

1 **A KDE-based random walk method for modeling reactive transport with complex**
2 **kinetics in porous media**

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12 **Key points**

- 13 • A Random Walk Particle Tracking Method capable to simulate reactions with
14 complex kinetics is presented
- 15 • Particles are equipped with optimal kernels to represent the uncertainty in the
16 particle position driven by subsampling a large population
- 17 • The method is implemented in a column transport model and tested for four
18 different reactive transport case examples

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23 **Abstract**

24 In recent years a large body of literature has been devoted to study reactive transport of
25 solutes in porous media based on pure Lagrangian formulations. Such approaches have
26 also been extended to accommodate second-order bimolecular reactions, in which the
27 reaction rate is proportional to the concentrations of the reactants. Rather, in some cases,
28 chemical reactions involving two reactants follow more complicated rate laws. Some
29 examples are (1) reaction rate laws written in terms of powers of concentrations, (2)
30 redox reactions incorporating a limiting term (e.g. Michaelis-Menten), or (3) any
31 reaction where the activity coefficients vary with the concentration of the reactants, just
32 to name a few. We provide a methodology to account for complex kinetic bimolecular
33 reactions in a fully Lagrangian framework where each particle represents a fraction of
34 the total mass of a specific solute. The method, built as an extension to the second-order
35 case, is based on the concept of optimal Kernel Density Estimator, which allows the
36 concentrations to be written in terms of particle locations, hence transferring the concept
37 of reaction rate to that of particle location distribution. By doing so, we can update the
38 probability of particles reacting without the need to fully reconstruct the concentration
39 maps. The performance and convergence of the method is tested for several illustrative
40 examples that simulate the Advection-Dispersion-Reaction Equation in a 1D
41 homogeneous column. Finally, a 2D example of application is presented evaluating the
42 need of fully describing non-linear chemical kinetics in a randomly heterogeneous
43 porous medium.

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46 **Index terms:** Groundwater Transport (1832), Computational Hydrology (1805),
47 Stochastic Hydrology (1869), Modeling (1847), Geochemical Modeling (1009)

48 **Keywords:** Reactive transport, complex kinetics, porous media, random walk, particle
49 tracking, Kernel Density Estimators

1. Introduction

Random Walk Particle Tracking Methods (RWPTMs) offer a convenient Lagrangian numerical approach to simulate solute transport in porous media. RWPTMs have been demonstrated to be particularly efficient in dealing with aquifer heterogeneities and non-reactive transport involving a large variety of complex processes such as non-Fickian transport and multiple porosity systems [Wen and Gómez-Hernández, 1996; LaBolle *et al.*, 1996; Sanchez-Vila and Solis-Delfin, 1999; Salamon *et al.*, 2006a, 2006b; Riva *et al.*, 2008; Delay and Bodin, 2001; Cvetkovic and Haggerty, 2002; Berkowitz *et al.*, 2006; Zhang and Benson, 2008; Dentz and Castro, 2009; Benson and Meerschaert, 2009; Tsang and Tsang, 2001; Huang *et al.*, 2003; Willmann *et al.*, 2013; Henri and Fernández-García, 2014, 2015]. This family of methods essentially consist of discretizing the solute mass (existing initially or injected through the boundaries with time) into a finite number of particles, each representing a fraction of the total mass, and then moving such particles according to simple relationships that represent the transport mechanisms considered (e.g., advection, dispersion or diffusion into stagnant zones). RWPTMs are mass conservative by construction, and avoid some of the inherent numerical difficulties associated with Eulerian approaches, i.e., numerical dispersion and oscillations [Salamon *et al.*, 2006a; Benson *et al.*, 2017].

However, several disadvantages have prevented the general use of RWPTMs in reactive transport problems with few limited exceptions. The main roadblock is that most chemical reactions are written in terms of concentrations (or chemical activities), which are not directly accessible at any given time, unless previously reconstructed from discrete particle information. At this stage, one needs to keep in mind that a naive reconstruction, such as the use of histograms, is an error prone process that can lead to

75 spurious fluctuations [e.g., *Boso et al.*, 2013]. Consequently, as concentrations - and in
76 some cases their gradients [e.g., *De Simoni et al.*, 2007] - are reaction drivers, errors can
77 propagate to reaction rates. Albeit recent works [*Fernàndez-Garcia and Sanchez-Vila*,
78 2011; *Pedretti and Fernàndez-Garcia*, 2013; *Schmidt et al.*, 2017] have shown that the
79 spurious fluctuations of the concentrations reconstructed from particles can be largely
80 minimized by using a post-processing analysis based on kernels, modeling complex
81 reactive transport problems with RWPTMs is still a challenge.

82

83 The focus of this paper is on kinetic chemical reactions. In this context, several methods
84 have been proposed in the literature to simulate reactive transport with RWPTMs.
85 Simple linear kinetic reactive transport problems such as first-order network reactions
86 and slow sorption can easily be treated with transition probabilities, without having to
87 estimate the concentrations during the course of the simulations [e.g., *Kinzelbach*, 1987;
88 *Andricevic and Foufoula-Georgiou*, 1991; *Michalak and Kitanidis*, 2000; *Henri and*
89 *Fernàndez-Garcia*, 2014, 2015]. Reconstruction here is an efficient post-processing tool
90 with little drawbacks.

91

92 However, the incorporation of non-linear chemical reactions involving more than one
93 chemical species into the RWPTM is remarkably cumbersome. In this case, one needs
94 to either re-estimate solute concentrations at any given time step or to use particle
95 proximity relationships. Both these approaches present important disadvantages, which
96 have hindered the widespread use of RWPTMs – since the most common processes in
97 geochemistry and biogeochemistry are complex, being non-linear, multi-species and
98 affected by water-rock interaction. The first approach is a hybrid Lagrangian-Eulerian
99 method by which reaction rates are determined from concentrations. Here, a

100 compromise between CPU time and the back and forth transformation of particles to
101 concentrations is necessary [Tompson, 1993; Tompson et al., 1996; Cui et al., 2014]; as
102 aforementioned, this process is either error-prone or computationally expensive. The
103 second approach is purely Lagrangian, and sophisticated search algorithms are needed
104 to calculate proximity relationships [Paster et al., 2014]. Along this line, Benson and
105 Meerschaert [2008] studied a simple bimolecular system ($A + B \rightarrow C$) with second-
106 order kinetics, and found that the probability of reaction of two isolated particles
107 depends on both thermodynamics and the probability of collocation of two particles.
108 Paster et al. [2013, 2014] extended these concepts to higher dimensions, and Ding and
109 Benson [2015] used this bimolecular type of reaction as a building block to simulate the
110 Michaelis-Menten enzyme kinetic model. Rahbaralam et al. [2015] demonstrated that
111 the support volume of particles in the probability of collocation can be determined by
112 using an optimal kernel bandwidth approach. This method speeds up the algorithm and
113 avoids incomplete mixing due to the use of a limited number of particles. A first field
114 application of the Benson and Meerschaert [2008] method has been recently presented
115 by Ding et al. [2017], who simulated the degradation of Carbon Tetrachloride at the
116 Schoolcraft, MI site, under anaerobic conditions. All existing variations of this method
117 share an important limitation: they can only reproduce second-order kinetics, with the
118 exception of those complex reactions that can be modeled as a combination of first-
119 order monomolecular reactions and second-order bimolecular reactions, such as the
120 aforementioned Michaelis-Menten enzyme kinetic model.

121

122 In some other Lagrangian approaches such as SPH [e.g. Tartakowsky and Meakin.
123 2005; Tartakovsky et al., 2007; Herrera et al., 2009, 2017] each particle represents a
124 volume of fluid, so concentrations are directly attributed to particles and

125 diffusion/dispersion is simulated by exchanging mass between particles. A similar
126 approach was used by *Benson and Bolster* [2016] to propose a particle tracking method
127 for the simulation of chemical reactions of arbitrary complexity, based on mass
128 exchange between particles which could contain any variety of chemical compounds.
129 *Engdahl et al.* [2017] recently generalized the capabilities of the method by coupling it
130 to the reaction engine PhreeqcRM [*Parkhurst and Wissmeier, 2015*]. Each particle can
131 be seen as a mobile bin containing a fixed volume of water, and reactions occur inside
132 particles according to the particle-specific solute concentrations. Some limitations can
133 be attributed to these kind of methods. For instance, one needs to artificially inject
134 empty particles in places where solutes can potentially diffuse, or to add immobile
135 particles and use very small time steps to represent linear sorption.

136

137 Most of these approaches to Lagrangian modeling of reactive transport use kernel
138 functions to account for either dispersion or reaction between particles. Kernels have
139 also been widely used in other fields of science like fluid mechanics [e.g., *Wu and Li,*
140 *2007; Yue et al., 2004*], computer vision and image processing [e.g., *Chang and Ansari,*
141 *2005; Stoessel and Sagerer, 2006; Takeda et al., 2007*], or 3D animation [e.g., *Ihmsen et*
142 *al., 2011*], just to name a few.

143

144 In this paper, we propose a new random walk particle tracking method capable of
145 simulating different sorts of complex kinetic reactions occurring between two reactants
146 (thus generalizing the existing methods to simulate second-order kinetics), while
147 maintaining the classical interpretation of a particle (a fraction of the total mass of a
148 given species). To simulate reactions, we determine the probability that any particle
149 reacts based on particle interactions, the reaction rate law and the stoichiometry. The

150 idea behind the proposed method is to equipped each particle with an optimal kernel
151 function that defines the particle support [*Fernàndez-Garcia and Sanchez-Vila, 2011;*
152 *Rahbaralam et al., 2015*] from the beginning of the simulation. For convenience,
153 complex reaction rates are expressed as the product of a second-order bimolecular
154 reaction and a compensation function (g) that depends on the reactant concentrations.
155 An approximate solution of the probability of reaction is then determined, providing a
156 fully Lagrangian approach that does not entail any kind of spatial discretization. The
157 probability of reaction is demonstrated to depend on the particle interaction, expressed
158 as the volume integral of the product between particle kernel functions, and on the
159 point-value of g at a weighted mid-position between the two particles.

160

161 We then show four example column transport (1D) applications to illustrate the
162 performance and the convergence of the method as a function of the initial number of
163 particles for different chemical systems. To achieve this, the random walk particle
164 tracking solution is compared with a highly-discretized finite difference solution that is
165 assumed to represent the exact solution. The four examples represent a wide sample of
166 the most common problems in biogeochemistry: two examples of non-linear aqueous
167 reactions and two examples of non-linear reactions considering the water-rock
168 interaction. Finally, a 2D example of application is presented evaluating the need of
169 fully describing non-linear chemical kinetics in a randomly heterogeneous porous
170 medium.

171

172 Although the example applications are 1D or 2D reactive transport problems in
173 stationary flow, the proposed method has no limitations regarding the number of spatial
174 dimensions or the effect of variable velocity with time (full 4D).

