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Dilution of reactive plumes: evolution of concentration statistics under diffusion and nonlinear reaction

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Abstract

Concentration fields of solutes in porous media often exhibit large fluctuations, driven by physical and chemical heterogeneity from the pore to the Darcy scale. For many applications, ranging from reactive transport modeling to toxicology, the knowledge of mean concentrations is not sufficient, and quantifying concentration variability is necessary. The probability density function (PDF) of concentration quantifies the frequency of occurrence of concentration values throughout a spatial domain. While evolution equations and analytical solutions for the concentration PDF exist for conservative solutes, less is known about its evolution under the joint action of transport and reaction. In this work, we investigate how dilution of a reactive plume by diffusion affects the statistics of concentrations. While mixing has no effect on first-order reactions, its coupling with nonlinear reactions leads to non-trivial effective kinetics relevant for a broad range of reactive transport problems. We study the evolution of the concentration PDF under diffusion and nonlinear reaction in one spatial dimension, which represents a critical step towards further coupling with heterogeneous advection. We show that the dependence of the scalar dissipation rate on concentration encodes the impact of diffusive transport on the concentration PDF and derive a dynamical equation for its time evolution. Using a weak-coupling approximation for the reaction and diffusion dynamics, we derive analytical predictions for the concentration PDF and its moments. Our results provide new insights into how diffusion and reaction control concentration variability and open new opportunities for coupling mixing models with chemical reactions.

Highlights

- We introduce a general framework quantifying the link between concentration PDFs and spatial concentration profiles.
- We derive a dynamical equation for the evolution of the concentration PDF under diffusion and nonlinear reaction in 1D.
- We derive analytical predictions for the concentration PDF and its moments using a weak-coupling approximation.

1 Introduction

Quantifying the variability in solute concentrations in the subsurface is of primary importance to a large range of applications, including reactive transport modeling (e.g., [1]), characterizing the natural chemical signature of groundwater systems (e.g., [2]), and assessing human health risks associated with contaminant transport (e.g., [3]). In particular, when reaction rates depend nonlinearly on available concentrations, effective reaction rates can differ by orders of magnitude from reaction rates determined under well-mixed conditions [4-7]. In such cases, knowledge of mean concentrations is not sufficient

39 to predict overall reaction rates, which requires additional knowledge about the spatial variability of
40 concentration values and local reaction rates.

41 Concentration probability density function (PDF) methods aim to quantify transport and reaction
42 processes in terms of the spatial statistics (i.e., frequency of occurrence of given values) of transported
43 scalars [8–11]. These methods were originally developed in the context of turbulent flows, where they
44 have been extensively employed to model both conservative transport [12–17] and reactive transport
45 with an emphasis on combustion [18–23]. More recently, these methods have gained popularity in the
46 context of porous media to study conservative [2, 24–33] and reactive [34–40] mixing. The statistics of
47 concentrations have been studied in relation to different types of fluctuations. The first approach is to
48 study concentration fluctuations with respect to an average transport model, such as the advection–
49 dispersion equation [24–26], in terms of a stochastic transport model such as the continuous time
50 random walk [28, 41]. Regarding, for instance, average concentrations at a given spatial position,
51 fluctuations typically arise from variability in particle transit times due to heterogeneity. A second
52 approach is to characterize uncertainty in concentrations due to uncertainty in model parameters, such
53 as flow velocities and reaction rates [29, 42–45]. These methods quantify the variability in concentra-
54 tions due to uncertainty in physical and chemical parameters. A third point of view is to consider
55 the variability in concentrations over the spatial extension of a solute plume which arises from known
56 transport and reaction processes. Even with homogeneous physical and chemical parameters, mean
57 concentrations and associated fluctuations evolve under the combined effect of transport and reaction.
58 In this context, the concentration PDF provides a useful tool to quantify the spatial frequency of
59 occurrence of different solute concentration values, and to provide information about the mixing state
60 of solute plumes without explicitly resolving the corresponding spatial profiles [31].

61 Here, we follow this last approach to study how the dilution of a reactive plume by diffusive mixing
62 affects concentration statistics (Fig. 1). In this context, evolution equations have been derived for the
63 conservative concentration PDF by quantifying the formation and interactions of lamellar structures
64 in concentration fields subject to advection and diffusion [30, 31, 46]. Recent developments have
65 extended these theories to mixing-limited bimolecular reactions [47]. Here, we consider a different
66 reactive transport problem in which mixing does not act to bring segregated reactants into contact
67 but rather to dilute a reactive plume. This system is relevant to a broad range of reactive transport
68 problems [6, 7], including situations where transported solute plumes react nonlinearly with a solid
69 phase as they get diluted by mixing. This leads to new dynamics that fundamentally differ from what
70 is known regarding mixing-limited reactions across diffusing or dispersing fronts [48–51].

71 We investigate the coupling of dilution by diffusive mixing with the nonlinear degradation of a single
72 species locally undergoing diffusion in one spatial dimensional and decaying at a rate proportional
73 to an arbitrary power of concentration (Fig. 1). We generalize the results of [7] for the evolution
74 of total mass and mean concentration to the evolution of the full concentration PDF, and we obtain
75 a dynamical equation for the latter in terms of the scalar dissipation rate [52–56], expressed as a
76 function of concentration. In addition to the mean concentration, the concentration PDF formulation
77 allows us to quantify higher-order concentration moments, such as the concentration variance, which
78 provides information about the variability in concentration values observed throughout a spatial do-
79 main. Building on the weak-coupling approximation developed in [7], we relate the evolution of the
80 concentration PDF and its moments to the evolution of the maximum concentration, and quantify the
81 resulting anomalous kinetics.

82 In the interest of developing and illustrating the new method proposed here, the class of reaction–
83 diffusion problems we analyze introduces significant simplifications. In particular, we consider a one-
84 dimensional problem and neglect heterogeneous advection effects. In addition, the weak-coupling
85 approach involves a Gaussian approximation for the solute plumes at late times. Although reaction
86 under diffusion or dispersion in the absence of advective heterogeneity has been studied in its own
87 right in the context of porous media [4, 57–61], these conditions may be seen as fundamental building
88 blocks in the theory of mixing in heterogeneous flows. In the presence of heterogeneous flow fields
89 characteristic of porous media, solute plumes are deformed into a collection of elongated structures
90 termed lamellae (Fig. 1) [31]. Using the Ranz transform [62], the resulting compression–diffusion–
91 reaction equation can be mapped onto a one-dimensional diffusion–reaction equation, which motivates

