive jumps for a given particle. Additionally, we find
 758 that the particle-preserving methods requires that $1 > k_f m_p / (4\pi\sqrt{\det(\mathbf{D})})$,
 759 where m_p is the initial particle mass.

760 Because of the lack of advection error and favorable computation times,
 761 the PT method can be used to examine the subtle changes to local reaction
 762 rates that arise in heterogeneous flow fields along with spatially heteroge-
 763 neous chemical distributions. At present, the particle methods have only

764 been extended to relatively simple reaction chains (e.g., Michaelis-Menton
765 [40]). Based on the advantages of the PT methods, an examination of fur-
766 ther extensions is warranted.

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773 Appendix A. Review of Finite-Difference Schemes

774 In multiple dimensions, there are several finite volume/finite difference
775 algorithms for scalar transport (see, e.g., [98]). An attractive component of
776 several schemes is the TVD requirement, which eliminates spurious oscilla-
777 tions and is a “single-pass” method. The TVD schemes can be applied in
778 single sequential 1- d sweeps by spatial operator splitting. However, these
779 schemes are 1st-order at best [98]. Other schemes can increase the order
780 of convergence accuracy with varying degrees of computational overhead,
781 such as stricter, smaller Courant number criteria, or predictor-corrector type
782 formulations. *Toro* (2009) provides an excellent overview [98]. Here, for ex-
783 position, we choose the TVD methods and show their optimal behavior in
784 1- d .

785 For concentrations q , the wave equation $q_t = -v \cdot q_x$ has an Euler approxi-
786 mation at the i^{th} location and the n^{th} timestep of $q_i^n = q_i - (\Delta t / \Delta x)(f_{i+1/2} -$
787 $f_{i-1/2})$, where f are the fluxes at cell faces. The lack of superscript im-
788 plies values from the previous $(n - 1)$ timestep. In the simplest case of
789 uniform positive velocity in 1- d and constant Δx , this simplifies to $q_i^n =$
790 $q_i - (v \Delta t / \Delta x)(q_{i+1/2} - q_{i-1/2})$. A first-order upwind or “donor-cell” scheme
791 uses $q_{i-1/2} = q_{i-1}$. Higher-order methods adjust the flux at a cell face to
792 represent the change in concentration over a timestep. This can be derived
793 in several ways [66, 67], including higher-order estimates of the concentration
794 derivatives or predictor-corrector techniques generally referred to as flux cor-
795 rected transport (FCT) (applications to hydrology problems include [52, 27]).
796 We will not investigate the FCT methods here, focusing instead on the ef-
797 ficient one-step TVD methods. The second-order methods use a (linear)

798 estimate of the slope S_i of the concentration in an upwind cell that leads to a
 799 change of flux over the timestep. Then integrating the linear change of con-
 800 centration over a timestep gives a new estimate of the upwind concentration

$$q_{i-1/2} = q_{i-1} + S_{i-1}(\Delta x - v\Delta t)/2 \quad (\text{A.1})$$

$$= q_{i-1} + S_{i-1}\Delta x(1 - \lambda)/2 \quad (\text{A.2})$$

801 A natural choice of slope $S_{i-1} = (q_i - q_{i-1})/\Delta x$ gives the Lax-Wendroff
 802 scheme. These calculated slopes will be discontinuous and can lead to over-
 803 shoot and oscillation, so the amount of allowable flux can be limited according
 804 to the values of neighboring slopes. If discontinuities are found, the slopes
 805 are adjusted. Replacing $S_{i-1}\Delta x$ in the last equation (A.1) with a general
 806 function and the difference in the two surrounding known concentrations
 807 $\phi(r_{i-1/2})(q_i - q_{i-1})$ gives the flux-limited form

$$q_{i-1/2} = q_{i-1} + \frac{(1 - \lambda)}{2}\phi(r_{i-1/2})(q_i - q_{i-1}) \quad (\text{A.3})$$

808 where $r_{i-1/2} = (q_{i-1} - q_{i-2})/(q_i - q_{i-1})$ is a ratio of upstream and down-
 809 stream gradients relative to the donor cell $i - 1$. Generalizations to vari-
 810 able velocity magnitude and direction are straightforward. For reference,
 811 the Lax-Wendroff 2^{nd} -order formula sets $\phi(r) = 1$ and leads to overshoot
 812 and oscillation. Various schemes have been developed based on eliminat-
 813 ing spurious fluctuations. A common method requires that the total vari-
 814 ation of q , given for example by $\int |dq/dx|dx$, must not increase. Given
 815 this constraint of total variation diminishment (TVD), and keeping the re-
 816 quirement that the solution be second-order accurate, *Sweby* [92] showed
 817 that the allowable values of $\phi(r)$ must lie in the shaded area of Figure
 818 A.1. Schemes that follow the bottom of the region are the most diffusive;
 819 schemes along the top are least (and can be compressive, leading to overly
 820 steep shock fronts). The four limiters shown on the plot—Roe’s superbee,
 821 (see [92]), Van Leer [100], minmod [83], and Leonard’s 3^{rd} -order [65, 31]
 822 —are chosen here to represent the range of behaviors. The first-order up-
 823 wind scheme uses $\phi(r) = 0$ and can obviously be coded without looking at
 824 three nodal concentrations per face and is faster. The 3^{rd} -order solution ad-
 825 justs the form of $\phi(r)$ based on the local value of λ (Fig. A.1) according to
 826 $\phi(r, \lambda) = \max[0, \min\{\min(2, 2r), \frac{1}{3}((2 - \lambda) + (1 + \lambda)r)\}]$.

827 For an illustration of the effects of the TVD schemes, the ADRE was
 828 coded in 1- d using operator splitting. Parameters were held the same as in

829 Section 4. The number of grid blocks was held at 512, or 1/4 the maximum
 830 number used in Section 4, roughly representing equivalent computational
 831 effort. For the square-pulse initial condition specified (Fig. 1), the least dif-
 832 fusive flux limiter (superbee) is clearly most accurate over the full range of
 833 Courant numbers tested (Fig. A.2). Based on this plot, one might assume
 834 that the superbee limiter is best; however, its compressive (anti-diffusive)
 835 nature is well suited to discontinuous concentrations. Smoother fields are
 836 artificially sharpened. To illustrate, a similar initial condition is specified in
 837 which equal, but Gaussian-shaped masses of reactants A and B are placed
 838 near each other (Fig. A.3). The total product masses are lower at $\lambda = 1$
 839 because the centers of A and B mass are farther apart, but it is clear that the
 840 superbee limiter is under-predicting the overlap and mixing of the plumes at
 841 later times (Fig. A.4). In fact, the reaction for $\lambda = 0.1$ has nearly ceased
 842 at the end of the simulation (not shown). Clearly, there is no optimal ad-
 843 vection scheme for all types of plumes or mixtures of Courant numbers that
 844 will be found in a heterogeneous flow field. It is also important to note
 845 that extending the higher-order TVD methods to multiple dimensions is not
 846 straightforward. Typically, the higher-order methods are applied sequentially
 847 in 1- d sweeps via directional operator-splitting. *LeVeque* [67] notes that any
 848 method that is TVD in 2- d is, at most, 1st-order accurate, although some
 849 multi-dimensional techniques appear to maintain higher-order accuracy in
 850 simultaneous multi-dimensional calculations (e.g., [96, 29]). Performing se-
 851 quential 1- d sweeps through a multi-dimensional domain is presently the
 852 best technique used in water resource applications (especially within readily-
 853 available codes), even though that method does not explicitly account for
 854 cross-derivatives that naturally come up in the addition of the higher-order
 855 anti-diffusion.