175

176 2. Second-order kinetic reactions

177 In order to lay the groundwork for the implementation of arbitrarily complex kinetic
178 reactions, we start by reviewing some concepts and then reformulating the mathematical
179 expressions corresponding to second-order bimolecular reactions. Let us consider a
180 simple bimolecular irreversible reaction $\alpha A + \beta B \rightarrow \gamma C$ with a reaction rate
181 proportional to the concentration of both reactants,

$$r(\mathbf{x}, t) = k_f c_A(\mathbf{x}, t) c_B(\mathbf{x}, t), \#(1)$$

182 where c_s is the concentration of the s th-species $\{s = A, B, C\}$, k_f is the forward reaction
183 coefficient, $\{\alpha, \beta, \gamma\}$ are the stoichiometric coefficients, and $r(\mathbf{x}, t)$ is the reaction rate at
184 the \mathbf{x} location and time t , defined as:

$$r(\mathbf{x}, t) = \frac{1}{\gamma} \frac{dc_C}{dt} = -\frac{1}{\alpha} \frac{dc_A}{dt} = -\frac{1}{\beta} \frac{dc_B}{dt} \#(2)$$

185 We refer to chemical reactions that follow equation (1) as second-order kinetic
186 reactions, also implying that the reaction is of first-order with respect to each reactant.

187 Although here we study an irreversible reaction, reversibility can be modeled as a
188 combination of a forward reaction and a backward reaction. Further details are given at
189 the end of section 3.

190

191 2.1. The particle pair annihilation method

192 *Benson and Meerschaert* [2008] found that this problem could be solved by simply
 193 analyzing how two isolated A and B particles react to form a C particle when $\alpha = \beta =$
 194 1. Although the original expression was developed for a general application, here we
 195 present it incorporating explicitly the effect of porosity for the particular case of porous
 196 media. In one dimension, the probability of reaction of these two particles in a given
 197 time interval Δt is given by the expression,

$$P(A \rightarrow C, \Delta t) = \phi^{-1} k_f \Delta t m \frac{1}{\sqrt{4\pi h^2}} \exp\left(-\frac{(X_A - X_B)^2}{4h^2}\right), \#(3)$$

198 which is obtained as the product of the probability that the two particles will occupy the
 199 same differential volume times the conditional probability that, upon collocation, the
 200 particles will react during the time step Δt . Equation (3) is written in terms of the
 201 particle mass m (or amount of substance, depending on how k_f is defined; thus, in this
 202 work the term *particle mass* is used in a general sense). Here, the mass of all particles is
 203 assumed equal to $m = \frac{\Omega \phi [A]_0}{N_0}$, where Ω is the initial volume occupied by the injected
 204 particles, ϕ is porosity, $[A]_0$ is the initial concentration of species A, and N_0 the number
 205 of A particles injected. Finally, $h = \sqrt{2D\Delta t}$ is the length of influence of one particle
 206 defined only in terms of local diffusion and/or dispersion.

207

208 Once the probability of reaction of two particles is calculated, chemical reactions in the
 209 random walk method can be incorporated by particle annihilation, i.e., when two
 210 particles react, they disappear. This means that the number of particles of the reactant
 211 species decreases as the simulation progresses, and numerical resolution problems may
 212 arise at low concentrations. This limitation was addressed by *Bolster et al.* [2016], who

213 showed that a change in the particle mass is also a valid alternative to particle
214 annihilation.

215

216 There is another strong limitation in the particle pair annihilation method. Chemical
217 reactions depend on the activities of the reactants rather than on their concentrations.
218 Thus, the aforementioned approach cannot reproduce second-order reactions correctly
219 unless the ionic strength is not affected by the reaction or its effect on the activity
220 coefficients is negligible. This is particularly relevant when modelling reactions that
221 have an important impact on the ionic strength of the solution.

222

223 **2.2. The optimal kernel approach**

224 **2.2.1 Representation of a particle**

225 The RWPTM satisfies the transport equation in the limit when the number of particles
226 approaches infinity. Considering that each i th particle associated with species s at time t
227 is located at a point \mathbf{X}_s^i , and that no size is attributed to it, its spatial distribution can be
228 expressed as a Dirac delta distribution and then the concentration of a given species can
229 be written formally as,

$$c_s(\mathbf{x}, t) = \frac{1}{\phi(\mathbf{x})} \sum_{i=1}^{n_s} m_s^i E \left\{ \delta \left(\mathbf{x} - \mathbf{X}_s^i(t) \right) \right\}, \#(4)$$

230 where m_s^i is the mass of the i th particle of species s , $\phi(\mathbf{x})$ is the location dependent
231 porosity, and $E\{\cdot\}$ is the expectation operator over all particle realizations. The
232 expectation of the Dirac delta function is the probability density function (pdf) of the
233 particle position, $p_s^i(\mathbf{x}; t)$. In practice, simulations cannot use an infinite number of

234 particles and the inference of $p_s^i(\mathbf{x}; t)$ becomes the Achilles heel of all random walk
 235 methods. Typically, the concentration field is estimated by averaging the mass over a
 236 fixed support volume $V(\mathbf{x})$ centered at the \mathbf{x} location. This can be achieved by counting
 237 the mass of particles in fixed bins or by projection functions [*Tompson and Gelhar,*
 238 *1990; Tompson et al., 1996*]. However, these methods suffer from the same problems as
 239 those associated with the estimation of pdfs through histograms, i.e., results depend on
 240 the discretization of the domain or the bin size.

241

242 An alternative approach was introduced by *Fernàndez-Garcia and Sanchez-Vila* [2011].
 243 The method recognizes the uncertainty associated with subsampling an infinite number
 244 of particles by equipping each particle with a pdf (the kernel function). The estimation
 245 of concentrations can then be written as a direct extension of (4),

$$c_s(\mathbf{x}, t) = \frac{1}{\phi(\mathbf{x})} \sum_{i=1}^{n_s} m_s^i W(\mathbf{x} - \mathbf{X}_s^i; \mathbf{H}_s), \#(5)$$

246 where \mathbf{H}_s is the kernel bandwidth matrix associated to species s and $W(\mathbf{u}; \mathbf{H})$ is the
 247 scaled kernel function, for which several shapes have been suggested, the most common
 248 one being the Gaussian kernel function,

$$W(\mathbf{u}; \mathbf{H}) = (2\pi)^{-\frac{d}{2}} |\mathbf{H}|^{-\frac{1}{2}} \exp\left(-\frac{1}{2} \mathbf{u}^T \mathbf{H}^{-1} \mathbf{u}\right), \#(6)$$

249 where d is the space dimension. In the Gaussian kernel (6), the bandwidth matrix is the
 250 covariance matrix. Expression (5) is valid for an infinite domain or away from the
 251 domain boundaries. The particular treatment of boundaries is discussed in the
 252 subsequent sections. Note that the concentration of a given species at any given \mathbf{x}
 253 location does not depend only on the subset of particles falling into an arbitrary bin, but

254 on all existing particles associated with that species. Assuming that $\mathbf{H}_s = h_s^2 \mathbf{I}_d$ (we will
 255 refer to this case later as the isotropic kernel) the optimal bandwidth h_s associated with
 256 a given species s (also denoted as particle support) can be determined based on the
 257 amount of particles n_s and their distribution in space, by minimizing the Asymptotical
 258 Mean Integrated Squared Error (*A-MISE*). This is a well-known procedure in statistics
 259 [e.g., *Silverman*, 1986; *Härdle*, 1991]. For a second-order kernel,

$$h_s = \left(\frac{d R(W)}{R(\nabla^2 p_s) \mu_2^2(W) n_s} \right)^{\frac{1}{d+4}}, \#(7)$$

260 where R is the L_2 norm of a function, μ_2 is the second moment, and p_s is the normalized
 261 concentration,

$$p_s(\mathbf{x}, t) = \frac{c_s(\mathbf{x}, t)}{\int_{\Omega^d} c_s(\mathbf{x}, t) d\mathbf{x}}, \#(8)$$

262 where Ω^d is the d -dimensional domain of the model. Note that, in this setup, the
 263 estimation of c_s is not explicit, i.e. the estimator (7) depends circularly on the estimation
 264 (5). Hence, one needs to either use an iterative method or make an assumption on the
 265 approximate shape of the particle plume. The former approach can be computationally
 266 intensive, whereas the latter can lead to a suboptimal bandwidth choice, hindering the
 267 convergence rate of the estimation with respect to the number of particles. We refer to
 268 *Engel et al.* [1994] for details on the calculation of h_s . Since p_s in RWPTMs changes
 269 over time, the kernel bandwidth matrix \mathbf{H}_s is a time-dependent variable that not only
 270 accounts for local diffusion and/or dispersion but also for the spreading and stretching
 271 of each particle plume. This approach has been used in subsurface hydrology to
 272 reconstruct key variables associated with a wide variety of problems, e.g., reaction rates
 273 and mixing measures [*Fernàndez-Garcia and Sanchez-Vila*, 2011], power-law tailing in

274 breakthrough curves [Pedretti and Fernàndez-Garcia, 2013], and human health risk
275 estimates [Siirila-Woodburn et al., 2015].

276

277 **2.2.2. The probability of reaction of a particle**

278 This section derives the probability of reaction of a given particle for a second order
279 reaction with arbitrary stoichiometric coefficients. For the derivation, we assume that
280 the problem domain Ω^d is infinite, so expression (5) is valid at any location. At the end
281 of section 3 it is discussed how the methodology can be adapted to simulate reactions
282 near the boundaries of a finite domain. The chemical reaction is still represented by
283 $\alpha A + \beta B \rightarrow \gamma C$ and the reaction rate follows equation (1). The probability that a particle
284 reacts in the time interval $[t, t + \Delta t]$ can be simply expressed as mass consumed per
285 unit of mass,

$$P(A^i \rightarrow C^k, \Delta t) = -\frac{\Delta m_A^i}{m_A^i}, \#(9)$$

$$P(B^j \rightarrow C^k, \Delta t) = -\frac{\Delta m_B^j}{m_B^j}. \#(10)$$

286 Here, A^i refers to the i th-particle associated with species A, $P(A^i \rightarrow C^k, \Delta t)$ is the
287 probability that A^i is transformed into a new particle C^k in the time interval Δt , and
288 Δm_A^i is the increment of mass of the particle A^i due to the chemical reaction. This
289 relationship was used by Salamon et al. [2007] and Henri and Fernàndez-Garcia [2014,
290 2015] to develop particle transition probabilities for modeling solute transport with
291 multi-rate mass transfer and network reactions. From the definition of reaction rate
292 given in (2), expressions (9) and (10) can be rewritten as:

$$P(A^i \rightarrow C^k, \Delta t) = \frac{\alpha}{m_A^i} \int_t^{t+\Delta t} \int_{\Omega^d} \phi r_A^i(\mathbf{x}, t') d\mathbf{x} dt' \approx \frac{\alpha}{m_A^i} \Delta t \int_{\Omega^d} \phi r_A^i(\mathbf{x}, t) d\mathbf{x}, \#(11)$$

$$P(B^j \rightarrow C^k, \Delta t) = \frac{\beta}{m_B^j} \int_t^{t+\Delta t} \int_{\Omega^d} \phi r_B^j(\mathbf{x}, t') d\mathbf{x} dt' \approx \frac{\beta}{m_B^j} \Delta t \int_{\Omega^d} \phi r_B^j(\mathbf{x}, t) d\mathbf{x}, \#(12)$$