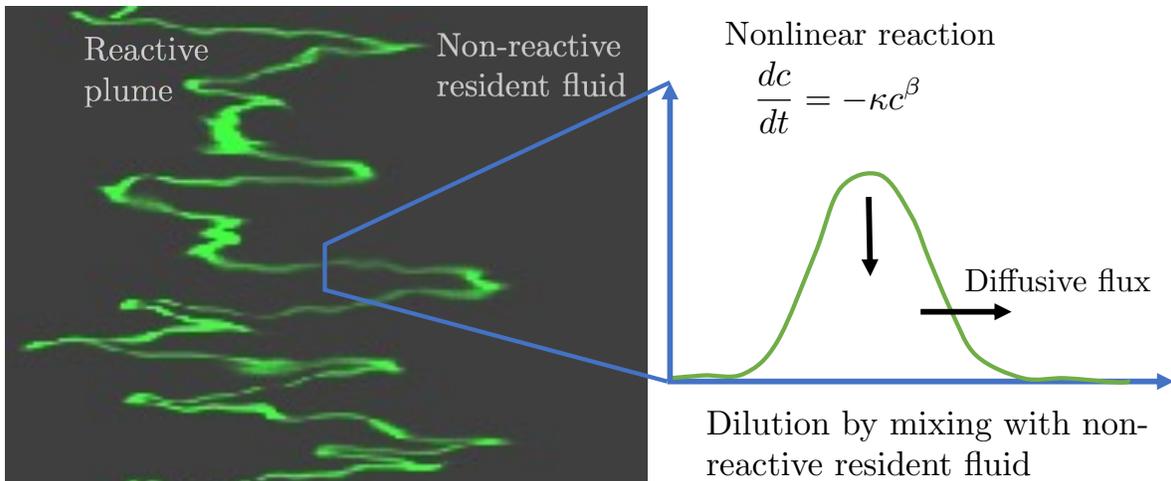


Figure 1: Illustration of the reactive transport problem under consideration (adapted from a simulation of transport at the Darcy scale in a heterogeneous permeability field [30]). We consider a plume of reactive solute (green) that undergoes nonlinear decay either by reaction with the solid, with another solute in excess everywhere, or with another solute that is well mixed inside the plume. The plume is diluted by mixing with the non-reactive resident fluid (black) while it reacts, leading to non-trivial effective reaction rates [7]. The latter are governed by the coupling of nonlinear reaction with the diffusive flux along concentration gradients. Here, we study the one-dimensional diffusion–reaction problem, which represents the first step towards solving the full advection–diffusion–reaction system.

92 the present study.

93 The paper is structured as follows. Section 2 introduces a general definition for the concentration
 94 PDF associated with a given spatial profile and explores its key properties. In Section 3, in light
 95 of these concepts, we derive a governing equation for the dynamics of the concentration PDF of a
 96 solute undergoing diffusion-induced dilution in one spatial dimension and nonlinear reaction described
 97 locally by a power-law decay of concentration. In this context, we also discuss the relationship between
 98 this simplified one-dimensional problem and reaction–diffusion in the presence of heterogeneous flows
 99 typically found in porous media, based on the Ranz transform. We then study the one-dimensional
 100 problem and the associated effective kinetics in terms of the weak-coupling approximation in Section 4.
 101 Conclusions and an overall discussion of the results are presented in Section 5. Some additional
 102 technical derivations are provided in the Appendices.

103 2 The concentration PDF

104 This section is concerned with providing a general definition of the concentration PDF associated with
 105 arbitrary spatial concentration profiles. We first present the general multispecies formulation, and then
 106 discuss the single-species case. We provide a detailed discussion of the properties of the concentration
 107 PDF, as well as of its numerical computation. The approach developed here, which forms the basis for
 108 the subsequent sections, builds on that introduced in [63] regarding Eulerian velocity PDFs. The main
 109 concepts behind the concentration PDF, which quantifies the spatial frequency of occurrence of different
 110 concentration values, are illustrated in Fig. 2 for a one-dimensional, single-species concentration profile.

111 Before proceeding, we introduce some notation that will be employed throughout. The concentra-
 112 tion $\underline{C}(\mathbf{x}; t)$ at a given location \mathbf{x} and time t , with $\underline{C} = (C_1, \dots, C_{n_s})$, is defined so that $\underline{C}(\mathbf{x}; t) d\mathbf{x}$ is
 113 the mass in an infinitesimal volume $d\mathbf{x}$ centered at $\mathbf{x} = (x_1, \dots, x_d)$ of each chemical species $1, \dots, n_s$.
 114 We use an underscore to denote quantities whose components relate to concentration species (of which
 115 there are a number n_s), and boldface to denote spatial vectors (which have components according to

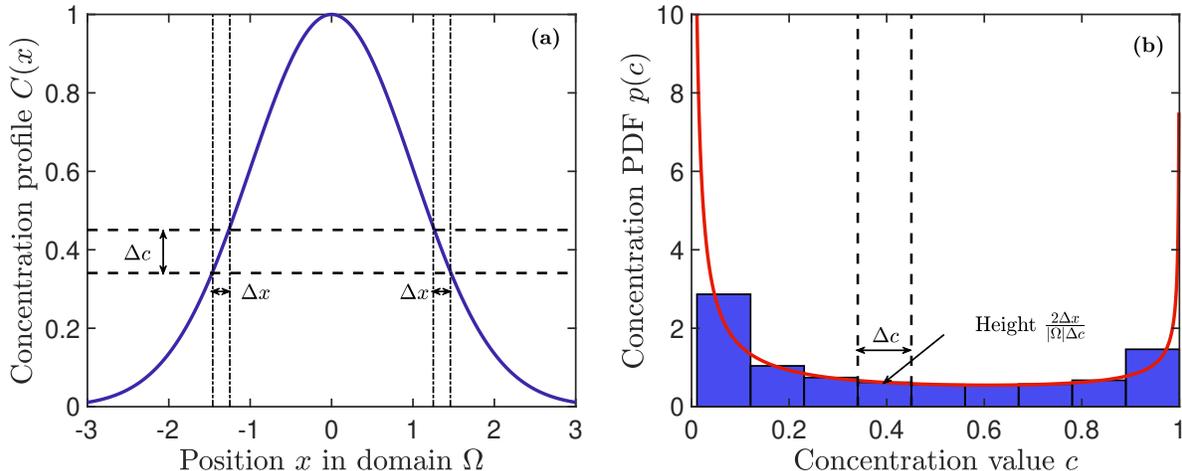


Figure 2: Illustration of the key concepts underlying the concentration PDF. **(a)**: Example spatial concentration profile, a Gaussian with unit variance and unit height, restricted to the spatial domain $\Omega = [-3, 3]$ of size $|\Omega| = 6$. **(b)**: Corresponding concentration PDF. Given a spatial profile, the concentration PDF quantifies the spatial frequency of occurrence of different concentration values $c = C(x)$ occurring at some position(s) x . When concentration values are discretized into bins of width Δc , the PDF value $p(c)$ is approximated by the fraction of the domain of the domain where the concentration c falls in this range, divided by Δc to obtain a probability density (bars in panel b). The continuous PDF (solid line in panel b) is obtained in the limit of infinitesimal bin widths dc . Each infinitesimal region dx around a point where $C(x) = c$ contributes a probability density $(dx/dc)/|\Omega| = 1/(|\Omega|dC(x)/dx)$. This causes a divergence of the PDF at the maximum concentration $c_M = 1$, where the gradient is zero, and contributes to a large value at the minimum concentration $c_m = C(3) = C(-3)$, where the gradient is small. These concepts are quantified and explored in detail throughout the text.