856 **Appendix B. Semi-Analytical Solutions for Mass of Product Pro-** 857 **duced**

858 Solutions are tractable under two end-member conditions: fast and slow
 859 reactions.

860 *Appendix B.1. Slow Reaction - A Perturbation Solution Approach*

861 In 1-d the ADRE (1) is given by

$$\frac{\partial C_i}{\partial t} + u \frac{\partial C_i}{\partial x} = D \frac{\partial^2 C_i}{\partial x^2} - k C_A C_B \quad i = A, B \quad (\text{B.1})$$

Figure A.1: Region of acceptable TVD flux-limiters [92]. Limiters for this study are the 2^{nd} -order maximally diffusive minmod (dash-dot line), minimally diffusive superbee (large dashes), intermediate Van Leer (small dashes), and Leonard's 3^{rd} -order, which depends on local Courant number and smoothly interpolates the region between $\lambda = [0, 1]$ (red solid lines).

Figure A.2: 1- d solutions to the adjacent square-pulse initial condition problem using different TVD advection schemes.

Figure A.3: 1- d versions of the two initial conditions of reactants A (red) and B (blue). The square pulses (dotted) mimic the original 2- d simulations in Section 4. An additional set of I.C.s is shown that place identical masses in nearby Gaussian pulses (solid red and blue curves).

Figure A.4: 1- d solutions to the adjacent Gaussian-pulse initial condition problem using different TVD advection schemes.

862 This equation can be rewritten in dimensionless forms by defining dimension-
 863 less variables $t^* = t \frac{u}{l}$, $x^* = x/l$, and $C^* = C/C_{ref}$, where l is a characteristic
 864 distance (e.g., the initial width of the plume in our simulations) and C_{ref}
 865 is a characteristic concentration (e.g., the initial concentration). For ease of
 866 notation we drop the stars and in dimensionless form (B.1) becomes

$$\frac{\partial C_i}{\partial t} + \frac{\partial C_i}{\partial x} = \frac{1}{Pe} \frac{\partial^2 C_i}{\partial x^2} - Da C_A C_B \quad i = A, B \quad (\text{B.2})$$

867 where $Pe = \frac{ul}{D}$ is the Peclet number and $Da = \frac{kC_0 l}{u}$ the Damköhler number.
 868 We are considering the limit of slow reactions and thus take Da as small.
 869 Doing this we can write the following expansion for concentration [99]:

$$C_i = \sum_{n=0}^{\infty} C_i^{(n)} Da^n \quad (\text{B.3})$$

870 Then at $O(Da^0)$

$$\frac{\partial C_i^{(0)}}{\partial t} + \frac{\partial C_i^{(0)}}{\partial x} = \frac{1}{Pe} \frac{\partial^2 C_i^{(0)}}{\partial x^2} \quad i = A, B \quad (\text{B.4})$$

871 Recognizing that the effect of advection is just a Gallilean shift, we move
 872 into a moving reference frame $z = x - t$ and

$$\frac{\partial C_i^{(0)}}{\partial t} = \frac{1}{Pe} \frac{\partial^2 C_i^{(0)}}{\partial z^2} \quad i = A, B \quad (\text{B.5})$$

873 In an infinite domain the solution to these equations is given by

$$C_i^{(0)} = \sqrt{\frac{Pe}{4\pi t}} \int_{-\infty}^{\infty} e^{\frac{-(z-\xi)^2 Pe}{4t}} C_i(t=0) d\xi \quad (\text{B.6})$$

874 At $O(Da^1)$

$$\frac{\partial C_i^{(1)}}{\partial t} = \frac{1}{Pe} \frac{\partial^2 C_i^{(1)}}{\partial z^2} - C_A^{(0)} C_B^{(0)} \quad i = A, B \quad (\text{B.7})$$

875 Given this equation and truncating series (B.3) for concentrations at $O(Da^1)$
 876 the total mass of the product will be given by

$$M(t) = Da \int_{-\infty}^{\infty} \int_0^t C_A^{(0)}(z, t') C_B^{(0)}(z, t') dt' dz \quad (\text{B.8})$$

877 Thus in principle for any initial condition we can now calculate the pro-
 878 duced mass to within approximation of the perturbation series. Any error
 879 introduced via numerical dispersion will manifest as an error in the concentra-
 880 tion fields $C_A^{(0)}(z, t')$ and $C_B^{(0)}(z, t')$ via a modified $Pe = (ul)/(D + D_{numerical})$,
 881 which will compound in an error in the resultant product mass.

882 The nonlinear and initial condition specific nature of the reaction makes
 883 it difficult to make general statements on how this error will manifest. For
 884 demonstration purposes, consider the following simple example, an infinite
 885 domain half filled with A and half filled with B , separated by a sharp interface
 886 at $x = 0$. At short times (i.e., when the diffusive length is much less than
 887 the initial plume width) this mimics the example setups studied in this work.
 888 For this setup the initial conditions are given by

$$\begin{aligned} C_A(t=0) &= 1 & -\infty < x < 0 \\ C_B(t=0) &= 1 & 0 < x < \infty \end{aligned} \quad (\text{B.9})$$

889 and zero elsewhere, which means

$$C_A^{(0)}(z, t) = \frac{1}{2} \operatorname{erfc} \left[\frac{z\sqrt{Pe}}{\sqrt{4t}} \right] \quad C_B^{(0)}(z, t) = 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{z\sqrt{Pe}}{\sqrt{4t}} \right] \quad (\text{B.10})$$

890 Thus solving (B.8) is trivial and gives

$$M(t) = \frac{2}{3} Da \sqrt{\frac{2}{\pi Pe}} t^{3/2} \quad (\text{B.11})$$

891 The key feature is that $M(t) \propto \frac{1}{\sqrt{Pe}}$, or in dimensional terms that the
 892 mass or product produced is proportional to $\sqrt{D}$. Given that in the Eulerian
 893 numerical models the dispersion coefficient will be $D = D_{actual} + D_{numerical}$,
 894 any error in the dispersion coefficient induced by numerical dispersion will
 895 increase the predicted amount of mass produced in this manner. The results
 896 for the specific initial conditions studied in this paper are cumbersome and
 897 provide little insight and are thus not shown. However, to leading order it
 898 can be shown that the initial condition studied in this paper has the same
 899 scaling.