293 where $r_A^i(\mathbf{x}, t)$ and $r_B^j(\mathbf{x}, t)$ are particle reaction rates. The products $\alpha r_A^i(\mathbf{x}, t)$ and
 294 $\beta r_B^j(\mathbf{x}, t)$ define the amount of particle mass consumed per unit volume of liquid in a
 295 unit of time. The particle reaction rates can be derived as it follows. Substituting (5) into
 296 (1), it is possible to find an expression of the total chemical reaction rate as a function of
 297 particle kernel distributions,

$$r(\mathbf{x}, t) = \frac{k_f}{\phi^2} \sum_{i=1}^{n_A} \sum_{j=1}^{n_B} m_A^i m_B^j W(\mathbf{x} - \mathbf{X}_A^i; \mathbf{H}_A) W(\mathbf{x} - \mathbf{X}_B^j; \mathbf{H}_B). \#(13)$$

298 The reaction rate of any particle A^i or B^j is determined, respectively, from the
 299 interaction of A^i with all existing B-particles and the interaction of B^j with all existing
 300 A-particles. Thus, the total reaction rate can be decomposed as

$$r(\mathbf{x}, t) = \sum_{i=1}^{n_A} r_A^i(\mathbf{x}, t) = \sum_{j=1}^{n_B} r_B^j(\mathbf{x}, t), \#(14)$$

301 where

$$r_A^i(\mathbf{x}, t) = \frac{k_f}{\phi^2} m_A^i \sum_{j=1}^{n_B} m_B^j W(\mathbf{x} - \mathbf{X}_A^i; \mathbf{H}_A) W(\mathbf{x} - \mathbf{X}_B^j; \mathbf{H}_B), \#(15)$$

$$r_B^j(\mathbf{x}, t) = \frac{k_f}{\phi^2} m_B^j \sum_{i=1}^{n_A} m_A^i W(\mathbf{x} - \mathbf{X}_A^i; \mathbf{H}_A) W(\mathbf{x} - \mathbf{X}_B^j; \mathbf{H}_B). \#(16)$$

302 Each term in the summation represents the interaction between two individual particles
 303 A^i and B^j . In the particular case of a Gaussian kernel function, the kernel product can be
 304 rewritten as

$$W(\mathbf{x} - \mathbf{X}_A^i; \mathbf{H}_A) W(\mathbf{x} - \mathbf{X}_B^j; \mathbf{H}_B) = W(\mathbf{x} - \mathbf{X}_{AB}^{ij}; \mathbf{H}_{AB}) W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B), \#(17)$$

305 where

$$\mathbf{H}_{AB} = (\mathbf{H}_A^{-1} + \mathbf{H}_B^{-1})^{-1}, \#(18)$$

$$\mathbf{X}_{AB}^{ij} = \mathbf{H}_{AB}(\mathbf{H}_A^{-1}\mathbf{X}_A^i + \mathbf{H}_B^{-1}\mathbf{X}_B^j), \#(19)$$

306 which means that the product of two Gaussian kernel density functions associated with
 307 particles A^i and B^j is proportional to another Gaussian kernel function centered at \mathbf{X}_{AB}^{ij}
 308 with a covariance matrix \mathbf{H}_{AB} . Figure 1 illustrates this equivalence in one dimension.
 309 This indicates that the reaction between two individual particles is occurring mostly
 310 around \mathbf{X}_{AB}^{ij} . The second kernel function on the right hand side of (17) is a constant
 311 scaling factor that only depends on the separation between particles.

312

313 In the case where \mathbf{H}_A and \mathbf{H}_B are isotropic ($\mathbf{H}_s = h_s^2 \mathbf{I}_d$), then it derives from (18) that
 314 \mathbf{H}_{AB} is also isotropic ($\mathbf{H}_{AB} = h_{AB}^2 \mathbf{I}_d$) and

$$h_{AB} = \sqrt{\frac{h_A^2 h_B^2}{h_A^2 + h_B^2}} \#(20)$$

315 is proportional to the harmonic mean of the squares of h_A, h_B . As aforementioned, \mathbf{X}_{AB}^{ij}
 316 is the position with maximum probability density of collocation of particles A^i and B^j ;
 317 in the isotropic case, expression (19) can be rewritten so that \mathbf{X}_{AB}^{ij} is simply the mid-

318 position of the particle pair weighted by their corresponding squared particle support,
 319 i.e.,

$$\mathbf{X}_{AB}^{ij} = \frac{\mathbf{X}_A^i h_B^2 + \mathbf{X}_B^j h_A^2}{h_A^2 + h_B^2}. \#(21)$$

320 In order to integrate expressions (11) and (12), we assume a locally constant porosity
 321 over the kernel product support centered at \mathbf{X}_{AB}^{ij} and represented by \mathbf{H}_{AB} . By
 322 substituting (15) and (16) into (11) and (12) respectively and integrating, we finally
 323 obtain that

$$P(A^i \rightarrow C^k, \Delta t) = \frac{\alpha k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{j=1}^{n_B} m_B^j W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B), \#(22)$$

$$P(B^j \rightarrow C^k, \Delta t) = \frac{\beta k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{i=1}^{n_A} m_A^i W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B). \#(23)$$

324 In the particular one-dimensional case where only one particle of each reactant is
 325 present, porosity ϕ is constant in space, $\alpha = \beta = 1$, $H_A = H_B = h^2$, and all particles
 326 share the same mass m , we have

$$P(A \rightarrow C, \Delta t) = P(B \rightarrow C, \Delta t) = \frac{k_f}{\phi} \Delta t m \frac{1}{\sqrt{4\pi h^2}} \exp\left(-\frac{(x_A - x_B)^2}{4h^2}\right), \#(24)$$

327 and we directly recover the probability of reaction between two isolated particles
 328 obtained by *Benson and Meerschaert* [2008]. We note that h in (24) is not $h = \sqrt{2D\Delta t}$
 329 but rather it is defined as an optimal kernel support that changes with time according to
 330 the number of particles remaining and the actual shape of the solute plume. We claim
 331 that this difference in the definition of h is very significant. *Benson and Meerschaert*
 332 [2008] simulate incomplete mixing by using a low number of uniform- randomly
 333 distributed particles, which limits the reaction rate after some time as the A-particles

334 become isolated from the B-particles (described by the authors as “islands of particles”).
 335 Along the same line, *Paster et al.* [2013, 2014] derive a relationship between the initial
 336 particle density and the noise of the initial condition, suggesting that the simulation of
 337 smoother initial conditions requires a higher number of particles. In contrast,
 338 *Rahbalaram et al.* [2015] show that using the adaptive kernel makes it possible to
 339 highly reduce the dependence of the numerical solution on the number of particles.
 340 Another important difference between the two approaches becomes evident when more
 341 than one particle of each reactant is present. In this case, the probability of reaction of a
 342 particle given by (22) or (23) can be seen as the sum of independent particle pair
 343 interactions. This is only satisfied by the particle pair annihilation method in the limit
 344 when $\Delta t \rightarrow 0$. Otherwise, the reaction between two particles is not a disjoint event.
 345 Section 4 provides the details of the new particle tracking algorithm.

346

347 **3. Extension to kinetic reactions with arbitrary reaction rate laws**

348 The challenge in extending second-order reactions to arbitrary reaction rate laws resides
 349 in that now the total reaction rate cannot be simply split into combinations of kernel
 350 functions between particle pairs. Consequently, the rate at which two particles react
 351 depends also on all other surrounding particles. In this case, without any loss of
 352 generality, it is convenient to represent the total reaction rate as the product of a second-
 353 order reaction times g , a function of any arbitrary shape involving the reactants’
 354 concentrations, and denoted as compensation function,

$$r(\mathbf{x}, t) = k_f c_A(\mathbf{x}, t) c_B(\mathbf{x}, t) g(c_A(\mathbf{x}, t), c_B(\mathbf{x}, t)). \#(25)$$

355 Applying $g = 1$ implies recovering (1). Substituting (5) into (25), and then
 356 decomposing as in (14) and substituting into (11) and (12), we now have,

357

$$P(A^i \rightarrow C^k, \Delta t) =$$

$$\frac{\alpha k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{j=1}^{n_B} m_B^j W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B) \int_{\Omega^d} W(\mathbf{x} - \mathbf{X}_{AB}^{ij}; \mathbf{H}_{AB}) g(c_A(\mathbf{x}, t), c_B(\mathbf{x}, t)) d\mathbf{x}, \#(26)$$

358

$$P(B^j \rightarrow C^k, \Delta t) =$$

$$\frac{\beta k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{j=1}^{n_A} m_A^j W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B) \int_{\Omega^d} W(\mathbf{x} - \mathbf{X}_{AB}^{ij}; \mathbf{H}_{AB}) g(c_A(\mathbf{x}, t), c_B(\mathbf{x}, t)) d\mathbf{x}, \#(27)$$

359

360 Because the compensation function $g(\mathbf{x}, t)$ depends on \mathbf{x} in a complex manner, the
 361 integration of (26) and (27) is no longer direct. To overcome this problem, we
 362 approximate this integral by localizing the function $g(\mathbf{x}, t)$ about the point $\mathbf{x} = \mathbf{X}_{AB}^{ij}$,
 363 i.e., at the centroid of the kernel product (see figure 1), using a truncated first-order
 364 Taylor series expansion (i.e., linearizing it in terms of location),

$$g(\mathbf{x}, t) \cong g(\mathbf{X}_{AB}^{ij}, t) + \nabla g(\mathbf{X}_{AB}^{ij}, t)^T (\mathbf{x} - \mathbf{X}_{AB}^{ij}) \#(28)$$

365 The validity of this approximation is subjected to the significance of higher order terms
 366 of g over the kernel product domain represented by \mathbf{H}_{AB} . Note that the truncation error
 367 will always converge towards zero with an increasing number of particles, namely, as
 368 \mathbf{H}_{AB} approaches the Dirac delta. Introducing (28) into (26) and (27), and given that the
 369 first moment of the kernel about its centroid equals zero, we obtain

$$P(A^i \rightarrow C^k, \Delta t) =$$

$$\frac{\alpha k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{j=1}^{n_B} m_B^j W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B) g(c_A(\mathbf{X}_{AB}^{ij}, t), c_B(\mathbf{X}_{AB}^{ij}, t)), \#(29)$$

$$P(B^j \rightarrow C^k, \Delta t) = \frac{\beta k_f}{\phi(\mathbf{X}_{AB}^{ij})} \Delta t \sum_{i=1}^{n_A} m_A^i W(\mathbf{X}_A^i - \mathbf{X}_B^j; \mathbf{H}_A + \mathbf{H}_B) g(c_A(\mathbf{X}_{AB}^{ij}, t), c_B(\mathbf{X}_{AB}^{ij}, t)). \#(30)$$

370 The evaluation of $g(c_A(\mathbf{X}_{AB}^{ij}, t), c_B(\mathbf{X}_{AB}^{ij}, t))$ in (29) and (30) requires an approximate
 371 solution of the concentrations of the species A and B at the specific location \mathbf{X}_{AB}^{ij} . One
 372 possibility is to estimate these concentrations directly using the kernel estimator given
 373 in (5). However, this would require an excessive amount of calculations. To minimize
 374 CPU time, here we estimated these concentrations as a linear interpolation of the
 375 concentrations obtained only at the particle positions, estimated a priori by (5). This is
 376 possible as long as \mathbf{X}_A , \mathbf{X}_{AB} and \mathbf{X}_B are aligned, i.e., \mathbf{H}_A and \mathbf{H}_B are isotropic, a
 377 condition that is inherently true in one dimension. This approach constitutes a
 378 simplification, and therefore it introduces some error in the solution. In the subsequent
 379 sections, we show that this error is small for a relatively low number of particles
 380 injected.