116 the spatial dimension d). We denote by $|A|$ the d -volume of a spatial domain A (volume for $d = 3$ -
117 dimensional A , area for $d = 2$, length for $d = 1$, and number of points for $d = 0$). As usual, $|\mathbf{a}|$ for a
118 vector \mathbf{a} denotes its Euclidean norm. We consider a spatial domain $\Omega(t)$ where the concentrations are
119 defined for each time t , and denote by $\mathbf{X}(t)$ a random variable with a uniform distribution over $\Omega(t)$.
120 The average with respect to $\mathbf{X}(t)$, i.e., the spatial average, is denoted by $\overline{\cdot}$. We also introduce, for
121 each time t , a random variable $\underline{C}(t)$ taking concentration values according to their spatial probability
122 of occurrence, and denote the average with respect to it (i.e., over concentrations) by $\langle \cdot \rangle$. As will be
123 discussed in more detail below, the two averages, while conceptually different, yield equivalent results.
124 That is, for an arbitrary function $f(\underline{c}, t)$ of concentrations \underline{c} and times t ,

$$\overline{f(\underline{C}[\mathbf{X}(t), t])} = \frac{1}{|\Omega(t)|} \int_{\Omega(t)} d\mathbf{x} f(\underline{C}[\mathbf{X}(t), t]) = \int_0^{\infty} d\underline{c} f(\underline{c}, t) p(\underline{c}; t) = \langle f[\underline{C}(t), t] \rangle, \quad (1)$$

125 where, at each time t , $p(\cdot; t)$ is the concentration PDF, to be formally defined momentarily.

126 2.1 General formulation for a multispecies system

127 At each time t , the concentration PDF $p(\cdot; t)$ is defined so that $p(\underline{c}; t) d\underline{c}$ is the probability, in the sense
128 of spatial frequency of occurrence, of finding a concentration in the infinitesimal vicinity $d\underline{c} = \prod_{j=1}^{n_s} dc_j$
129 of \underline{c} in the domain $\Omega(t)$. According to this definition, we have

$$p(\underline{c}; t) = \overline{\delta[\underline{c} - \underline{C}[\mathbf{X}(t); t]]} = \frac{1}{|\Omega(t)|} \int_{\Omega(t)} d\mathbf{x} \delta[\underline{c} - \underline{C}(\mathbf{x}; t)], \quad (2)$$

130 where $\delta(\cdot)$ is the Dirac delta. Intuitively, this expression encodes the fact that the contributions to the
 131 probability of having a value \underline{c} of concentration at time t correspond to points \mathbf{x} where $\underline{C}(\mathbf{x}; t) = \underline{c}$,
 132 which are “counted” by the Dirac delta in accordance with the continuous nature of concentrations
 133 (for the general theory of PDFs as averages of Dirac deltas, see, e.g., [64]). This corresponds to the
 134 continuum limit described in Fig. 2.

135 The concentration PDF contains information about the full structure of point statistical variability
 136 of concentrations. According to the definition, Eq. (2), moments of concentration, such as the
 137 component-wise mean concentrations $\langle \underline{C}(t) \rangle$ and variances $\sigma_c^2 = \langle \underline{C}^2(t) \rangle - \langle \underline{C}(t) \rangle^2$ (representing not
 138 a spatial variance but variability with respect to the mean concentration), may be computed given
 139 knowledge of the PDF, and agree with those obtained from the spatial profile. In particular,

$$\langle \underline{C}(t) \rangle = \int_0^\infty d\underline{c} \underline{c} p(\underline{c}; t) = \frac{M(t)}{|\Omega(t)|} = \overline{\underline{C}[\mathbf{X}(t); t]}, \quad (3)$$

140 where the total component masses are given by

$$\underline{M}(t) = \int_{\Omega(t)} d\mathbf{x} \underline{C}(\mathbf{x}; t). \quad (4)$$

141 It is important to note that $\Omega(t)$ may be time-dependent, but its size $|\Omega(t)|$ must be finite at all
 142 times, because a uniformly-distributed random variable $\mathbf{X}(t)$ does not exist in an infinite domain.
 143 Intuitively, this is related to the fact that the concentration PDF is defined in terms of the spatial
 144 frequency of occurrence of concentration values. Thus, if the total component masses are finite, most
 145 regions in an infinite domain $\Omega(t)$ must have a vanishing concentration, and $p(\underline{c}; t) = 0$ for all $\underline{c} \neq 0$,
 146 so that we must have trivially $p(\underline{c}; t) = \delta(\underline{c})$ by normalization. In practice, as will be discussed in more
 147 detail below, this means that in order to define a non-trivial concentration PDF we must consider
 148 either a finite, fixed reference domain Ω , or a minimum concentration threshold c_m such that $\Omega(t)$ is
 149 the region where concentrations are above this threshold. Finally, we note that, in an infinite periodic
 150 system, the concentration PDF may be naturally defined over a single period. The previous argument
 151 can be circumvented in this case because the total mass in such an infinite system is infinite, although
 152 the mass per period is finite.

153 2.2 Single-species formulation

154 Writing the concentration PDF in a more useful analytical form requires changing variables in the
 155 Dirac delta in Eq. (2), in order to identify the spatial points \mathbf{x} that contribute to the integral for a
 156 given value of concentration \underline{c} . In other words, we must invert the relations $\underline{C}(\mathbf{x}; t) = \underline{c}$, which form
 157 a set of n_s constraints in d dimensions. These constraints are not necessarily independent, and this is
 158 a difficult problem in general from an analytical perspective. We now derive a simple analytical form
 159 for the single-species case. We write $C = C_1$ and $c = c_1$ for the single species component. A numerical
 160 computation procedure, also valid for the general multispecies PDF, is discussed in Appendix A.