900 *Appendix B.2. Fast Reactions*

901 Now if we consider the other extreme when Da is large, we can treat the
 902 reaction as instantaneous, which in previous studies has been shown to be a
 903 good assumption for $Da > 10$ [86]. Under this assumption A and B cannot
 904 coexist, meaning that the lesser will be consumed entirely. Now following the
 905 development of *Gramling et al.* (2002) [47], define two conservative pseudo-
 906 tracers as

$$U_A = C_A + C_P \quad U_B = C_B + C_P \quad (\text{B.12})$$

907 These are governed by a conservative transport equation because upon
 908 summation of the ADREs (1) for C_A and C_P , the reaction terms disappear
 909 (because A and B disappear at the same rate as P by stoichiometry). For
 910 the initial conditions considered in B.1

$$\begin{aligned} U_A(t=0) &= 1 & -\infty < x < 0 \\ U_B(t=0) &= 1 & 0 < x < \infty \end{aligned} \quad (\text{B.13})$$

911 which means that at all times

$$U_A(t) = \frac{1}{2} \operatorname{erfc} \left[\frac{(x-ut)\sqrt{Pe}}{\sqrt{4t}} \right] \quad U_B(t) = 1 - \frac{1}{2} \operatorname{erfc} \left[\frac{(x-ut)\sqrt{Pe}}{\sqrt{4t}} \right] \quad (\text{B.14})$$

912 Now since A and B cannot coexist, the concentration of product is given by

$$C_P = \min(U_A, U_B) \quad (\text{B.15})$$

913 and the total mass of product for the semi-infinite sources (following [47]) is
 914 given by

$$M = \int_{-\infty}^{\infty} C_P dx = 2 \int_0^{\infty} U_A dx = 2 \sqrt{\frac{t}{Pe\pi}} \quad (\text{B.16})$$

915 A more accurate equation for the finite (in the x -direction) sources is

$$M_C(t) = \sqrt{\frac{4t}{\pi Pe}} \left(1 - e^{-\frac{Pe}{4t}} \right) + 1 - \operatorname{erf} \left[\sqrt{\frac{Pe}{4t}} \right] \quad (\text{B.17})$$

Figure B.1: Evolution of the mass of product in the 20,000 particle simulations in a homogeneous velocity field (symbols), along with the solution to the analytical expression (B.17).

916 which recovers (B.16) for $l \rightarrow \infty$. The 20,000 particle simulations follow
 917 formula (B.17) fairly closely at later time (Fig. B.1) using the initial condition
 918 $l = 15.6$ m for an estimation of the scaling length. The early time discrepancy
 919 is most likely due to the fact that our reactions are not instantaneous, but
 920 take some time (albeit small) to develop.

921 *Appendix B.3. Slow reactions generalized to a higher order reaction $-kC_A^n C_B^m$*

922 To demonstrate how these effect might be influenced for higher order
 923 reactions, consider taking $r = -kC_A^n C_B^m$. Following the same procedures as
 924 above for slow reactions (i.e. Appendix B.1) the total mass produced will be

$$M(t) = \int_0^t \int_{-\infty}^{\infty} Da \frac{Pe^{\frac{n+m}{2}}}{(4\pi t')^{\frac{n+m}{2}}} \prod_{i=1}^n \int_{-\infty}^0 e^{\frac{-(x-\xi_i)^2 Pe}{4t'}} d\xi_i \prod_{j=1}^m \int_0^{\infty} e^{\frac{-(x-\eta_j)^2 Pe}{4t'}} d\eta_j dx dt' \quad (\text{B.18})$$

925 Now rescale all the length scales by $\sqrt{\frac{Pe}{4t'}}$, i.e.

$$\xi' = \xi \sqrt{\frac{Pe}{4t'}} \quad \eta' = \eta \sqrt{\frac{Pe}{4t'}} \quad x = x \sqrt{\frac{Pe}{4t'}} \quad (\text{B.19})$$

926 Then

$$M(t) = \int_0^t \int_{-\infty}^{\infty} Da \sqrt{\frac{4t'}{Pe}} \frac{1}{\pi^{\frac{n+m}{2}}} \prod_{i=1}^n \int_{-\infty}^0 e^{-(x-\xi_i)^2} d\xi_i \prod_{j=1}^m \int_0^{\infty} e^{-(x-\eta_j)^2} d\eta_j dx dt' \quad (\text{B.20})$$

927 which gives

$$M(t) = W \frac{2Da}{3} \sqrt{\frac{2}{Pe}} t^{3/2} \quad (\text{B.21})$$

928 where the constant W is given by

$$W = \frac{1}{\pi^{\frac{n+m}{2}}} \int_{-\infty}^{\infty} \prod_{i=1}^n \int_{-\infty}^0 e^{-(x-\xi_i)^2} d\xi_i \prod_{j=1}^m \int_0^{\infty} e^{-(x-\eta_j)^2} d\eta_j dx \quad (\text{B.22})$$

929 The specific value of W is unimportant to the central message. From
 930 (B.21) we see again that the total amount of mass produced has the same
 931 proportionality as before of $M(t) \propto \frac{1}{\sqrt{Pe}}$. At this point it is not clear how to
 932 generalize the fast reactions scenario to higher order reactions.

933 *Appendix B.4. Error Estimates*

934 The foregoing sections of this Appendix show that the mass produced is
 935 roughly proportional to $\sqrt{D}$. This allows the construction of some rules-of-
 936 thumb for error estimation. The ratio of mass produced with numerical error
 937 to mass produced without error is $\sqrt{D_{actual} + D_{numerical}} / \sqrt{D_{actual}}$. Therefore
 938 the excess amount of mass produced in error expressed as a fraction of the
 939 real amount is $Error = \sqrt{1 + D_{numerical}/D_{actual}} - 1$. For isotropic, fixed
 940 D_{actual} in our first-order upwind scheme, we have

$$Error = \sqrt{1 + \frac{|v|\Delta x}{2D_{actual}} (1 - |v|\Delta t/\Delta x)} - 1 \quad (\text{B.23})$$

Figure B.3: Histogram (blue bars) of velocity magnitude in the heterogeneous domain pictured in Fig 8. Estimates of the excess mass production error (red curves) by the upwind advection algorithm as a function of velocity (hence grid Peclet and Courant numbers) for fixed dispersion value $0.001 \text{ m}^2/\text{d}$ and a velocity-dependent dispersion with $\alpha_L = 0.03 \text{ m}$. The right-hand labels are for excess error as a multiple of the real production value.

941 In the case of velocity-dependent dispersion in which the longitudinal disper-
 942 sion is given by $D_{actual} = \alpha_L |v|$, the error is

$$Error = \sqrt{1 + \frac{\Delta x}{2\alpha_L}(1 - |v|\Delta t/\Delta x)} - 1 \quad (\text{B.24})$$

943 The latter of these two errors is greater for regions of smaller velocity in
 944 the domain, as the former goes to zero for $|v| \rightarrow 0$. Figure B.3 shows the
 945 magnitude of these two error estimates for reasonable values in the exam-
 946 ple heterogeneous domain ($\Delta x = 1 \text{ m}$, $\max(v) = 1.46 \text{ m/d}$), along with
 947 a histogram of the velocities within the (log-normal) K field. For a large
 948 portion of the domain experiencing low velocity, the error is greater for a
 949 velocity-dependent dispersion.

950 Appendix C. PT simulation of anisotropic dispersion and reaction.

951 We solve (1) via PT using operator-splitting as follows: The finite-time
 952 discretized Langevin equation applied to each particle's position $\mathbf{X}$ for the
 953 backward Kolmogorov transport portion of equation (1) follows $\mathbf{X}_{t+\Delta t} =$
 954 $\mathbf{X}_t + (\mathbf{v} + \nabla \mathbf{D})\Delta t + \mathbf{B}W$, where $\mathbf{B} = \sqrt{2\Delta t \mathbf{D}}$ after $\mathbf{D}$ is diagonalized
 955 by rotation into a coordinate system along the flow direction, and W is a
 956 standard multiGaussian random vector [60].