381

382 In the case where the reaction is reversible, it can be solved by combination of a
 383 forward and a backward reaction probability [*Benson and Meerschaert, 2008*]. For
 384 example, if the backward reaction is a first-order decay, i.e.,

$$\frac{1}{\gamma} \frac{dc_C}{dt} = k_f c_A(\mathbf{x}, t) c_B(\mathbf{x}, t) - k_b c_C(\mathbf{x}, t), \#(31)$$

385 where k_b is the backward reaction coefficient, then the probability of backward reaction
 386 is simply,

$$P(C^k \rightarrow A^i + B^j, \Delta t) = \gamma k_b \Delta t, \#(32)$$

387 and the mass of the disappearing particle C^k has to be distributed between the generated
388 particles A^i and B^j in proportion to their stoichiometric coefficients. This, just like the
389 separate treatment of transport and reaction described in the following section,
390 constitutes a split operator approach, which implies that the time step Δt should not be
391 too large in order to avoid error and instabilities.

392

393 Expressions (29) and (30) were derived under the assumption that particles are not at
394 close distance from the domain boundaries. Should this condition not be fulfilled,
395 different methods exist in the literature to make KDE valid near domain boundaries. A
396 simple one, in principle only valid for regular boundaries, is the reflection method
397 [Silverman, 1986]: for every particle that is at close distance from a boundary (beneath
398 some significance threshold) an identical virtual particle is placed as a reflection on the
399 other side of that boundary. This complies with mass conservation inside the domain
400 ($\int_{\Omega^d} c_s(\mathbf{x}, t) d\mathbf{x} = \sum_{i=1}^{n_s} m_s^i$), and also imposes a zero-gradient boundary condition.
401 Then, the methodology that we describe in this paper can be used as long as the virtual
402 particles are considered in the computation of the right hand side of (29) and/or (30).

403

404 **4. The random walk algorithm**

405 In the proposed method, reactive transport is solved in two stages, one corresponding to
406 the chemical reactions, and another one to the standard advection-dispersion equation.
407 This split operator approach is known in the literature as RT [Simpson and Landman,
408 2007]. Of course, other split operator approaches could also be implemented in a similar
409 way. Morshed and Kaluarachchi [1995] show that operator splitting in non-linear
410 reactive transport can have significant restrictions on the time step size to obtain

411 accurate solutions. *Simpson and Landman* [2007] show that the error associated to
 412 operator splitting can be removed by using an alternating scheme provided Δt is
 413 sufficiently small. *Paster et al.* [2014] derive some practical criteria for the selection of
 414 the time step in a Lagrangian model of reactive transport with second order kinetics. In
 415 this work, the time step was simply chosen small enough in each example to reach
 416 convergence of the solution. Alternatively, an adapted time step can be estimated by
 417 fixing the maximum probability of reaction. This way, the time step is respectively
 418 small or large at stages where the reaction is fast or slow.

419

420 The procedure used in this work to simulate kinetic reactions based on the probabilities
 421 determined by (29) can be written as it follows: First, for each time step Δt , the
 422 probability of reaction of only one of the reactants (A or B) is estimated. For simplicity,
 423 and without any loss of generality, we will assume it to be the reactant A. Then, a
 424 uniform $[0, 1]$ random number μ is drawn for each A-particle and compared to the
 425 corresponding probability of reaction, $P(A^i \rightarrow C^k, \Delta t)$. If $\mu \leq P(A^i \rightarrow C^k, \Delta t)$, it is
 426 considered that particle A^i does not react and the algorithm continues with the next A-
 427 particle. On the contrary, if $\mu > P(A^i \rightarrow C^k, \Delta t)$, the A-particle reacts with a number of
 428 nearby B-particles (the closest ones). To satisfy stoichiometry, the number of B-
 429 particles reacting with the A-particle, denoted here as n_r , is a positive integer value that
 430 should fulfill the following expression,

$$\alpha \sum_{j=1}^{n_r} m_B^j = \beta m_A^i. \#(33)$$

431 When the reaction occurs, one C-particle is injected at each \mathbf{X}_{AB}^{ij} position located
 432 between the reacting particle pairs $\{A^i, B^j\}$. These reacting particle pairs disappear after

433 that. Again, by stoichiometry, the mass associated with each new C-particle should
434 fulfill that

$$\sum_{k=1}^{n_r} m_C^k = \frac{\gamma}{\alpha + \beta} \left(m_A^i + \sum_{j=1}^{n_r} m_B^j \right). \#(34)$$

435 If all particles associated with a given species share a constant mass, these expressions
436 reduce to the following simple relationships,

$$\frac{m_A}{m_B} = \frac{\alpha}{\beta} n_r, \#(35)$$

$$m_C = \frac{\gamma}{\beta} m_B. \#(36)$$

437 To satisfy (35) when n_r is a real value, this expression simply requires to slightly
438 modify the particle mass associated with the reactants prior to the beginning of the
439 simulation. In the case of an instantaneous injection or to reproduce an initial condition,
440 this will imply choosing an adequate ratio between the number of particles of each
441 reactant. A valid alternative, not implemented in this work although perfectly
442 compatible with the presented method, is to change the particle mass upon reaction
443 [Bolster *et al.*, 2016], using (9) and (10) to determine the particle mass variation from
444 the computed probability. Another alternative is to decide the reaction of particle pairs
445 {A,B} based on Bernoulli trials with a probability of failure determined by $f = n_r -$
446 $F(n_r)$. Here, $F(x)$ is the floor function defined as the greatest integer less than or equal
447 to x . However, in this case, stoichiometry is only fulfilled in an average sense. The
448 latter approach is used in Example 1.

449

450 After this, following the standard random walk method, each particle is moved
451 according to a drift term and a Brownian motion to respectively simulate advection and
452 dispersion,

$$\mathbf{X}_s^i(t + \Delta t) = \mathbf{X}_s^i(t) + \mathbf{v}_s(\mathbf{X}_s^i(t)) \Delta t + \mathbf{E}_s(\mathbf{X}_s^i(t)) \boldsymbol{\xi} \sqrt{\Delta t}, \#(37)$$

453 where $\mathbf{X}_s^i(t)$ is the i th particle position associated with species s , \mathbf{v}_s is the particle
454 velocity associated with species s given by $\mathbf{v}_s = \frac{\mathbf{q}}{\phi R_s} + \frac{1}{\phi R_s} \nabla \cdot (\phi \mathbf{D}_s)$, R_s is the
455 retardation factor associated with species s , \mathbf{D}_s is the local hydrodynamic dispersion
456 tensor associated with species s , \mathbf{E}_s is the Brownian displacement matrix determined by
457 $\mathbf{E}_s \mathbf{E}_s^T = 2\mathbf{D}_s/R_s$, and $\boldsymbol{\xi}$ is a vector of d standard normally distributed random numbers.
458 Note that the method can directly support species-dependent properties such as effective
459 particle velocity (affected by retardation) and dispersion. Note also that alternative
460 equations to the advection-dispersion could be used in this step (e.g., Continuous Time
461 Random Walks), as the processes of transport and reaction are fully decoupled.

462

463 **5. Performance and convergence of the method**

464 Four simple hypothetical case examples were solved using the proposed methodology to
465 evaluate the performance and convergence of the method as a function of the number of
466 injected particles. The selected problems illustrate a wide range of possible applications.
467 For each problem, we simulate reactive transport in a one-dimensional column of unit
468 (1 m^2) cross-section, with constant velocity, porosity, and dispersion, to emphasize only
469 the relevance of the complex reactions. The parameter values adopted in each example
470 are given in tables 1-4.

471

472 Simulations are performed in a Monte Carlo framework consisting of 100 random walk
473 particle tracking realizations. Results are compared with those obtained from a very
474 finely discretized finite difference solver for the ADRE with explicit time stepping and
475 upwind differences in space for the advection term, which was checked for spatial and
476 temporal convergence. The finite difference solution is assumed to represent the true
477 solution. As explained in the previous section and although other approaches could be
478 used, we assigned equal mass to all particles belonging to the same species so that
479 stoichiometry is fulfilled exactly. Whenever possible, we imposed that the ratio of the
480 reactant masses matches that of the stoichiometric coefficients, i.e., $n_r = 1$ in (35). The
481 method was implemented in a Random Walk Particle Tracking code written in Matlab.
482 At the start of each simulation, 5000 particles of each reactant were injected following
483 Gaussian distributions in space characterized by the mean, the standard deviation and
484 the total amount of substance indicated in tables 1-4. In all cases, the concentration of
485 all compounds in the inflow is zero at all times.

486

487 The support of each species was estimated through (7) by assuming a Gaussian shape of
488 the particle plume. This leads to a suboptimal approximation of the particle support
489 volume written as [e.g. *Silverman*, 1986],

$$h_s = 1.06 \sigma_{x,s} n_s^{-\frac{1}{5}}, \#(38)$$

490 where the index s denotes the chemical species, n_s is the number of particles of the s th
491 species, and $\sigma_{x,s}$ is the standard deviation of the particle positions of the s th species at a
492 given time.

493

494 **5.1. Description of the chemical systems**

495 **Example 1. A Generic reaction with fractional exponents**

496 In this first example, we consider a generic kinetic reaction with arbitrary stoichiometric
497 coefficients, $\alpha A + \beta B \rightarrow \gamma C$. The reaction rate is written as

$$r(x, t) = k_f c_A c_B g(c_A, c_B), \#(39)$$

498 where the compensation function g in this case is

$$g(c_A, c_B) = c_A^{\theta_A - 1} c_B^{\theta_B - 1}. \#(40)$$

499 Here, θ_A and θ_B are arbitrary real values, often (but not always) associated with the
500 stoichiometric coefficients. To illustrate that any reaction with fractional exponents can
501 be properly simulated, we chose $\theta_A = \alpha = 2.3$ and $\theta_B = \beta = 1.3$. The parameters
502 adopted during the simulations are summarized in Table 1.