161 Assuming $C(\cdot; t)$ to be smooth, the Dirac delta can be expressed as a simple-layer integral [65],

$$\delta[c - C(\mathbf{x}; t)] = \int_{\Lambda(c; t)} dS(\mathbf{y}) \frac{\delta(\mathbf{x} - \mathbf{y})}{|\nabla C(\mathbf{y}; t)|}, \quad (5)$$

162 where $dS(\mathbf{x})$ is the $(d - 1)$ -area element at point \mathbf{x} on the $(d - 1)$ -surface consisting of the points
 163 in the domain at time t at which the concentration has value c , and which do not constitute a local
 164 extremum (or zero-gradient inflection point). Formally, this surface is defined as $\Lambda(c; t) = \{\mathbf{x} \in \Omega(t) \mid$
 165 $C(\mathbf{x}; t) = c \wedge |\nabla C(\mathbf{x}; t)| \neq 0\}$. Note that, for the one-dimensional example in Fig. 2, $\Lambda(c) = 2$ for all
 166 concentrations strictly between the minimum and maximum values. This is discussed in more detail

167 in Section 2.4. Substituting Eq. (5) in Eq. (2), we find

$$p(c; t) = \int_{\Lambda(c; t)} \frac{dS(\mathbf{x})}{|\Omega(t)||\nabla C(\mathbf{x}; t)|}. \quad (6)$$

168 This form corresponds to the intuitive notion of a change of variables mentioned above: it expresses
 169 the contribution to the probability density of a given value c of concentration as a spatial integral over
 170 the spatial region where the concentration takes the required value (see also Fig. 2). This spatial region
 171 has dimensionality one less than the full space due to the constraint $C(\mathbf{x}; t) = c$. This result holds
 172 for smooth, non-constant $C(\cdot; t)$. The contributions of concentrations found near spatial concentration
 173 extrema and in extended regions of constant concentration are discussed below.

174 Equation (6) can also be expressed so as to highlight the role of concentration gradients associated
 175 with a given concentration in determining the value of the PDF. To this end, consider the harmonic
 176 average $g_h(c; t)$ of the concentration gradient magnitudes in $\Lambda(c; t)$. By definition, it is given by

$$g_h(c; t) = \left[\frac{1}{|\Lambda(c; t)|} \int_{\Lambda(c; t)} \frac{dS(\mathbf{x})}{|\nabla C(\mathbf{x}; t)|} \right]^{-1}. \quad (7)$$

177 Substituting this definition in Eq. (6) immediately yields the simple form

$$p(c; t) = \frac{|\Lambda(c; t)|}{|\Omega(t)|g_h(c; t)}. \quad (8)$$

178 The proportionality to the inverse of a concentration gradient magnitude is a consequence of the
 179 fact that $p(c; t)$ is a density, i.e., a probability per unit concentration. Spatial regions where the
 180 concentration gradient is low correspond to a higher density around the corresponding concentration
 181 value due to the slow variation. To understand this, consider a surface $\Lambda(c; t)$ over which the gradient
 182 magnitude $g_h(c; t) = |\nabla C|$ is homogeneous and therefore equal to its harmonic average. A small
 183 variation dc of concentration occurs over a distance $dz = dc/g_h(c; t)$ along the concentration gradient.
 184 The gradient is locally perpendicular to the surface of constant concentration, so that the spatial
 185 volume associated with an occurrence of concentration in $[c, c + dc]$ is $|\Lambda(c; t)|dz$. Correspondingly,
 186 the contribution to the probability $p(c; t)dc$ of concentration in this range is $|\Lambda(c; t)|dz/|\Omega(t)|$. Thus,
 187 its contribution to the concentration PDF $p(c; t)$ is $|\Lambda(c; t)|/[|\Omega(t)|g_h(c; t)]$, in agreement with Eq. (8).
 188 This is illustrated for a one-dimensional profile in Fig. 2. More generally, if the gradient is not constant
 189 over the surface, the same argument can be applied locally, using the area element dS introduced above
 190 and the volume element $dSdz$. The inverse proportionality to the harmonic average then arises due to
 191 the inverse proportionality of the local contributions to the inverse gradient magnitude, which must
 192 be integrated over. This provides an intuitive explanation for Eq. (6) and recovers Eq. (8).

193 2.3 Extrema and constant-concentration regions

194 We now study the impact on the concentration PDF of local extrema of the spatial concentration
 195 profile, at which $|\nabla C(\mathbf{x}; t)| = 0$. Near an extremum c_0 at position \mathbf{x}_0 and time t , we have $C(\mathbf{x}_0 +$
 196 $\Delta\mathbf{x}; t) \approx c_0 + \Delta\mathbf{x} \cdot H(\mathbf{x}_0; t)\Delta\mathbf{x}/2$ and $\nabla C(\mathbf{x}; t) \approx H(\mathbf{x}_0; t)\Delta\mathbf{x}$, where $H(\mathbf{x}_0; t)$ is the Hessian matrix
 197 of concentration at position \mathbf{x}_0 and time t , with components $H_{ij}(\mathbf{x}_0; t) = \nabla_i \nabla_j C(\mathbf{x}; t)|_{\mathbf{x}=\mathbf{x}_0}$. We find
 198 that in $d = 1$ the PDF of concentration behaves in a vicinity Δc of c_0 as

$$p(c_0 + \Delta c; t) \approx \left(|\Omega(t)| \sqrt{\Delta c \left. \frac{\partial^2 C(\mathbf{x}; t)}{\partial x^2} \right|_{\mathbf{x}=\mathbf{x}_0}} \right)^{-1}, \quad (9)$$

199 to first order in $|\Delta c| \ll c_0$, for $\Delta c < 0$ near a maximum and $\Delta c > 0$ near a minimum. This type
 200 of divergent behavior due to a spatial maximum can be observed in Fig. 2. We note that this is an

201 integrable divergence, that is, the integral of $p(\cdot; t)$ converges near c_0 as necessary for a PDF. This
 202 result is a direct consequence of the fact that for a smooth function near an extremum the behavior of
 203 the function is quadratic, and the behavior of its derivative is linear. We have assumed the extremum is
 204 non-degenerate, so that the second derivative is nonzero; otherwise, higher order terms are important
 205 and the behavior is different.