957 The velocities are calculated at cell faces following an iterative solution of
 958 the continuity equation for constant-density fluid $\nabla \cdot K \nabla h = 0$ followed by
 959 $\mathbf{v} = -K \nabla h / \theta$. Constant values of h at the left and right boundaries, along
 960 with no-flow $\nabla h \cdot \mathbf{n} = 0$ along the top and bottom boundaries maintain
 961 the desired mean gradient from left to right. The K is constant within
 962 each rectilinear volume (cell), porosity θ is constant everywhere, and $\mathbf{v}$ is
 963 calculated at cell faces and linearly interpolated to each particle's location
 964 within the cells. Dispersion components for each particle use these linearly-
 965 interpolated velocities. Because the calculation of the gradients of dispersion
 966 coefficients at the exact particle location are relatively time consuming by
 967 bilinear interpolation (see [60]), we make a simplification that the gradients
 968 can be well approximated as constant within each cell. This follows directly
 969 from the linear velocity interpolation and linear dispersion dependence on
 970 velocity. For example, in 2- d with indices i, j in the x, y -directions, the
 971 components D_{xx} and D_{yx} are calculated at the $i - 1/2$ and $i + 1/2$ faces,
 972 while D_{yy} and D_{xy} are calculated at the $j - 1/2$ and $j + 1/2$ faces. So for
 973 the i, j block, $\frac{dD_{xx}}{dx} = (D_{xx}(i + 1/2) - D_{xx}(i - 1/2))/\Delta x$, $\frac{dD_{yx}}{dx} = (D_{yx}(i +$
 974 $1/2) - D_{yx}(i - 1/2))/\Delta x$, $\frac{dD_{yy}}{dy} = (D_{yy}(j + 1/2) - D_{yy}(j - 1/2))/\Delta y$, $\frac{dD_{xy}}{dy} =$
 975 $(D_{xy}(j + 1/2) - D_{xy}(j - 1/2))/\Delta y$.

976 In the operator-split method, we enforce zero-diffusive flux BCs in the
 977 random walk by reflecting all particles back into the domain [e.g., 85]. Par-
 978 ticles that move by advection into boundary cells are removed, enforcing
 979 $J = \mathbf{n} \cdot \mathbf{v}C$, where $\mathbf{n}$ is the unit normal to the boundary and the relation of
 980 concentration to particle mass is thought of as the spatial convolution of any
 981 particle's mass with some kernel function with unit integral in d -dimensions.
 982 A nice discussion of all types of boundary conditions for advection and dis-
 983 persion via the PT method is given by *Koch and Nowak* [58].

984 Reactions between particles may either follow the formulas given in [11]
 985 or [18] for particle-killing or particle-preserving methods, respectively. For
 986 the latter, each A particle with unique mass $m_A(t)$ at time t is chosen

987 and sequentially subjected to reaction with nearby B particles with unique
988 mass m_B . The change in masses for a single reaction are $dm_A = dm_B =$
989 $-\Delta t k_f m_B(t) m_A(t) v(\mathbf{s})$. Then the net change sums over all reaction partner
990 pairs $m_A(t + \Delta t) = m_A(t) + \sum dm_A$. The co-location density $v(\mathbf{s})$ given a
991 separation vector $\mathbf{s}$ between an A and B particle pair is given by a multi-
992 Gaussian

$$v(\mathbf{s}) = \frac{1}{(8\pi\Delta t)^{d/2} |\mathbf{D}|^{1/2}} \exp\left(-\frac{1}{8\Delta t} \mathbf{s}' \mathbf{D}^{-1} \mathbf{s}\right). \quad (\text{C.1})$$

993 The search radius for nearby particles was restricted to $3\sqrt{8 \max(D_{ij})\Delta t}$, and
994 the kd-tree algorithm [14] for nearby particle searching was used as coded in
995 the “rangesearch” algorithm in matlab.

996 We assume, for calculation speed, that the dispersion tensor is simply that
997 of the “central” A particle. The differences in dispersion tensors between the
998 A and each nearby B particle was ignored, i.e., $\mathbf{D} = \mathbf{D}_A$. For isotropic
999 dispersion, the above procedure was used with $\mathbf{D} = D\mathbf{I}$.

- 1000 [1] Apello, C. A. J., Postma, D., 2005. Geochemistry, Groundwater and
1001 Pollution, 2nd Edition. CRC Press.
- 1002 [2] Audigane, P., Gaus, I., Czernichowski-Lauriol, I., Pruess, K., Xu, T.,
1003 2007. Two-dimensional reactive transport modeling of CO2 injection
1004 in a saline aquifer at the Sleipner site, North Sea. Am. J. Sci. 307 (7),
1005 974–1008.
1006 URL <http://www.ajsonline.org/cgi/content/abstract/307/7/974>
- 1007 [3] Avesani, D., Herrera, P., Chiogna, G., Bellin, A., Dumbser, M., 6 2015.
1008 Smooth particle hydrodynamics with nonlinear moving-least-squares
1009 weno reconstruction to model anisotropic dispersion in porous media.
1010 Advances in Water Resources 80 (0), 43–59.
1011 URL <http://www.sciencedirect.com/science/article/pii/S0309170815000627>
- 1012 [4] Ayuso, B., Marini, L. D., 2009. Discontinuous Galerkin methods for
1013 advection-diffusion-reaction problems. SIAM J. Numer. Anal. 47 (2),
1014 1391–1420.
- 1015 [5] Bakker, M., Hemker, K., 2004. Analytic solutions for groundwater
1016 whirls in box-shaped, layered anisotropic aquifers. Advances in Water
1017 Resources 27 (11), 1075–1086.
1018 URL <http://www.sciencedirect.com/science/article/pii/S0309170804001344>

- 1019 [6] Barry, D., Prommer, H., Miller, C., Engesgaard, P., Brun, A., Zheng,
1020 C., 2002. Modelling the fate of oxidisable organic contaminants in
1021 groundwater. *Advances in Water Resources* 25 (8–12), 945 – 983.
1022 URL <http://www.sciencedirect.com/science/article/pii/S0309170802000441>
- 1023 [7] Battiato, I., Tartakovsky, D. M., 2011. Applicability regimes for macro-
1024 scopic models of reactive transport in porous media. *J. Contam. Hydrol.*
1025 120-121, 18–26.
- 1026 [8] Battiato, I., Tartakovsky, D. M., Tartakovsky, A. M., Scheibe, T., 2009.
1027 On breakdown of macroscopic models of mixing-controlled heteroge-
1028 neous reactions in porous media. *Adv. Water Resour.* 32, 1664–1673.
- 1029 [9] Bechtold, M., Vanderborght, J., Ippisch, O., Vereecken, H., 2011. Effi-
1030 cient random walk particle tracking algorithm for advective-dispersive
1031 transport in media with discontinuous dispersion coefficients and water
1032 contents. *Water Resour. Res.* 47 (10), W10526–.
1033 URL <http://dx.doi.org/10.1029/2010WR010267>
- 1034 [10] Benson, D. A., Carey, A. E., Wheatcraft, S. W., 1998. Numerical ad-
1035 vective flux in highly variable velocity fields exemplified by saltwater
1036 intrusion. *J. Contam. Hydrol.* 34, 207–233.
- 1037 [11] Benson, D. A., Meerschaert, M. M., Dec. 2008. Simulation of chemical
1038 reaction via particle tracking: Diffusion-limited versus thermodynamic
1039 rate-limited regimes. *Water Resour. Res.* 44, W12201.
1040 URL <http://dx.doi.org/10.1029/2008WR007111>
- 1041 [12] Benson, D. A., Meerschaert, M. M., 2009. A simple and efficient ran-
1042 dom walk solution of multi-rate mobile/immobile mass transport equa-
1043 tions. *Adv. Water Resour.* 32, 532–539.
- 1044 [13] Benson, D. A., Meerschaert, M. M., Revielle, J., Jan. 2013. Fractional
1045 calculus in hydrologic modeling: A numerical perspective. *Advances*
1046 *in Water Resources* 51 (0), 479–497.
1047 URL <http://www.sciencedirect.com/science/article/pii/S0309170812000899>
- 1048 [14] Bentley, J. L., 1975. Multidimensional binary search trees used for as-
1049 sociative searching. *Communications of the Association for Computing*
1050 *Machinery* 18, 509–517.