503

504 **Example 2. Aerobic Michaelis-Menten degradation considering linear**
505 **sorption of organic carbon**

506 In this example we reproduce the aerobic biodegradation of an organic chemical
507 compound dissolved in groundwater. The organic compound (CH_2O) is subject to linear
508 sorption, with a retardation factor $R = 3$. Microbial growth and decay is neglected, and
509 the dissolved organic carbon is assumed to react with dissolved oxygen to form carbon
510 dioxide and water, $\text{CH}_2\text{O} + \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}$. The reaction rate follows the Michaelis-
511 Menten kinetic model written here as

$$r(x, t) = k_f c_{\text{CH}_2\text{O}} c_{\text{O}_2} g(c_{\text{CH}_2\text{O}}, c_{\text{O}_2}), \#(41)$$

512 with function g being defined in this case as

$$g(c_{\text{CH}_2\text{O}}, c_{\text{O}_2}) = \frac{1}{k_{\text{CH}_2\text{O}} + c_{\text{CH}_2\text{O}}} \frac{1}{k_{\text{O}_2} + c_{\text{O}_2}}. \#(42)$$

513 $k_{\text{CH}_2\text{O}}$ and k_{O_2} are the half-saturation constants associated with the dissolved organic
 514 carbon and oxygen, respectively.

515

516 The plume of oxygen rapidly migrates towards the organic chemical compound with an
 517 effective retardation of $R = 1$. We assumed that the carbon dioxide produced by the
 518 chemical reaction remains dissolved in groundwater as $\text{CO}_2(\text{aq})$. The degradation
 519 constant value and the half-saturation constant values are taken from *Rolle et al.* [2008]
 520 and *Nagy et al.* [2009]. The parameters adopted during the simulations are summarized
 521 in Table 2.

522

523 **Example 3. Calcite precipitation**

524 This example simulates the precipitation of calcium carbonate that takes place at the
 525 contact fringe of two moving solute plumes of Ca^{2+} and CO_3^{2-} . Remarkably, we
 526 consider the effect of the nontrivial activity coefficients involved in the chemical
 527 reaction. We neglect the changes in the hydraulic properties of the porous medium
 528 resulting from precipitation. Back-dissolution is also omitted. The chemical reaction is
 529 formally written as $\text{Ca}^{2+} + \text{CO}_3^{2-} \rightarrow \text{CaCO}_3(\text{s})$. The rate of precipitation is represented
 530 by [e.g., *Nancollas, 1979*],

$$r(x, t) = k_{obs}(\Omega - 1), \#(43)$$

531 where k_{obs} is an observed or effective rate constant and Ω is the saturation state. We can
 532 rewrite this expression as:

$$r(x, t) = k' c_{\text{Ca}^{2+}} c_{\text{CO}_3^{2-}} \left(\gamma_{\text{Ca}^{2+}} \gamma_{\text{CO}_3^{2-}} - \frac{k_{eq}}{c_{\text{Ca}^{2+}} c_{\text{CO}_3^{2-}}} \right). \#(44)$$

533 Here, $\gamma_{Ca^{2+}}$, $\gamma_{CO_3^{2-}}$ are the activity coefficients of Ca^{2+} and CO_3^{2-} , respectively, k_{eq} is
 534 the equilibrium or solubility constant, and $k' = k_{obs}/k_{eq}$. From this, the compensation
 535 function associated with this chemical reaction is expressed as

$$g(c_{Ca^{2+}}, c_{CO_3^{2-}}) = \gamma_{Ca^{2+}} \gamma_{CO_3^{2-}} - \frac{k_{eq}}{c_{Ca^{2+}} c_{CO_3^{2-}}}. \#(45)$$

536 We assume that Ca^{2+} and CO_3^{2-} are the only ions with significant concentrations in the
 537 solution. Then, by using the extended Debye-Hückel formula, the activity coefficients
 538 $\gamma_{Ca^{2+}}$ $\gamma_{CO_3^{2-}}$ are calculated as,

$$\log_{10}(\gamma_{Ca^{2+}} \gamma_{CO_3^{2-}}) = -4k_1 \left(\frac{1}{\frac{1}{\sqrt{2(c_{Ca^{2+}} + c_{CO_3^{2-}})}} + k_2 \mathring{a}_{Ca^{2+}}} + \frac{1}{\frac{1}{\sqrt{2(c_{Ca^{2+}} + c_{CO_3^{2-}})}} + k_2 \mathring{a}_{CO_3^{2-}}} \right), \#(46)$$

539 where $k_1 = 0.018846 \text{ m}^{3/2}/\text{mol}^{1/2}$ and $k_2 = 0.103755 \text{ m}^{3/2}/\text{mol}^{1/2} \text{ nm}$ for water at
 540 25°C (assuming that the density of water is $\rho_w = 1 \text{ Kg}/\text{dm}^3$), and $\mathring{a}_{Ca^{2+}}$, $\mathring{a}_{CO_3^{2-}}$ are the
 541 hydrated radii of the respective ions [Garrels and Christ, 1965]. Values for k_{obs} , k_{eq}
 542 were taken from *van Breukelen* [2003] and *Appelo and Postma* [2005], respectively.
 543 The parameters adopted during the simulations are summarized in Table 3.

544

545 **Example 4. Acidic dissolution of Fluorite:**

546 This example describes the acidic dissolution of fluorite. The chemical reaction is
 547 $CaF_2 + 2H^+ \rightarrow Ca^{2+} + 2HF^0$, and the dissolution rate is typically represented by
 548 [Zhang *et al.*, 2006],

$$r(x, t) = k S_s (c_{H^+}^2/c_{Ca^{2+}})^\alpha, \#(47)$$

549 Where S_s is the mineral (CaF_2) surface per cubic meter of the porous medium, and k
 550 and α are experimental parameters. Zhang and coworkers found that at 25°C $\log k$
 551 ranged approximately between -2 and -4 for different experimental conditions,
 552 whereas α had values between 0.495 and 1.146 . Here, we chose $\log k = -4$ and
 553 $\alpha = 0.8$, so that

$$r(x, t) = k S_s c_{\text{H}^+}^{\theta_{\text{H}^+}} c_{\text{Ca}^{2+}}^{\theta_{\text{Ca}^{2+}}}, \#(48)$$

554 where $\theta_{\text{H}^+} = 1.6$ and $\theta_{\text{Ca}^{2+}} = -0.8$. This kinetic model resembles that of the example
 555 1, but with the presence of a negative exponent in the concentration of Ca^{2+} . We
 556 consider that Fluorite is everywhere in the system and in high amounts, and so S_s is a
 557 constant. Then the model has only one reactant and two products, although one of the
 558 products has an influence on the reaction rate. This means that, for this particular case,
 559 injection of the product particles is performed directly on the position of the reacting
 560 particle. We neglect the changes in the hydraulic properties of the porous medium
 561 resulting from dissolution. The chemical reaction can be embedded in (24) by defining
 562 that

$$g(c_{\text{H}^+}, c_{\text{Ca}^{2+}}) = c_{\text{H}^+}^{\theta_{\text{H}^+}-1} c_{\text{Ca}^{2+}}^{\theta_{\text{Ca}^{2+}}-1}, \#(49)$$

563 and $k S_s = k_f$. In this case, two overlapping plumes of H^+ and Ca^{2+} are injected at the
 564 same initial location (note that the reaction rate has an asymptote in case of total
 565 absence of Ca^{2+}). The parameters adopted during the simulations are summarized in
 566 Table 4.

567

568 **5.2. Results**

569 Figures 2-9 compare the random walk solution obtained at the end of the simulation
570 time with the corresponding finite difference solution for each reactive transport
571 problem. The random walk solution is presented in terms of the mean concentration of
572 the different chemical species and its standard deviation (the shaded zone delimits ± 1
573 standard deviation) obtained from 100 realizations. For completeness, the corresponding
574 evolution of the total mass of the different chemical species remaining in the column
575 during the simulation are also depicted in these figures. Considering that the reactive
576 transport problems were simulated with only 5000 particles, a good match is obtained
577 for all cases.

578

579 We note that larger deviations from the finite difference solution can be seen at the
580 concentration peaks. This is mostly attributed to the fact that the suboptimal
581 approximation of the particle support volume directly affects the calculation of the
582 probabilities in (29) through the estimation of concentrations in the compensation
583 function g . This effect is seen most significant when g deviates from zero-order
584 (corresponding to second-order kinetic reactions, where there is no need for
585 compensation).

586

587 The approximation (38) used to determine the particle support volume h_s is only valid
588 for Gaussian distributions of the species' concentrations. This is particularly not
589 satisfied for calcium ion in the acidic dissolution of Fluorite (see Figure 8). Hence,
590 errors in the estimation of the resulting concentration map in this case example are
591 slightly larger than in the others. In practice, the use of such an approximation of h_s
592 (known as the rule-of-thumb in statistics), implies that more particles are needed to

593 match the exact solution. Yet, the use of (7) may become computationally expensive in
594 reactive transport problems otherwise.

595

596 Figure 10 shows the average relative error (ϵ_r) and the coefficient of variation (CV_r) of
597 the increase in the total amount of substance at the end of the simulation, calculated
598 over 100 realizations by comparison with the finite difference solution,

$$\epsilon_r = \frac{\langle M_{PT} \rangle - M_{FD}}{\Delta M_{FD}}, \#(50)$$

$$CV_r = \frac{\sqrt{\langle M_{PT}^2 \rangle - \langle M_{PT} \rangle^2}}{|\Delta M_{FD}|}, \#(51)$$

599 where M_{PT} is the total mass of a given chemical compound obtained at the final
600 simulation time, $\langle \cdot \rangle$ is the mean operator over all realizations, M_{FD} is the total mass of
601 the chemical compound obtained with finite difference at the end of the simulation time,
602 and ΔM_{FD} is the total mass variation of the chemical compound obtained with the finite
603 difference method. The mean relative error ϵ_r represents the systematic error associated
604 to one realisation, whereas CV_r accounts for its random variability. Note that the sum of
605 the squares of these two parameters is the Mean Squared Error (MSE) of ΔM_{PT} ,
606 normalized by ΔM_{FD}^2 . Results show that the proposed random walk method converges
607 towards the exact solution with an increasing number of particles. It also demonstrates
608 that not many particles are needed to simulate non-linear chemical reactions with
609 sufficient accuracy.

610 **6. Importance of chemical kinetics in heterogeneous aquifers: An example**

611 A two-dimensional implementation of the proposed method in a heterogeneous aquifer
612 is given in this section. The objective of this example is to illustrate the application of

613 the presented random walk approach in a more realistic setting. In doing this, we
614 analyze the need of fully describing non-linear chemical kinetics in heterogeneous
615 porous media.

616 We study a reactive transport problem in a 2D rectangular confined aquifer with
617 dimensions of $100 \times 50 \text{ m}^2$. The aquifer is characterized by a randomly generated log-
618 normally distributed hydraulic conductivity field $Y = \ln K$ with a mean of $\langle Y \rangle = 3$ and
619 a variance of $\sigma_Y^2 = 1$. The Y field follows an isotropic exponential covariance function
620 model with integral scale of $I_Y = 5 \text{ m}$. The other aquifer properties are assumed
621 homogeneous. Groundwater flow is considered at steady-state and subject to constant
622 head conditions at the lateral boundaries and impermeable conditions otherwise. As a
623 result, the mean flow direction is oriented in the x-direction and characterized by a
624 mean hydraulic gradient of 0.00622. The flow problem is solved with a finite-difference
625 code, MODFLOW-2000 [Harbaugh *et al.*, 2000], with a domain discretized into regular
626 cells of size 0.5 m. The resulting cell face flows were used to compute the random walk
627 particle velocities according to the hybrid interpolation method suggested by LaBolle *et*
628 *al.* [1996].