206 In arbitrary dimension, we provide an argument based on dimensional analysis. First, note that
 207 the qualitative behavior near an extremum is determined by the Hessian determinant $|H|$ and the
 208 distance $|\Delta\mathbf{x}|$ to the maximum; thus, the gradient near an extremum obeys $|\nabla C| \propto |H|^{1/d}|\Delta\mathbf{x}|$, and
 209 the concentration changes as $|\Delta c| \propto |\nabla c||\Delta\mathbf{x}| \propto |H|^{1/d}\Delta x^2$. The second equation gives $|\Delta\mathbf{x}| \propto$
 210 $|H|^{-1/(2d)}|\Delta c|^{1/2}$, and substituting in the first leads to $p(c_0 + \Delta c) \approx |\Lambda(c_0 + \Delta c; t)|/|\Omega(t)||\nabla C| \propto$
 211 $|\Lambda(c_0 + \Delta c; t)|/|\Omega(t)||H|^{1/(2d)}|\Delta c|^{1/2}$. Substituting $|\Lambda(c_0 + \Delta c; t)| \propto |\Delta\mathbf{x}|^{d-1}$ for the $(d-1)$ -area of
 212 the surface of concentration $c_0 + \Delta c$ yields

$$p(c_0 + \Delta c; t) \propto \frac{|\Delta c|^{d/2-1}}{|\Omega(t)||H|^{1/2}}. \quad (10)$$

213 Thus, there is no divergence in $d \geq 2$. In $d = 2$, extrema of the spatial concentration correspond to
 214 extrema of the concentration PDF, and in $d = 3$ they correspond to zeros. As before, we have assumed
 215 that the minimum is non-degenerate, i.e., $|H| \neq 0$. As a simple example of degeneracy, consider a
 216 concentration field which is constant along the second and third dimensions, and exhibits a regular
 217 extremum along the first dimension. As expected, the divergence as the extremum is neared then
 218 depends only on the distance Δx along the first dimension, and the square-root divergence of the
 219 concentration PDF characteristic of $d = 1$ is recovered.

220 If $C(\cdot; t)$ is constant in space (i.e., the concentration is homogeneous), or if we relax the smoothness
 221 assumption so that $|\nabla C(\cdot; t)|$ may be zero in open sets by letting $C(\cdot; t)$ be non-differentiable at their
 222 boundary (i.e, piecewise-smooth), these sets may contribute additional terms to the concentration PDF.
 223 Consider first that the concentration is piecewise-constant. Each set $\Omega_i(t)$ where the concentration
 224 takes a given position-independent value $c_i(t)$ at time t is associated with a probability $|\Omega_i(t)|/|\Omega(t)|$.
 225 Note that there must be a finite number $N(t)$ of such constant-concentration sets at each time, and thus
 226 a finite number of corresponding concentration values, because open sets have nonzero measure and
 227 sets corresponding to different concentrations are disjoint, so that $|\Omega(t)| = \sum_{i=1}^{N(t)} |\Omega_i(t)|$. Therefore,

$$p(c; t) = \sum_{i=1}^{N(t)} \frac{|\Omega_i(t)|}{|\Omega(t)|} \delta[c - c_i(t)]. \quad (11)$$

228 The Dirac deltas express the fact that concentration takes a single specific value within spatially-
 229 homogeneous regions. If the concentration is piecewise-smooth and non-constant over certain parts
 230 of the domain, Eq. (8) may be applied separately to each such region, and the contributions of all
 231 constant and non-constant regions summed over to obtain the full concentration PDF.

232 2.4 One-dimensional Gaussian profile

233 As a relevant example which will play a central role in Section 3, we consider a single-species Gaussian
 234 concentration profile in $d = 1$ spatial dimension (Fig. 1), characterized by spatial variance $\sigma^2(t)$ and
 235 total mass $M(t)$:

$$C(x; t) = \frac{M(t)}{\sqrt{2\pi\sigma^2(t)}} \exp\left[-\frac{x^2}{2\sigma^2(t)}\right]. \quad (12)$$

236 The corresponding regions of constant concentration c are zero-dimensional, $\Lambda(c; t) = \{x | x = \pm x_c(c; t)\}$.
 237 Inverting $C(x; t) = c$ for x ,

$$x_c(c; t) = \sqrt{2\sigma^2(t) \ln[c_M(t)/c]}, \quad (13)$$

238 where

$$c_M(t) = \frac{M(t)}{\sqrt{2\pi\sigma^2(t)}} \quad (14)$$

239 is the maximum concentration at time t . The zero-dimensional area element on $\Lambda(c; t)$ is a sum of
 240 point measures concentrated at the two points $\pm x_c(c; t)$ where the concentration takes a given value,
 241 $dS(x) = (\delta[x + x_c(c; t)] + \delta[x - x_c(c; t)]) dx$. For all $c < c_M(t)$, $|\Lambda(c; t)| = 2$ because it consists of
 242 two points. The gradient of concentration magnitudes at $\pm x_c(c; t)$ have the same value, so that their
 243 harmonic average is equal to this value and given by

$$g_h(c; t) = |\nabla C(x; t)|_{x=\pm x_c(c; t)} = \sqrt{\frac{2c^2 \ln[c_M(t)/c]}{\sigma^2(t)}}. \quad (15)$$

244 As discussed in Section 2, we must consider a finite domain in order for the concentration PDF
 245 to be well-defined. This can be conveniently achieved through one of two possible approaches. The
 246 first considers a fixed (i.e., time-independent) reference domain Ω centered at $x = 0$. In this case,
 247 a time-dependent minimum concentration $c_m(t) = c_M(t) \exp\{-|\Omega|^2/[8\sigma^2(t)]\}$ is found at the fixed
 248 domain boundaries. Alternatively, we fix a (time-independent) minimum concentration c_m , and con-
 249 sider $\Omega(t) = \{x|C(x; t) > c_m\}$, the time-dependent spatial domain where concentration are above the
 250 minimum value. In this case, c_m can be thought of as a lower detection limit, and the concentration
 251 PDF as being computed over the region of space where non-zero concentration is detected. In either
 252 case, using Eq. (8) leads to the concentration PDF

$$p(c; t) = \frac{H[c_M(t) - c]H[c - c_m(t)]}{2c\sqrt{\ln[c_M(t)/c] \ln[c_M(t)/c_m(t)]}}, \quad (16)$$

253 where under the second approach $c_m(t) = c_m$ is constant. This PDF is illustrated in Fig. 2, and it
 254 agrees with the result reported, e.g., in [30]. By noting that $|\Omega(t)| = 2x_c[c_m(t); t]$ and using Eqs. (13)
 255 and (14), we find

$$|\Omega(t)| = \frac{2M(t)}{c_M(t)} \sqrt{\frac{\ln[c_M(t)/c_m(t)]}{\pi}}, \quad (17)$$

256 and the concentration PDF can thus also be expressed as

$$p(c; t) = \frac{M(t)H[c_M(t) - c]H[c - c_m(t)]}{|\Omega(t)|c c_M(t) \sqrt{\pi \ln[c_M(t)/c]}}. \quad (18)$$

257 Note that, for fixed t , setting $c = c_M(t) - \Delta c$ and expanding to first order in Δc recovers the expected
 258 $\Delta c^{-1/2}$ divergence due to the presence of a spatial maximum discussed in Section 2.3. For small
 259 concentrations compared to the peak value, this PDF scales as $1/c$ with logarithmic corrections.