- 1051 [15] Bokanowski, O., Zidani, H., 2007. Anti-dissipative schemes for advec-
 1052 tion and application to Hamilton–Jacobi–Bellmann equations 30 (1),
 1053 1–33–.
 1054 URL <http://dx.doi.org/10.1007/s10915-005-9017-0>
- 1055 [16] Bolster, D., de Anna, P., Benson, D. A., Tartakovsky, A. M., 2012.
 1056 Incomplete mixing and reactions with fractional dispersion. *Advances*
 1057 *in Water Resources* 37, 86–93.
- 1058 [17] Bolster, D., Dentz, M., Borgne, T. L., 2011. Hyper mixing in shear
 1059 flow. *Water Resources Research* 47, W09602.
- 1060 [18] Bolster, D., Paster, A., Benson, D. A., 2016. A particle number con-
 1061 serving Lagrangian method for mixing-driven reactive transport. *Water*
 1062 *Resources Research* 52 (2), 1518–1527.
 1063 URL <http://dx.doi.org/10.1002/2015WR018310>
- 1064 [19] Bolster, D., Valdés-Parada, F. J., LeBorgne, T., Dentz, M., Carrera,
 1065 J., 2011. Mixing in confined stratified aquifers. *Journal of Contaminant*
 1066 *Hydrology* 120, 198–212.
- 1067 [20] Boso, F., Bellin, A., Dumbser, M., 2013. Numerical simulations of so-
 1068 lute transport in highly heterogeneous formations: A comparison of
 1069 alternative numerical schemes. *Advances in Water Resources* 52, 178–
 1070 189.
- 1071 [21] Burchard, H., Rennau, H., 2008. Comparative quantification of
 1072 physically and numerically induced mixing in ocean models. *Ocean*
 1073 *Modelling* 20 (3), 293–311.
 1074 URL <http://www.sciencedirect.com/science/article/pii/S146350030700128X>
- 1075 [22] Chakraborty, P., Meerschaert, M. M., Lim, C. Y., 2009. Parameter es-
 1076 timation for fractional transport: A particle-tracking approach. *Water*
 1077 *Resour. Res.* 45 (10), W10415–.
 1078 URL <http://dx.doi.org/10.1029/2008WR007577>
- 1079 [23] Chiogna, G., Bellin, A., 2013. Analytical solution for reactive solute
 1080 transport considering incomplete mixing within a reference elementary
 1081 volume. *Water Resources Research* 49 (5), 2589–2600.
 1082 URL <http://dx.doi.org/10.1002/wrcr.20200>

- 1083 [24] Chiogna, G., Hochstetler, D. L., Bellin, A., Kitanidis, P. K., Rolle,
1084 M., 2012. Mixing, entropy and reactive solute transport. *Geophysical*
1085 *Research Letters* 39 (20).
- 1086 [25] Chiogna, G., Rolle, M., Bellin, A., Cirpka, O. A., Nov. 2014. Helicity
1087 and flow topology in three-dimensional anisotropic porous media.
1088 *Advances in Water Resources* 73 (0), 134–143.
1089 URL <http://www.sciencedirect.com/science/article/pii/S0309170814001341>
- 1090 [26] Cirpka, O. A., de Barros, F. P. J., Chiogna, G., Rolle, M., Nowak, W.,
1091 Jun. 2011. Stochastic flux-related analysis of transverse mixing in two-
1092 dimensional heterogeneous porous media. *Water Resour. Res.* 47 (6),
1093 W06515–.
- 1094 [27] Cirpka, O. A., Frind, E. O., Helmig, R., 1999. Numerical methods
1095 for reactive transport on rectangular and streamline-oriented grids.
1096 *Advances in Water Resources* 22 (7), 711 – 728.
1097 URL <http://www.sciencedirect.com/science/article/pii/S0309170898000517>
- 1098 [28] Cockburn, B., Shu, C., 1998. The local discontinuous Galerkin method
1099 for time-dependent convection-diffusion systems. *SIAM Journal on Nu-*
1100 *merical Analysis* 35 (6), 2440–2463.
- 1101 [29] Colella, P., Mar. 1990. Multidimensional upwind methods for hyper-
1102 bolic conservation laws. *Journal of Computational Physics* 87 (1),
1103 171–200.
1104 URL <http://www.sciencedirect.com/science/article/pii/002199919090233Q>
- 1105 [30] Constantinescu, E. M., Sandu, A., Carmichael, G. R., 2008. Modeling
1106 atmospheric chemistry and transport with dynamic adaptive resolu-
1107 tion. *Computational Geosciences* 12 (2), 133–151.
1108 URL <http://dx.doi.org/10.1007/s10596-007-9065-7>
- 1109 [31] Datta-Gupta, A., Lake, L. W., Pope, G. A., Sephernoori, K., King,
1110 M. J., 1991. High-resolution monotonic schemes for reservoir fluid flow
1111 simulation. *In Situ*, 289–317.
- 1112 [32] de Anna, P., Dentz, M., Tartakovsky, A., Le Borgne, T., 2014. Fila-
1113 mentary structure of mixing fronts controls reaction kinetics in porous
1114 media flows. *Geophysical Research Letters*, in press.