629 The reactive transport problem is similar to the one defined in example 2 but considers a
630 two-dimensional heterogeneous porous media. A schematic representation of the system
631 is shown in Figure 11. A plume of dissolved organic matter, retarded with respect to
632 groundwater by linear sorption, passes after some time through an oxygen plume. The
633 chemical reaction follows the Michaelis-Menten kinetic model with the same
634 formulation and parameter values as given in example 2. Table 2 shows the values of
635 the parameters. The concentrations of the reactants are initially uniform in two separate
636 rectangular areas depicted in Figure 11 and zero everywhere else in the domain. The
637 concentration of all compounds in the inflow water is zero at all times.

638 The fast method of *Botev et al.* [2010] was used to determine the kernel bandwidth with
639 a slight modification: the anisotropic kernel bandwidth matrix \mathbf{H} obtained by this
640 method was transformed into an isotropic bandwidth by matching the determinants, i.e.,
641 $h^2 = \det(\mathbf{H})$. As explained in section 3, the use of isotropic kernels facilitates the
642 computation of the compensation function g at the \mathbf{X}_{AB}^{ij} location by linear interpolation.
643 However, the kernel obtained by this approach is suboptimal compared to the original
644 method by *Botev et al.* [2010], and presumably produced a slower convergence with
645 respect to the number of particles.

646 The convergence of the random walk solution was controlled by choosing a small
647 enough time step and by performing a sensitivity analysis with respect to the number of
648 particles. As expected, the convergence occurred for a higher number of particles
649 compared to the 1D examples. Nevertheless, by using only 32,768 particles of each
650 reactant, the estimated error in the total amount of product generated was below 1% as
651 compared to the solution obtained with 131,072 particles. Figure 12 shows the three
652 particle plumes at different moments of the simulation (for a better visualization, only a
653 random subsample of 5,000 particles is shown), and the corresponding KDE
654 reconstruction of the product concentrations.

655

656 The actual impact of the reaction kinetics on the problem solution depends on whether
657 mixing or chemical kinetics is the limiting process. In order to illustrate this, we
658 compare the evolution of the CO_2 production with the following equivalent second-
659 order reaction,

$$r(\mathbf{x}, t) = \frac{k_f}{k_{\text{CH}_2\text{O}} k_{\text{O}_2}} c_{\text{CH}_2\text{O}} c_{\text{O}_2},$$

660 for three different values of k_f ranging from five times smaller to five times higher than
661 the value given in Table 2. Figure 13 shows that for a very fast reaction rate the process
662 is mixing-limited (in this case mixing is driven by the difference in the retardation
663 coefficients), and therefore the reaction kinetics do not have a significant effect on the
664 results. These kind of reactions can be modeled as instantaneous (ref. xavi), as long as
665 the mixing process is well represented by the transport model. On the other hand, in
666 slow reactions, the reaction kinetics can make a very important difference in the results.

667 7. Conclusions

668 We have presented a new random walk particle tracking method to simulate reactions
669 with complex kinetics involving two reactants. Reactive transport is solved in two
670 stages: the first one corresponding to the chemical reactions, and the second one to the
671 standard advection-dispersion equation. The method is based on the representation of
672 particles by optimal kernel functions. This way, we derived the probability that a given
673 particle reacts with any particle associated with other reactants. In the proposed
674 methodology, complex kinetic reactions require linearizing a function of the local
675 concentrations at the location of highest probability density of encounter between
676 potentially reactive particle pairs. The implementation of the probability of reaction in
677 random walk models has been achieved in this paper by particle annihilation, but other
678 approaches such as particle mass variations can easily be incorporated.

679

680 In addition, two simple relationships should be satisfied to fulfill stoichiometry: one
681 relating the mass of interacting particles with the stoichiometric coefficients, and
682 another one relating the mass of particles produced from reactions with the
683 stoichiometric coefficients. In practice, the first relationship requires a careful choice of

684 the mass of the particles injected. The second relationship determines the mass of
685 particles produced from the chemical reaction.

686

687 Several synthetic examples demonstrate the potential applicability of the method in a
688 wide range of applications, ranging from reaction-rate laws with fractional exponents to
689 acidic dissolution and precipitation systems with nontrivial activity coefficients. Results
690 have shown that a good match with a finite difference solution is obtained with
691 relatively few particles. The method has been demonstrated to converge to the solution
692 with an increasing number of particles. This rate of convergence depends on the type of
693 chemical reaction, i.e., on the shape of the compensation function g . Finally, a 2D
694 example dealing with non-linear Michaelis-Menten biodegradation in a randomly
695 heterogeneous aquifer is provided to illustrate the capabilities of the method in a more
696 realistic setting.

697

698

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702 69768-R (MINECO/FEDER). GS acknowledges financial support by AGAUR. The
703 paper provides all the information needed to replicate the results. The codes and the
704 output data from the simulations are freely available from the authors upon request.

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860 **Tables**861 *Table 1: Simulation parameter values used in example 1.**

	A	B	C
$(\mu_x, \sigma_x)_{initial}$	(40, 6)	(50, 6)	—
$m_{initial}$	1 mol	1 mol	0
α, β, γ	2.3	1.3	1
θ (eq. 37)	2.3	1.3	—
R	1	1	1
<hr/>			
k_f	6 (mol/m³)^{-2.6} day⁻¹		
q	0.3 m/day		
ϕ	0.25		
D	0.4 m²/day		
τ	80 days		

862 * $(\mu_x, \sigma_x)_{initial}$ are the mean and standard deviation defining the initial normal distribution of
863 solute particles in space, $m_{initial}$ is the total amount of substance at the start of the simulation,
864 and τ is the total simulated time. The other variables are defined in the text.

865 *Table 2: Simulation parameter values used in example 2.**

	CH₂O	O₂	CO₂
$(\mu_x, \sigma_x)_{initial}$	(70, 2)	(50, 8)	—
$m_{initial}$	1 mol	1 mol	0
α, β, γ	1	1	1
K_{CH_2O}, K_{O_2} (eq.39)	1.6667 mol/m³	0.0156 mol/m³	—
R	3	1	1
<hr/>			
k_f	0.15 (mol/m³) day⁻¹		

q	0.32 m/day
ϕ	0.25
D	0.5 m²/day
τ	65 days

866 * $(\mu_x, \sigma_x)_{initial}$ are the mean and standard deviation defining the initial normal distribution of
867 solute particles in space, $m_{initial}$ is the total amount of substance at the start of the simulation,
868 and τ is the total simulated time. The other variables are defined in the text.

869

870 *Table 3: Simulation parameter values used in example 3.**

	Ca²⁺	CO₃²⁻	CaCO₃
$(\mu_x, \sigma_x)_{initial}$	(25, 5)	(35, 8)	—
$m_{initial}$	2.5 mol	2.5 mol	0
α, β, γ	1	1	1
$\hat{a}_{Ca^{2+}}, \hat{a}_{CO_3^{2-}}$ (eq. 43)	0.6 nm	0.5 nm	—
R	1	1	∞
<hr/>			
k_{obs}	0.002 (mol/m³)^{-2.6} day⁻¹		
k_{eq}	10^{-2.3} (mol/m³)²		
q	0.1 m/day		
ϕ	0.25		
D	0.15 m²/day		
τ	100 days		

871 * $(\mu_x, \sigma_x)_{initial}$ are the mean and standard deviation defining the initial normal distribution of
872 solute particles in space, $m_{initial}$ is the total amount of substance at the start of the simulation,
873 and τ is the total simulated time. The other variables are defined in the text.

874

875 *Table 4: Simulation parameter values used in example 4.**

	H⁺	Ca²⁺	HF⁰
$(\mu_x, \sigma_x)_{initial}$	(90, 5)	(90, 20)	—
$m_{initial}$	2 mol	4 mol	0
α, β, γ	2	1	2

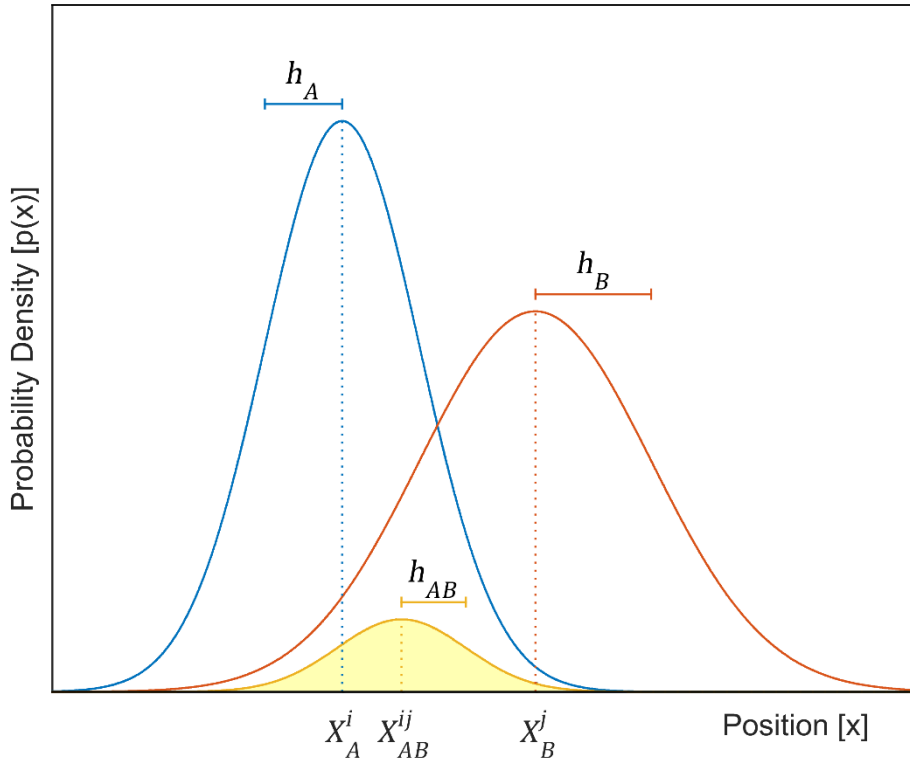
θ (eq. 45)	1.6	-0.8	-
R	1	1	1
k_f	0.72 (mol/m ³) ^{0.2} day ⁻¹		
q	0.5 m/day		
ϕ	0.25		
D	0.4 m ² /day		
τ	7 days		

876 * $(\mu_x, \sigma_x)_{initial}$ are the mean and standard deviation defining the initial normal distribution of
877 solute particles in space, $m_{initial}$ is the total amount of substance at the start of the simulation,
878 and τ is the total simulated time. The other variables are defined in the text.