260 Using these results and Eq. (12), it can be verified by direct computation that the mean concen-
 261 tration is given by

$$\langle C(t) \rangle = \overline{C(X; t)} \approx \frac{M(t)}{|\Omega(t)|} = \frac{c_M(t)}{2} \sqrt{\frac{\pi}{\ln[c_M(t)/c_m(t)]}}, \quad (19)$$

262 and for the second moment of concentration we have

$$\langle C^2(t) \rangle = \overline{C^2(X; t)} \approx \frac{M(t)c_M(t)}{\sqrt{2}|\Omega(t)|} = \frac{c_M^2(t)}{2} \sqrt{\frac{\pi}{2 \ln[c_M(t)/c_m(t)]}}, \quad (20)$$

263 where the approximation corresponds to approximating the total mass $M(t)$ in the infinite domain
 264 by the mass within $\Omega(t)$, over which concentration is larger than $c_m(t)$. Note that, in particular, this
 265 approximation requires $c_M(t) \gg c_m(t)$, that is, the lower detection limit must be small compared to
 266 the peak concentration. Under the same approximation, the variance of concentration is thus

$$\sigma_c^2(t) \approx \frac{\pi c_M^2(t)}{4 \ln[c_M(t)/c_m(t)]} \left[\sqrt{\frac{2 \ln[c_M(t)/c_m(t)]}{\pi}} - 1 \right], \quad (21)$$

267 or equivalently

$$\frac{\sigma_c^2(t)}{\langle C(t) \rangle^2} \approx \sqrt{\frac{2 \ln[c_M(t)/c_m(t)]}{\pi}} - 1. \quad (22)$$

268 Note that the mean and variance of concentration represent the mean value and the associated vari-
 269 ability in the frequency of occurrence of concentration values found throughout the domain. They
 270 differ from the more common metrics of mean plume position, which here is zero, and spatial or plume
 271 variance, which here is $\sigma^2(t)$.

272 3 Concentration PDF evolution under nonlinear reaction and 273 diffusion

274 In this section, we apply the concepts developed above to the single-species, one-dimensional reaction-
 275 diffusion problem

$$\frac{\partial C(x; t)}{\partial t} = D \frac{\partial^2 C(x; t)}{\partial x^2} - r[C(x; t)], \quad (23)$$

276 where the reaction rate as a function of concentration has the form

$$r(c) = \kappa c^\beta, \quad (24)$$

277 with $\beta > 0$ the order of the reaction and κ the reaction rate constant in units of $[C^{1-\beta}T^{-1}]$. Under-
 278 standing the role and dynamics of concentration statistics under one-dimensional reaction-diffusion
 279 represents a fundamental first step towards treating more complex reaction problems in heterogeneous
 280 flow fields. In this connection, we discuss the Ranz transform, which was developed to quantify mixing
 281 and reaction in the context of turbulence and combustion problems [62, 66] and has more recently been
 282 employed to study these phenomena in porous media [30, 67, 68]. The goal of the Ranz transform is to
 283 exploit the fact that material elements in an incompressible flow tend to orient themselves according
 284 to the principal directions of strain-induced stretching (Fig. 1), forming thin lamellar structures (lines
 285 in 2D or sheets in 3D) [48, 69–74, 74–76].

286 Due to incompressibility, the thickness of such a material element along the principal axis of com-
 287 pression is given by $s(t) = s(0)A(0)/A(t)$, where $A(t)$ is its area (or length in 2D). Assuming that local
 288 compression is well described by a first-order Taylor expansion of the flow, and neglecting concentra-
 289 tion gradients on the surface in comparison to normal gradients along the compression direction ζ , the
 290 advection-diffusion-reaction equation becomes [30, 67, 74, 75]

$$\frac{\partial C}{\partial t} = -\frac{\zeta}{s} \frac{ds}{dt} \frac{\partial C}{\partial \zeta} + D \frac{\partial^2 C}{\partial \zeta^2} - r(C). \quad (25)$$

291 These approximations provide a very good description of transport at high Péclet number [30, 74, 75].
 292 Applying the Ranz transform [62],

$$\tau = \int_0^t dt' \frac{s^2(0)}{s^2(t')}, \quad \xi = \frac{s(0)}{s(t)} \zeta, \quad (26)$$

293 reduces Eq. (25) to a diffusion-reaction equation in the new time τ and rescaled transverse coordinate
 294 ξ , which takes into account the history of advective deformation:

$$\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial \xi^2} - \frac{s^2}{s_0^2} r(C). \quad (27)$$

295 Thus, the full advection-diffusion-reaction problem reduces to a collection of one-dimensional diffusion-
 296 reaction problems over lamellae. Solving this problem remains highly nontrivial, as it requires deter-
 297 mining the statistics of thicknesses $s(t)$ and those of lamella coalescence (overlapping) [30, 46, 67,
 298 68, 77, 78], and the solution of the one-dimensional reaction-diffusion problem (27) for given $s(\tau)$,
 299 where the reaction rate becomes time-dependent according to a rescaling by $s^2(\tau)/s_0^2$. Treating the
 300 full problem is beyond the scope of this work. Here, we restrict ourselves to the purely-diffusive case,
 301 Eq. (23), which corresponds to setting $s^2/s_0 = 1$ in Eq. (27), with the power-law reaction rate (24).

302 The dynamics remain nontrivial even under this simplified scenario. When the reaction is nonlinear
 303 (order β nonzero and different from unity), the effective kinetics, representing the overall reaction rate
 304 for a given amount of available mass, depend on the spatial variability of concentration. In other
 305 words, the global reaction rate $dM(t)/dt$ for the total mass is not given by $\kappa M^\beta(t)$, except when
 306 $\beta = 1$ or when the system is well mixed, i.e., uniformly characterized by a single concentration value.
 307 Similar considerations apply to the reaction rate in terms of the mean concentration instead of the total
 308 mass. Nonetheless, knowledge of the point statistics of concentration as encoded in the concentration
 309 PDF is sufficient to fully characterize the global reaction rate, which can be obtained by integrating
 310 Eq. (23) over the domain $\Omega(t)$. Using integration by parts, the diffusive term can be seen to contribute
 311 $2D|\partial C/\partial x|$ evaluated at the domain boundaries, which we neglect under the assumption of a small
 312 lower detection limit c_m as above, we obtain

$$\frac{dM(t)}{dt} = - \int_0^\infty dc r(c) p(c; t) = -\kappa \int_0^\infty dc c^\beta p(c; t), \quad (28)$$

313 where in the last equality we have expressed the integral of the reactive contribution in terms of the
 314 concentration PDF using its definition, Eq. (2).