- 1115 [33] de Anna, P., Jimenez-Martinez, J., Tabuteau, H., Turuban, R.,
 1116 Le Borgne, T., Derrien, M., Méheust, Y., 2013. Mixing and reaction
 1117 kinetics in porous media: an experimental pore scale quantification.
 1118 *Environmental Science & Technology* 48 (1), 508–516.
- 1119 [34] de Barros, F. P., Dentz, M., 2016. Pictures of blockscale transport:
 1120 Effective versus ensemble dispersion and its uncertainty. *Advances in*
 1121 *Water Resources* 91, 11 – 22.
 1122 URL <http://www.sciencedirect.com/science/article/pii/S0309170816300549>
- 1123 [35] de Barros, F. P. J., Dentz, M., Kock, J., Nowak, W., 2012. Flow topol-
 1124 ogy and scalar mixing in spatially heterogeneous flow fields. *Geophys.*
 1125 *Res. Lett.* 39, L08404.
- 1126 [36] De Simoni, M., Carrera, J., Sanchez-Vila, X., Guadagnini, A., 2005. A
 1127 procedure for the solution of multicomponent reactive transport prob-
 1128 lems. *Water Resources Research* 41 (11).
- 1129 [37] De Simoni, M., Sanchez-Vila, X., Carrera, J., Saaltink, M., 2007. A
 1130 mixing ratios-based formulation for multicomponent reactive transport.
 1131 *Water Resources Research* 43 (7).
- 1132 [38] Dentz, M., Le Borgne, T., Englert, A., Bijeljic, B., 2011. Mixing,
 1133 spreading and reaction in heterogeneous media: A brief review. *Journal*
 1134 *of Contaminant Hydrology* 120, 1–17.
- 1135 [39] Ding, D., Benson, D., Paster, A., Bolster, D., 2012. Modeling bimolec-
 1136 ular reactions and transport in porous media via particle tracking. *Ad-*
 1137 *vances in Water Resources* 53, 56–65.
- 1138 [40] Ding, D., Benson, D. A., 2015. Simulating biodegradation under
 1139 mixing-limited conditions using michaelis-menten (monod) kinetic
 1140 expressions in a particle tracking model. *Advances in Water Resources*
 1141 76, 109 – 119.
 1142 URL <http://www.sciencedirect.com/science/article/pii/S0309170814002462>
- 1143 [41] Doi, M., 1976. Stochastic theory of diffusion-controlled reaction. *Jour-*
 1144 *nal of Physics A: Mathematical and General* 9, 1479–1495.
- 1145 [42] Edery, Y., Scher, H., Berkowitz, B., Jan. 2009. Modeling bimolecular
 1146 reactions and transport in porous media. *Geophys. Res. Lett.* 36 (2),

1147 L02407.
1148 URL <http://dx.doi.org/10.1029/2008GL036381>

1149 [43] Engdahl, N. B., Benson, D. A., Bolster, D., Nov 2014. Predicting the
1150 enhancement of mixing-driven reactions in nonuniform flows using mea-
1151 sures of flow topology. *Phys. Rev. E* 90, 051001.
1152 URL <http://link.aps.org/doi/10.1103/PhysRevE.90.051001>

1153 [44] Fernàndez-Garcia, D., Sanchez-Vila, X., 2011. Optimal reconstruction
1154 of concentrations, gradients and reaction rates from particle distribu-
1155 tions. *Journal of Contaminant Hydrology* 120, 99–114.

1156 [45] Gillespie, D. T., 1977. Exact stochastic simulation of coupled chemical
1157 reactions. *J. Phys. Chem.* 81 (25), 2340–2361.

1158 [46] Gillespie, D. T., 2000. The chemical Langevin equation. *J. Chem. Phys.*
1159 113 (1), 297–306.

1160 [47] Gramling, C., Harvey, C., Meigs, L., JUN 1 2002. Reactive transport
1161 in porous media: A comparison of model prediction with laboratory
1162 visualization. *Environmental Science & Technology* 36 (11), 2508–2514.

1163 [48] Hammond, G. E., Lichtner, P. C., Sep. 2010. Field-scale model for the
1164 natural attenuation of uranium at the Hanford 300 area using high-
1165 performance computing. *Water Resour. Res.* 46 (9), W09527.
1166 URL <http://dx.doi.org/10.1029/2009WR008819>

1167 [49] Hansen, S. K., Scher, H., Berkowitz, B., Jul. 2014. First-principles
1168 derivation of reactive transport modeling parameters for particle track-
1169 ing and pde approaches. *Advances in Water Resources* 69 (0), 146–158.

1170 [50] Henshaw, W. D., Schwendeman, D. W., Nov. 2003. An adaptive
1171 numerical scheme for high-speed reactive flow on overlapping grids.
1172 *Journal of Computational Physics* 191 (2), 420–447.
1173 URL <http://www.sciencedirect.com/science/article/pii/S0021999103003231>

1174 [51] Herrera, P. A., Valocchi, A. J., Beckie, R. D., Jul. 2010. A multidimen-
1175 sional streamline-based method to simulate reactive solute transport
1176 in heterogeneous porous media. *Advances in Water Resources* 33 (7),
1177 711–727.
1178 URL <http://www.sciencedirect.com/science/article/pii/S0309170810000424>

- 1179 [52] Hills, R. G., Fisher, K. A., Kirkland, M. R., Wierenga, P. J., 1994.
1180 Application of flux-corrected transport to the las cruces trench site.
1181 Water Resources Research 30 (8), 2377–2385.
1182 URL <http://dx.doi.org/10.1029/94WR01216>
- 1183 [53] Huang, C.-S., Xiao, F., Arbogast, T., 2015. Fifth order multi-moment
1184 weno schemes for hyperbolic conservation laws. J. Sci. Comput. 64,
1185 477–507.
- 1186 [54] Isaacson, S. A., 2013. A convergent reaction-diffusion master equation.
1187 The Journal of Chemical Physics 139 (5), 054101.
1188 URL <http://scitation.aip.org/content/aip/journal/jcp/139/5/10.1063/1.4816377>
- 1189 [55] Johnson, J. W., Nitao, J. J., Knauss, K. G., 2004. Reactive transport
1190 modelling of co2 storage in saline aquifers to elucidate fundamental pro-
1191 cesses, trapping mechanisms and sequestration partitioning. Geological
1192 Society, London, Special Publications 233 (1), 107–128.
- 1193 [56] Keating, E. H., Hakala, J. A., Viswanathan, H., Carey, J. W., Pawar,
1194 R., Guthrie, G. D., Fessenden-Rahn, J., 2013. CO₂ leakage impacts
1195 on shallow groundwater: Field-scale reactive-transport simulations
1196 informed by observations at a natural analog site. Applied Geochem-
1197 istry 30, 136 – 147, geochemical Aspects of Geologic Carbon Storage.
1198 URL <http://www.sciencedirect.com/science/article/pii/S0883292712002223>
- 1199 [57] Ketcheson, D. I., Parsani, M., LeVeQue, R. J., 2013. High-order wave
1200 propagations algorithms for hyperbolic systems. SIAM J. SCI. COM-
1201 PUT. 35 (1), A351–A377.
- 1202 [58] Koch, J., Nowak, W., 2014. A method for implementing dirichlet
1203 and third-type boundary conditions in PTRW simulations. Water Re-
1204 sources Research 50 (2), 1374–1395.
1205 URL <http://dx.doi.org/10.1002/2013WR013796>
- 1206 [59] Kuzmin, D., 2010. A Guide to Numerical Methods for Transport Equa-
1207 tions. Friedrich-Alexander-Universität Erlangen-Nürnberg.
- 1208 [60] Labolle, E. M., Fogg, G. E., Tompson, A. F. B., 1996. Random-walk
1209 simulation of transport in heterogeneous porous media: Local mass-
1210 conservation problem and implementation methods. Water Resour.
1211 Res. 32 (3), 583–593.