879

880

881 **Figures**

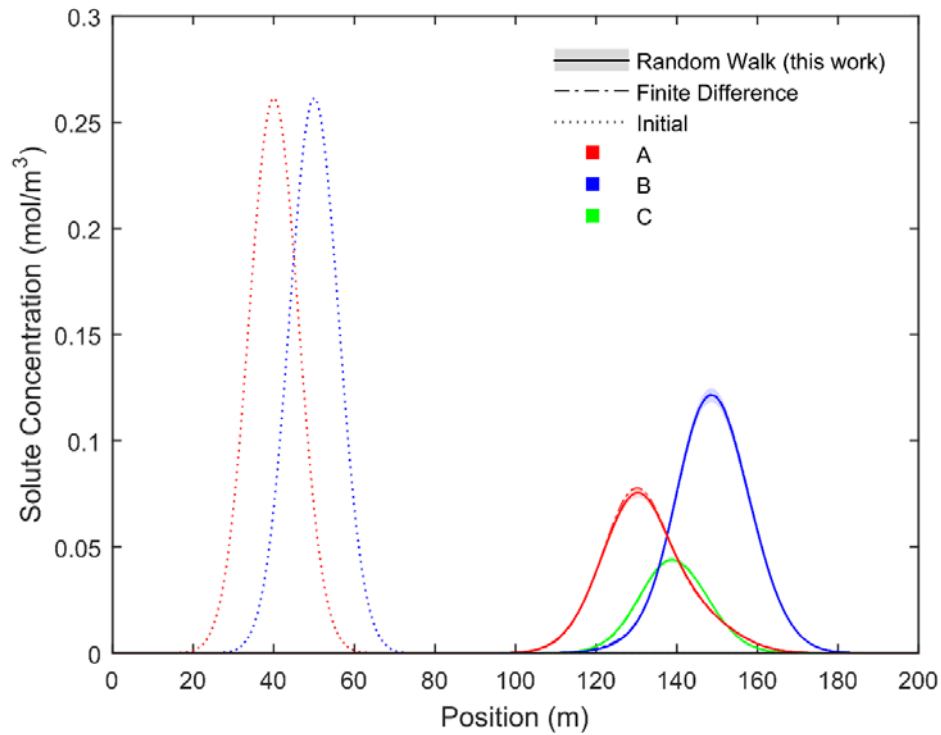


882

883 Figure 1: Schematic example of a product between two Gaussian pdf's in one
884 dimension. The product (yellow) is another Gaussian function centered in X_{AB} and with

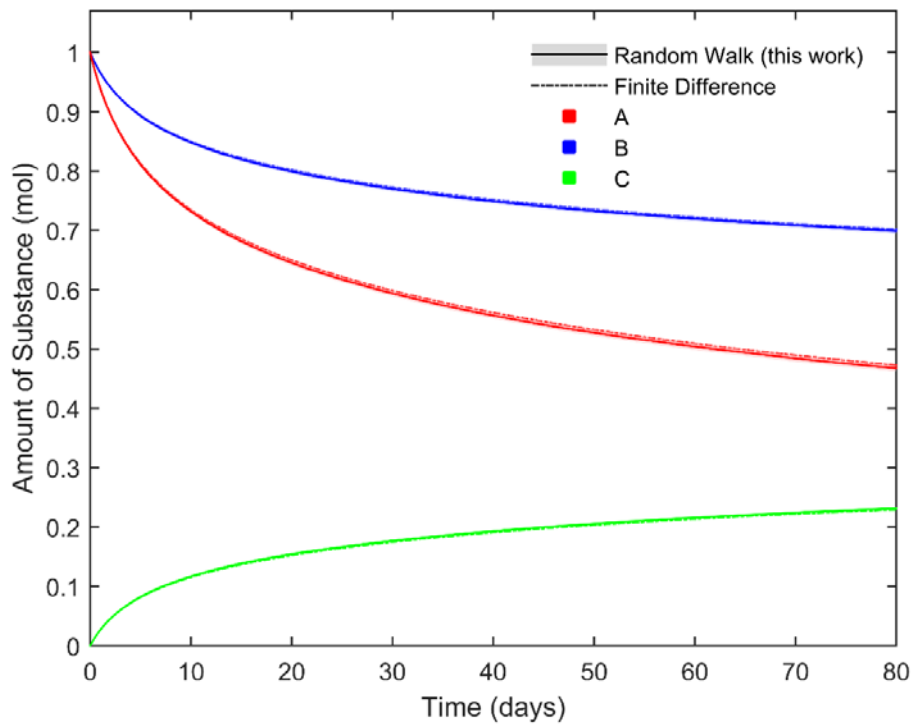
885 a standard deviation $h_{ab} = \sqrt{H_{AB}}$. Its integral over x is the probability of collocation of
886 the two particles.

887



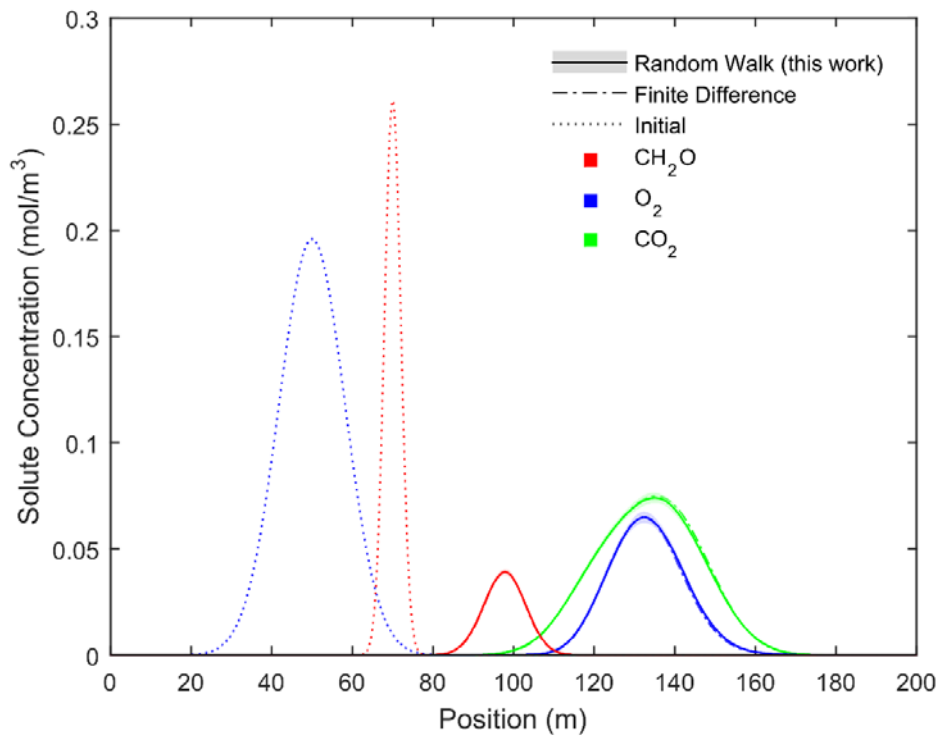
888

889 *Figure 2: Solute concentrations in example 1, at the start of the simulation and after 80*
890 *days. The error zone around the Particle Tracking curves indicates ± 1 standard*
891 *deviation.*



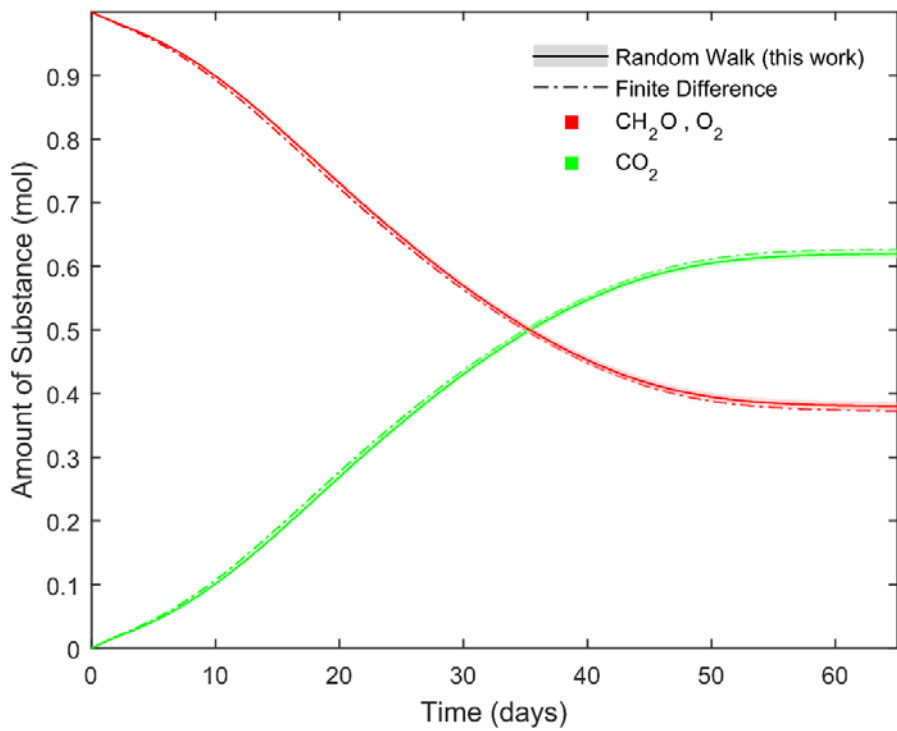
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893 *Figure 3: Evolution in time of the total amount of substance of each compound in*
 894 *example 1. The error zone around the Particle Tracking curves indicates ± 1 standard*
 895 *deviation.*



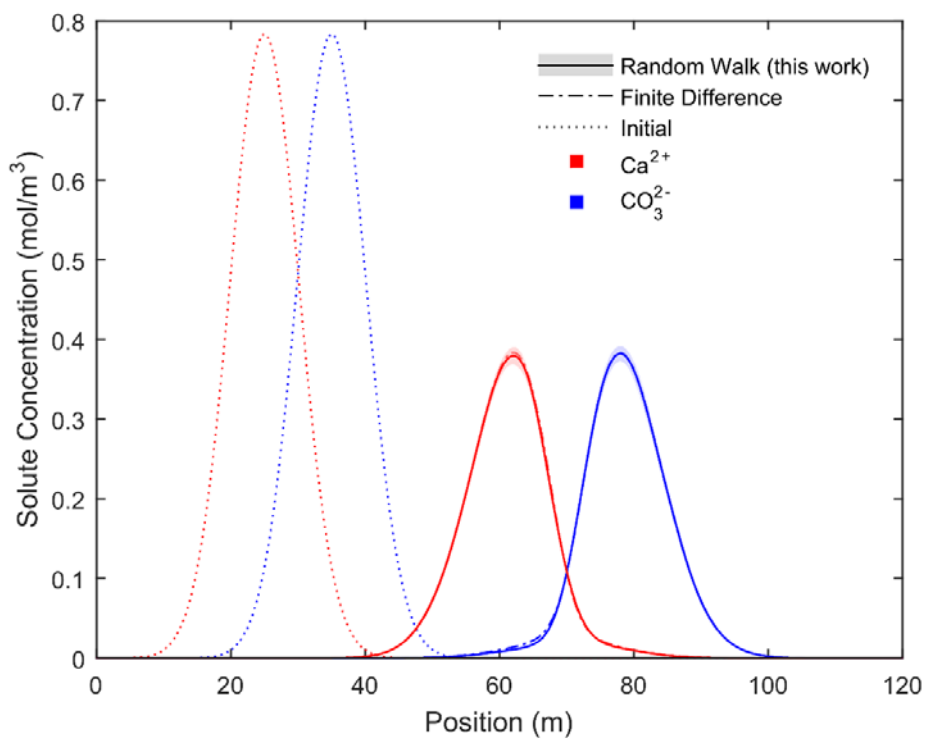
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897 *Figure 4: Solute concentrations in example 2, at the start of the simulation and after 65*
 898 *days. The error zone around the Particle Tracking curves indicates ± 1 standard*
 899 *deviation.*