315 In what follows, we will first derive a dynamical equation for the evolution of the concentration
 316 PDF, in terms of a concentration-dependent scalar dissipation rate. We will then discuss and employ
 317 the Gaussian spatial profile arising from the weak-coupling approximation of [7] to directly compute
 318 the evolution of the concentration PDF using the results of Section 2.4, and compare it to the PDF
 319 obtained from numerical solutions of Eq. (23).

320 3.1 Dynamical equation for the concentration PDF

321 The concentration PDF evolves under the combined action of transport and reaction processes. The
 322 structure of the reaction–diffusion equation (23), where transport and reaction terms locally contribute
 323 independently to the evolution of the concentration field, ensures that the same holds for the evolution
 324 of the concentration PDF for each value of concentration. We thus seek to express its evolution as

$$\frac{\partial p(c; t)}{\partial t} = \Delta p_D(c; t) + \Delta p_R(c; t), \quad (29)$$

325 where the two contributions respectively represent the effect of diffusion and reaction. Note that, while
 326 this independence holds locally, the global reaction dynamics (i.e., the evolution of the total mass and
 327 other global quantities such as the concentration mean and variance) are affected by the dynamical
 328 evolution of the plume through the combined effect of transport and reaction. These dynamics will
 329 be discussed in detail in Section 4 using a weak-coupling approximation. We focus in what follows on
 330 the case of a fixed minimum detection limit c_m and a time-varying domain $\Omega(t)$ where concentrations
 331 are above c_m . This choice avoids the introduction of an arbitrary domain devoid of physical meaning,
 332 and corresponds more closely to real-world situations, where a lower detection limit always exists.
 333 Nonetheless, note that the introduction of a fixed reference domain may be appropriate if one is in
 334 fact interested in a specific spatial region, and the formalism can be easily adapted to that case.

335 As shown in Appendix B, the reactive contribution in Eq. (29) is given by

$$\Delta p_R(c; t) = \frac{\partial r(c) p(c; t)}{\partial c} + p(c; t) p(c_m; t) r(c_m). \quad (30)$$

336 Note that it is completely determined given knowledge of the concentration PDF and local reaction
 337 rate as a function of concentration. The first term represents the net change in the probability density
 338 of concentration c due to reaction, and the second term guarantees the PDF remains normalized by
 339 accounting for reactive decay of concentrations below the threshold value c_m .

340 It should be clear that, in general, knowledge of the frequencies of occurrence of concentration
 341 values, as expressed by $p(c; t)$, is not sufficient to determine their evolution under transport. This is

342 because concentration fluxes due to advection and diffusion are sensitive to the spatial gradients in the
 343 concentration profiles. Thus, without additional information, an equation for the concentration PDF,
 344 which encodes only the point statistics of concentration, cannot be closed. However, it is possible to
 345 express the concentration PDF's evolution in terms of an additional mixing metric, which corresponds
 346 to the scalar dissipation rate (see, e.g., [53, 54]),

$$\chi_x(x; t) = (\nabla C) \cdot (D \nabla C), \quad (31)$$

347 expressed as a function of concentration. We make the simplifying assumption that the initial con-
 348 centration profile $C(x, 0)$ is symmetric about the origin and monotonically decreasing away from it
 349 (as happens, e.g., for a Gaussian profile or a square pulse). In that case, these properties hold for all
 350 times, so that a given concentration value is associated with a single concentration gradient magnitude,
 351 simplifying the description. Under these assumptions, the concentration-dependent scalar dissipation
 352 rate is given by

$$\chi(c; t) = \chi_x[\pm x_c(c; t); t] = D g_h^2(c; t), \quad (32)$$

353 where the harmonic average gradient magnitude g_h is equal to the gradient magnitude at both points
 354 $\pm x_c$ where the concentration is equal to c . As shown in Appendix B, we have for the transport
 355 contribution:

$$\Delta p_D(c; t) = p(c; t) \left[\frac{1}{4} \frac{\partial \ln \chi(c; t)}{\partial c} \frac{\partial \chi(c; t)}{\partial c} - \frac{1}{2} \frac{\partial^2 \chi(c; t)}{\partial c^2} - \frac{p(c_m; t)}{2} \frac{\partial \chi(c; t)}{\partial c} \Big|_{c=c_m} \right], \quad (33)$$

356 where the first and second terms arise from the impact of diffusion on the concentration gradients
 357 associated with a given concentration value, and the third term is due to the change in domain size
 358 due to concentrations dropping below c_m by diffusion.

359 Substituting Eqs. (30) and (33) in Eq. (29), we conclude that the combined effect of transport and
 360 reaction leads to

$$\begin{aligned} \frac{\partial p(c; t)}{\partial t} = \frac{\partial r(c)p(c; t)}{\partial c} + & \left[\frac{1}{4} \frac{\partial \ln \chi(c; t)}{\partial c} \frac{\partial \chi(c; t)}{\partial c} - \frac{1}{2} \frac{\partial^2 \chi(c; t)}{\partial c^2} \right. \\ & \left. + \left(r(c_m) - \frac{1}{2} \frac{\partial \chi(c; t)}{\partial c} \Big|_{c=c_m} \right) p(c_m; t) \right] p(c; t). \end{aligned} \quad (34)$$

361 This equation shows that the dynamical evolution of the concentration PDF for this problem is fully
 362 determined given knowledge of the local reaction rates $r(c)$ and the concentration-dependent scalar
 363 dissipation rate $\chi(c; t)$. The first (reactive) term on the right-hand side has the form of an advective
 364 contribution: the reaction rate $r(c)$ functions as an advective “velocity” (units of inverse concentration
 365 per time) generating a net flux of probability towards lower concentrations. The remaining contri-
 366 butions have the form of concentration-dependent sink/source terms. The first two terms in square
 367 brackets, which are governed by the scalar dissipation rate, encode the impact on the PDF of changes
 368 in concentration values and the associated gradients due to diffusive transport. The remaining terms
 369 concern the reactive and diffusive fluxes of probability towards concentration values below the de-
 370 tection limit. These affect the concentration PDF through the normalization across the remaining
 371 concentration values, since $\int_{c_m}^{c_M(t)} dc p(c; t) = 1$ by definition.

372 As discussed in the introduction, the scalar dissipation rate has been studied in connection with
 373 mixing in porous media. By clarifying its role in the evolution of the concentration PDF, this approach
 374 provides a promising departure point for upscaling of reaction dynamics under transport.

375 4 Concentration dynamics under the weak-coupling approxi- 376 mation

377 The weak-coupling approximation developed in [7] simplifies the full reaction–diffusion dynamics of
 378 Eq. (23) by assuming that, after a time on the order of the diffusion time, the concentration profile

379 remains Gaussian as for the conservative problem, but with a spatial variance and mass that are affected
 380 by reaction. We briefly review this approach before applying the theory and concepts developed here
 381 to analyze the evolution of concentration statistics.