- [61] Le Borgne, T., Dentz, M., Bolster, D., Carrera, J., de Dreuzy, J.-R., Bour, O., 2011. Persistence of incomplete mixing: A key to anomalous transport. *Phys. Rev. E* 84,, 015301(R).
- [62] Le Borgne, T., Dentz, M., Bolster, D., Carrera, J., De Dreuzy, J.-R., Davy, P., 2010. Non-Fickian mixing: Temporal evolution of the scalar dissipation rate in heterogeneous porous media. *Advances in Water Resources* 33 (12), 1468–1475.
- [63] Le Borgne, T., Dentz, M., Villermanx, E., 2013. Stretching, coalescence, and mixing in porous media. *Physical Review Letters* 110 (20), 204501.
- [64] Le Borgne, T., Ginn, T. R., Dentz, M., 2014. Impact of fluid deformation on mixing-induced chemical reactions in heterogeneous flows. *Geophysical Research Letters* 41 (22), 7898–7906.
URL <http://dx.doi.org/10.1002/2014GL062038>
- [65] Leonard, B., Jun. 1991. The ultimate conservative difference scheme applied to unsteady one-dimensional advection. *Computer Methods in Applied Mechanics and Engineering* 88 (1), 17–74.
URL <http://www.sciencedirect.com/science/article/pii/004578259190232U>
- [66] LeVeque, R. J., 1992. *Numerical Methods for Conservation Laws*, 2nd Edition. *Lectures in Mathematics*, ETH Zurich. Birkhauser Verlag.
- [67] LeVeque, R. J., 2002. *Finite Volume Methods for Hyperbolic Problems*. Cambridge University Press.
- [68] LeVeque, R. J., 2005. *Numerical Methods for Conservation Laws*, 2nd Edition. Birkhäuser.
- [69] Lichtner, P. C., Hammond, G. E., Lu, C., Karra, S., Bisht, G., Andre, B., Mills, R. T., Kumar, J., 2013. PFLOTRAN user manual. Tech. rep.
- [70] Lv, Y., Ihme, M., 2014. Discontinuous Galerkin method for multicomponent chemically reacting flows and combustion. *Journal of Computational Physics* 270, 105 – 137.
URL <http://www.sciencedirect.com/science/article/pii/S0021999114002101>

- 1242 [71] Maier, U., Bürger, C. M., 2013. An accurate method for transient par-
 1243 ticle tracking. *Water Resources Research* 49 (5), 3059–3063.
 1244 URL <http://dx.doi.org/10.1002/wrcr.20236>
- 1245 [72] Mansell, R. S., Ma, L., Ahuja, L. R., Bloom, S. A., 2002. Adaptive grid
 1246 refinement in numerical models for water flow and chemical transport
 1247 in soil florida agricultural exp. stn. journal series no. r-08979. 1.
 1248 URL <http://dx.doi.org/10.2136/vzj2002.2220>
- 1249 [73] Navarre-Sitchler, A. K., Maxwell, R. M., Siirila, E. R., Hammond,
 1250 G. E., Lichtner, P. C., 2013. Elucidating geochemical response of shal-
 1251 low heterogeneous aquifers to {CO₂} leakage using high-performance
 1252 computing: Implications for monitoring of {CO₂} sequestration.
 1253 *Advances in Water Resources* 53, 45 – 55.
 1254 URL <http://www.sciencedirect.com/science/article/pii/S0309170812002679>
- 1255 [74] Nitao, J. J., June 2000. Reference Manual for the NUFT Flow and
 1256 Transport Code, Version 3.0. Lawrence Livermore National Laboratory.
- 1257 [75] Oldenburg, C. M., Lewicki, J. L., Dobeck, L., Spangler, L., 2009. Mod-
 1258 eling gas transport in the shallow subsurface during the zert co₂ release
 1259 test. *Transport in Porous Media* 82 (1), 77–92.
 1260 URL <http://dx.doi.org/10.1007/s11242-009-9361-x>
- 1261 [76] Paster, A., Bolster, D., Benson, D. A., 2013. Particle tracking and the
 1262 diffusion-reaction equation. *Water Resour. Res.* 49, 1–6.
- 1263 [77] Paster, A., Bolster, D., Benson, D. A., Apr. 2014. Connecting the
 1264 dots: Semi-analytical and random walk numerical solutions of the
 1265 diffusion–reaction equation with stochastic initial conditions. *Journal*
 1266 *of Computational Physics* 263 (0), 91–112.
 1267 URL <http://www.sciencedirect.com/science/article/pii/S0021999114000473>
- 1268 [78] Pedretti, D., Fernández-Garcia, D., Sep. 2013. An automatic locally-
 1269 adaptive method to estimate heavily-tailed breakthrough curves from
 1270 particle distributions. *Advances in Water Resources* 59 (0), 52–65.
 1271 URL <http://www.sciencedirect.com/science/article/pii/S0309170813000869>
- 1272 [79] Pollock, D. W., 1988. Semianalytical computation of path lines for
 1273 finite-difference models. *Ground Water* 26 (6), 743–750.
 1274 URL <http://dx.doi.org/10.1111/j.1745-6584.1988.tb00425.x>

- 1275 [80] Porta, G., Ceriotti, G., Thovert, J.-F., 2016. Comparative assessment
1276 of continuum-scale models of bimolecular reactive transport in porous
1277 media under pre-asymptotic conditions. *Journal of Contaminant*
1278 *Hydrology* 185–186, 1 – 13.
1279 URL <http://www.sciencedirect.com/science/article/pii/S0169772215300474>
- 1280 [81] Prommer, H., August 2006. PHT3D: A Reactive Multicomponent
1281 Transport Model for Saturated Porous Media. <http://www.pht3d.org>.
- 1282 [82] Prommer, H., Barry, D., Davis, G., 2002. Modelling of physical and
1283 reactive processes during biodegradation of a hydrocarbon plume
1284 under transient groundwater flow conditions. *Journal of Contaminant*
1285 *Hydrology* 59 (1–2), 113 – 131, the 2000 Contaminated Site Remedia-
1286 tion Conference: From Source Zones to Ecosystems.
1287 URL <http://www.sciencedirect.com/science/article/pii/S0169772202000785>
- 1288 [83] Roe, P. L., Baines, M. J., 1982. Algorithms for advection and shock
1289 problems. In: Viviand, H. (Ed.), *Proc. 4th GAMM conference on Nu-*
1290 *merical Methods in Fluid Mechanics*.
- 1291 [84] Salamon, P., Fernández-Garcia, D., Gómez-Hernández, J. J., 2006.
1292 Modeling mass transfer processes using random walk particle track-
1293 ing. *Water Resour. Res.* 42 (11), W11417–.
1294 URL <http://dx.doi.org/10.1029/2006WR004927>
- 1295 [85] Salamon, P., Fernández-Garcia, D., Gómez-Hernández, J. J., 2006. A
1296 review and numerical assessment of the random walk particle tracking
1297 method. *Journal of Contaminant Hydrology* 87 (3–4), 277 – 305.
1298 URL <http://www.sciencedirect.com/science/article/pii/S0169772206000957>
- 1299 [86] Sanchez-Vila, X., Dentz, M., Donado, L. D., 2007. Transport-controlled
1300 reaction rates under local non-equilibrium conditions. *Geophysical Re-*
1301 *search Letters* 34 (10).
- 1302 [87] Sanchez-Vila, X., Fernández-Garcia, D., Guadagnini, A., 2010. Inter-
1303 pretation of column experiments of transport of solutes undergoing
1304 an irreversible bimolecular reaction using a continuum approximation.
1305 *Water Resources Research* 46 (12).
- 1306 [88] Schwede, R. L., Cirpka, O. A., Nowak, W., Neuweiler, I., 2008. Impact
1307 of sampling volume on the probability density function of steady state