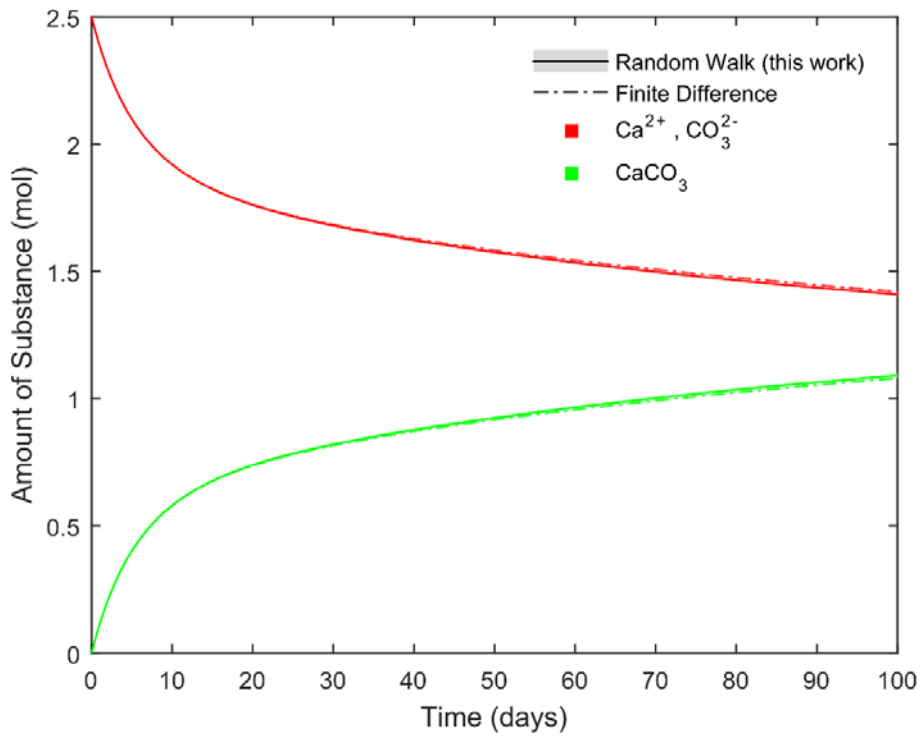
900

901 *Figure 5: Evolution in time of the total amount of substance of each compound in*
 902 *example 2. The error zone around the Particle Tracking curves indicates ± 1 standard*
 903 *deviation.*



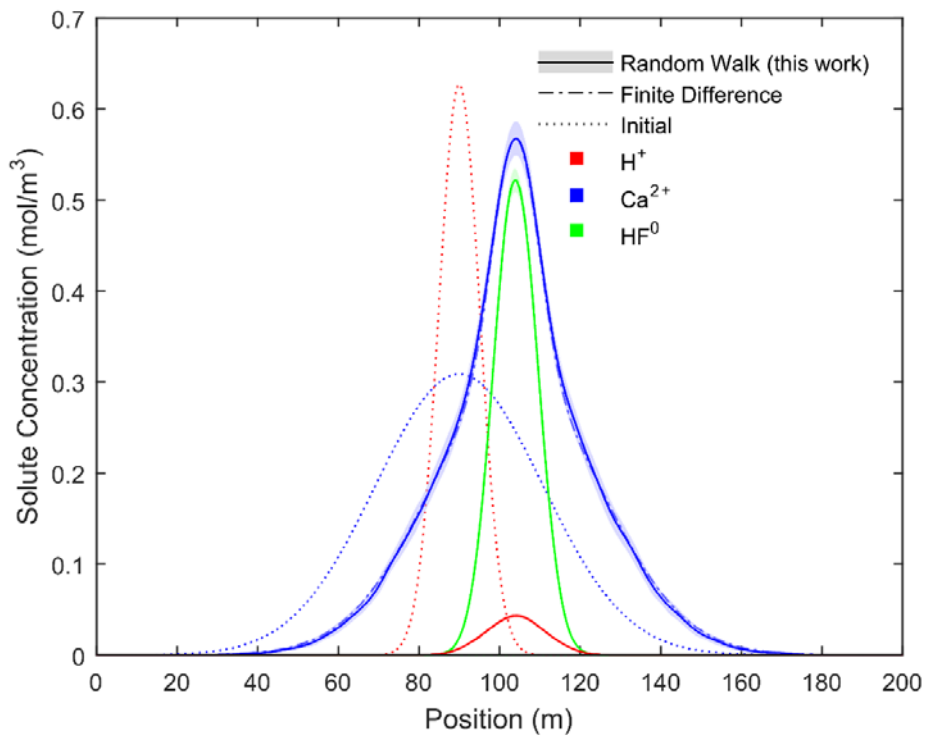
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905 *Figure 6: Solute concentrations in example 3, at the start of the simulation and after*
 906 *100 days. The error zone around the Particle Tracking curves indicates ± 1 standard*
 907 *deviation.*



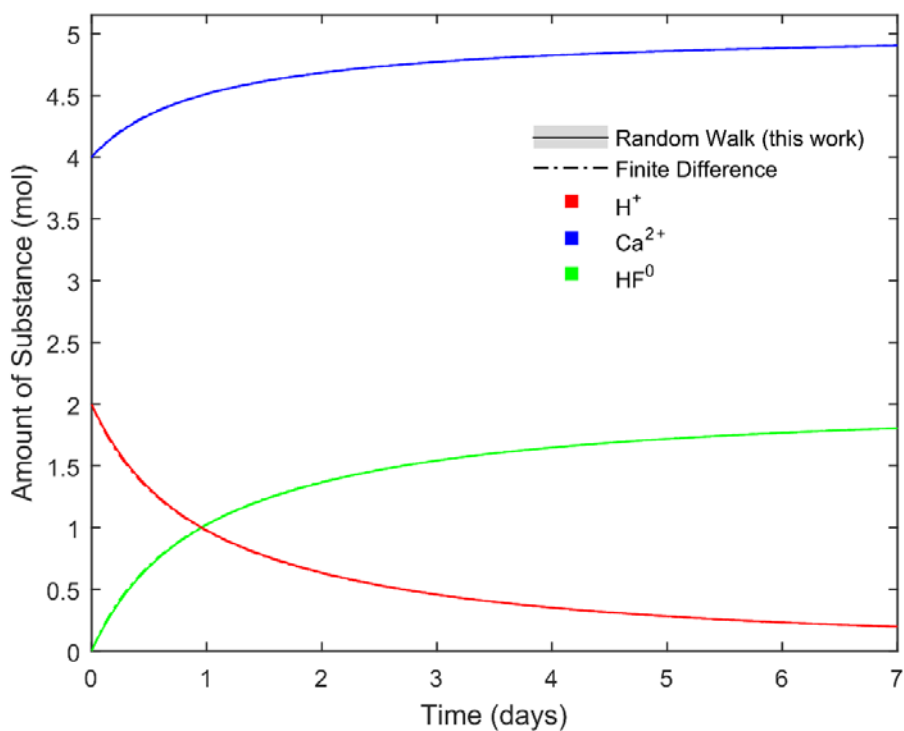
908

909 *Figure 7: Evolution in time of the total amount of substance of each compound in*
 910 *example 3. The error zone around the Particle Tracking curves indicates ± 1 standard*
 911 *deviation.*



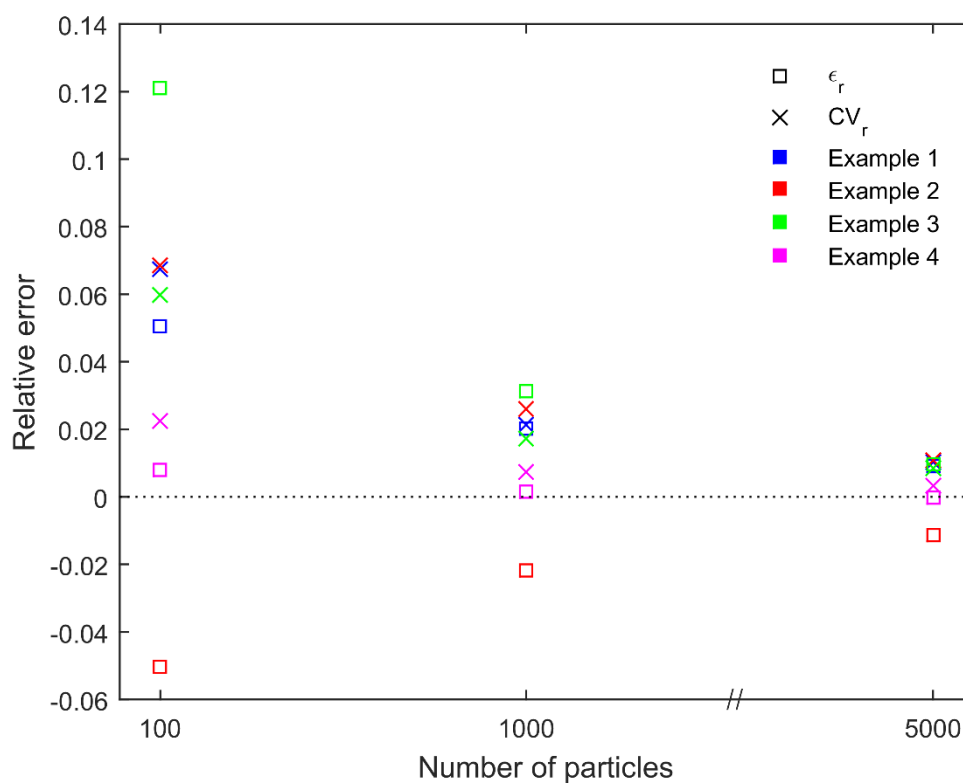
912

913 *Figure 8: Solute concentrations in example 4, at the start of the simulation and after 7*
 914 *days. The error zone around the Particle Tracking curves indicates ± 1 standard*
 915 *deviation.*



916

917 *Figure 9: Evolution in time of the total amount of substance of each compound in*
 918 *example 4. The error zone around the Particle Tracking curves indicates ± 1 standard*
 919 *deviation.*



920

921 *Figure 10: The two measured error components for different initial number of particles*
 922 *of the reactants.*