- 1308 concentration. Water Resources Research 44 (12), W12433, w12433.
1309 URL <http://dx.doi.org/10.1029/2007WR006668>
- 1310 [89] Smolarkiewicz, P. K., 1984. A fully multidimensional positive definite
1311 advection transport algorithm with small implicit diffusion. Journal of
1312 Computational Physics 54 (2), 325 – 362.
1313 URL <http://www.sciencedirect.com/science/article/pii/0021999184901219>
- 1314 [90] Steefel, C. I., October 2009. CrunchFlow Software for Modeling Mul-
1315 ticomponent Reactive Flow and Transport CrunchFlow CRUNCH-
1316 FLOW, Software for Modeling Multicomponent Reactive Flow and
1317 Transport, USER’S MANUAL. Earth Sciences Division, Lawrence
1318 Berkeley National Laboratory, Berkeley, CA 94720 USA.
- 1319 [91] Steefel, C. I., Appelo, C. A. J., Arora, B., Jacques, D., Kalbacher, T.,
1320 Kolditz, O., Lagneau, V., Lichtner, P. C., Mayer, K. U., Meeussen, J.
1321 C. L., Molins, S., Moulton, D., Shao, H., Šimůnek, J., Spycher, N.,
1322 Yabusaki, S. B., Yeh, G. T., 2014. Reactive transport codes for sub-
1323 surface environmental simulation. Computational Geosciences 19 (3),
1324 445–478.
1325 URL <http://dx.doi.org/10.1007/s10596-014-9443-x>
- 1326 [92] Sweby, P. K., Oct. 1984. High resolution schemes using flux limiters
1327 for hyperbolic conservation laws. SIAM Journal on Numerical Analysis
1328 21 (5), 995–1011.
1329 URL <http://www.jstor.org/stable/2156939>
- 1330 [93] Tambue, A., Lord, G., Geiger, S., May 2010. An exponential integrator
1331 for advection-dominated reactive transport in heterogeneous porous
1332 media. Journal of Computational Physics 229 (10), 3957–3969.
1333 URL <http://www.sciencedirect.com/science/article/pii/S0021999110000604>
- 1334 [94] Tartakovsky, A. M., Meakin, P., Scheibe, T. D., Eichler West,
1335 R. M., 2007. Simulations of reactive transport and precipitation with
1336 smoothed particle hydrodynamics. Journal of Computational Physics
1337 222 (2), 654–672.
- 1338 [95] Tartakovsky, A. M., Tartakovsky, D. M., Scheibe, T. D., Meakin, P.,
1339 2008. Hybrid simulations of reaction-diffusion systems in porous media.
1340 SIAM Journal on Scientific Computing 30 (6), 2799–2816.

- 1341 [96] Thuburn, J., 1996. Multidimensional flux-limited advection schemes.
 1342 Journal of Computational Physics 123 (1), 74 – 83.
 1343 URL <http://www.sciencedirect.com/science/article/pii/S0021999196900066>
- 1344 [97] Tompson, A., Dougherty, D., JUL 1992. Particle-grid methods for re-
 1345 acting flows in porous-media with application to Fisher equation. Appl.
 1346 Math. Model. 16 (7), 374–383.
- 1347 [98] Toro, E. F., 2009. Riemann Solvers and Numerical Methods for Fluid
 1348 Dynamics, A Practical Introduction (3rd edition). Springer.
- 1349 [99] Van Dyke, M., 1975. Perturbation Methods in Fluid Mechanics.
 1350 Parabolic Press, Stanford.
- 1351 [100] van Leer, B., 1974. Towards the ultimate conservative difference
 1352 scheme. ii. Monotonicity and conservation combined in a second-order
 1353 scheme. J. Comput. Phys. 14, 361–370.
- 1354 [101] van Zon, J. S., ten Wolde, P. R., Apr. 2005. Simulating biochemical
 1355 networks at the particle level and in time and space: Green’s function
 1356 reaction dynamics. Phys. Rev. Lett. 94 (12), 128103–.
- 1357 [102] von Smoluchowski, M., 1917. Versuch einer mathematischen theorie der
 1358 koagulationskinetik kolloider lösungen. Z. Phys. Chem 92, 124–168.
- 1359 [103] Werth, C. J., Cirpka, O. A., Grathwohl, P., 2006. Enhanced mixing and
 1360 reaction through flow focusing in heterogeneous porous media. Water
 1361 Resources Research 42 (12), W12414, w12414.
 1362 URL <http://dx.doi.org/10.1029/2005WR004511>
- 1363 [104] White, M., Oostrom, M., October 1997. STOMP, Subsurface Transport
 1364 Over Multiple Phases. Pacific Northwest National Laboratory, Rich-
 1365 land, WA, report pnsl-11218 Edition.
- 1366 [105] Wolfsberg, A. V., Freyberg, D. L., 1994. Efficient simulation of single
 1367 species and multispecies transport in groundwater with local adaptive
 1368 grid refinement. Water Resources Research 30 (11), 2979–2991.
 1369 URL <http://dx.doi.org/10.1029/93WR02749>

- 1370 [106] Xu, T., Sonnenthal, E., Spycher, N., Zheng, L., June 2014.
 1371 TOUGHREACT V3.0-OMP Reference Manual: A Parallel Simula-
 1372 tion Program for Non-Isothermal TOUGHREACT V3.0-OMP Ref-
 1373 erence Manual: A Parallel Simulation Program for Non-Isothermal
 1374 Multiphase Geochemical Reactive Transport. Earth Sciences Divi-
 1375 sion, Lawrence Berkeley National Laboratory University of California,
 1376 Berkeley, CA 94720, draft Edition.
- 1377 [107] Yeh, G.-T., Sun, J., Jardine, P. M., Burgos, W. D., Fang, Y., Li,
 1378 M.-H., Siegel, M. D., May 2004. HYDROGEOCHEM 5.0: A Three-
 1379 Dimensional Model of Coupled Fluid Flow, Thermal Transport, and
 1380 HYDROGEOCHEMical Transport through Variably Saturated Con-
 1381 ditions: Version 5.0. OAK RIDGE NATIONAL LABORATORY.
- 1382 [108] Zhang, Y., Benson, D. A., Meerschaert, M. M., LaBolle, E. M., Scheff-
 1383 fler, H.-P., AUG 2006. Random walk approximation of fractional-order
 1384 multiscaling anomalous diffusion. Phys. Rev. E 74 (2, Part 2).
- 1385 [109] Zheng, C., Wang, P. P., 1999. MT3DMS: A Modular Three-
 1386 Dimensional Multispecies Transport Model for simulation of advection,
 1387 dispersion and chemical reactions of contaminants in groundwater sys-
 1388 tems; documentation and user's guide. U.S. Army Engineer Research
 1389 and Development Center, Vicksburg, MS, contract report serdp-99-1
 1390 Edition.
- 1391 [110] Zyvoloski, G., 1997. Summary of the Models and Methods for the
 1392 FEHM Application – A Finite-Element Heat- and Mass-Transfer Code.
 1393 Los Alamos National Laboratory Tables, Los Alamos, NM 87545,
 1394 United States.