382 4.1 Problem setup and nondimensionalization

383 We will focus here, as in [7], on a rectangular pulse initial condition, corresponding to constant con-
 384 centration $c_0 = M_0/s_0$ over a domain $\Omega(t)$ centered at the origin and of initial width $s_0 = |\Omega(0)|$. This
 385 setup correspond to a Dirac delta initial condition for the PDF, $p(c; 0) = \delta(c - c_0)$. The initial condition
 386 allows for meaningful direct comparison with the well-mixed batch problem in the domain $\Omega(0)$, which
 387 corresponds to the purely-reactive scenario in the absence of diffusion. In that case, $D = 0$, so that
 388 the scalar dissipation rate $\chi \equiv 0$, and we denote the associated uniform solution for concentration as
 389 a function of time as $c_B(t)$.

390 In addition, in order to meaningfully compare the behavior of the system across different parameter
 391 values, it is convenient to nondimensionalize concentration according to the initial concentration c_0 ,
 392 position according to the initial width s_0 , and time according to the characteristic reaction time [7]
 393 $\tau_R = \kappa^{-1}c_0^{1-\beta}$. Thus, denoting nondimensionalized quantities by an asterisk, nondimensional time
 394 is given by t_*/τ_R , positions by $x_* = x/s_0$, and concentrations by $C_* = C/c_0$, seen as a function of
 395 nondimensional times and positions. Functions of these quantities, such as the concentration PDF, are
 396 nondimensionalized accordingly; further details may be found in Appendix D. In what follows, we work
 397 exclusively in nondimensional units and drop the asterisks for notational brevity. The nondimensional
 398 transport equation is given by

$$\frac{\partial C(x; t)}{\partial t} = \frac{1}{2 \text{Da}} \frac{\partial^2 C(x; t)}{\partial x^2} - r[C(x, t)], \quad (35)$$

399 where we have introduced the Damköhler number

$$\text{Da} = \frac{\tau_D}{\tau_R}, \quad \tau_D = \frac{s_0^2}{2D}. \quad (36)$$

400 A large Damköhler number corresponds to fast reaction compared to the diffusion time τ_D associated
 401 with the nondimensionalization lengthscale s_0 , and a low Damköhler number to slow reaction. Note
 402 that Eq. (34) for the evolution of the concentration PDF remains unchanged when all intervening
 403 quantities are nondimensionalized.

404 4.2 Early times – Batch dynamics

405 Under the weak-coupling approximation, up to times on the order of the diffusion time, the concen-
 406 tration distribution is approximated as not having deformed substantially with respect to the initial
 407 condition, here a square pulse of unit width in nondimensional coordinates. Thus, up to nondimen-
 408 sional time $t = \text{Da}$, the system is taken to evolve according to reaction in a batch reactor. Since
 409 variations in the spatial distribution up to this time are considered negligible and not resolved, under
 410 this approximation the concentration PDF remains a Dirac delta for $t \leq \text{Da}$, $p(c; t) \approx \delta[c - c_B(t)]$. We
 411 have (see also Appendix E):

$$\frac{dc_B}{dt} = -c_B^\beta. \quad (37)$$

412 The special case $\beta = 1$ corresponds to linear reactions. Decay is then exponential, $c_B(t) = \exp(-t)$.
 413 In this classical case, reaction and transport dynamics are fully decoupled: the exact solution of the
 414 full reactive transport problem is simply the conservative transport solution, multiplied by $\exp(-t)$ to
 415 account for mass loss due to reaction. For nonlinear reactions, $\beta \neq 1$, integrating Eq. (37) yields

$$c_B(t) = [1 - (1 - \beta)t]^{1/(1-\beta)}. \quad (38)$$

416 In nondimensional units, the total mass and concentration coincide for batch dynamics, because
 417 the width of the pulse is approximated as constant and equal to the initial unit width in this time

418 window. Thus, for $t < \text{Da}$ we approximate $M(t) \approx c_B(t)$. Note that for $\beta < 1$ the batch reaction is
 419 fully depleted in a finite time

$$t_f^B = \frac{1}{1 - \beta}. \quad (39)$$

420 If $t_f^B < \text{Da}$, the full dynamics are thus simply treated as a well-mixed batch reactor.

421 4.3 Late times – Gaussian profile

422 For times $t < \text{Da}$, [7] have verified that the dynamics are reasonably well approximated by a well-mixed
 423 batch reactor, disregarding transport and spatial variability in concentration. We thus focus now on
 424 times $t \geq \text{Da}$, for which spatial concentration variability cannot be neglected. Starting at $t = \text{Da}$, when
 425 diffusion has had sufficient time to deform the concentration pulse, the weak-coupling approximation
 426 consists in approximating the spatial profile as a Gaussian, whose properties are governed by the
 427 combined effect of reaction and diffusion as detailed below. Consider first Eq. (34) for the dynamical
 428 evolution of the concentration PDF. Under the Gaussian approximation, the scalar dissipation rate
 429 can be computed analytically. From Eqs. (12) and (13) for the Gaussian profile and (77b) for the
 430 scalar dissipation rate, we find

$$\chi(c; t) = \frac{2\pi c_M^2(t) c^2 \ln[c_M(t)/c]}{\text{Da } M^2(t)} H[c_M(t) - c] H[c - c_m], \quad (40)$$

431 where we have used Eq. (14) to express the spatial variance in terms of the mass and peak concentration.
 432 Note that, expanding the logarithm in Taylor series for small Δc near the peak value, $c = c_M(t) - \Delta c$,
 433 we find that the scalar dissipation rate approaches zero linearly with Δc . At low concentrations
 434 compared to the peak value, it scales as c^2 with logarithmic corrections. Using Eq. (40), Eq. (34) for
 435 the evolution of the concentration PDF becomes

$$\begin{aligned} \frac{\partial p(c; t)}{\partial t} = \frac{\partial c^\beta p(c; t)}{\partial c} + & \left\{ \frac{1 + 2 \ln[c_M(t)/c]}{2 \ln[c_M(t)/c]} \right. \\ & \left. + \left(1 - 2 \ln \frac{c_M(t)}{c_m} + c_m^{\beta-1} \right) c_m p(c_m; t) \right\} \frac{\pi c_M^2(t) p(c; t)}{\text{Da } M^2(t)}. \end{aligned} \quad (41)$$

436 Consider first the conservative case, corresponding to omitting the reactive terms involving c^β and
 437 c_m^β . As explained above, we consider a Gaussian initial condition at $t = \text{Da}$, and take the detection
 438 limit to be sufficiently low for the mass corresponding to concentrations above c_m to be approximately
 439 equal to the total mass for all times of interest. Then, $M(t) = 1$, and the peak concentration is given
 440 by Eq. (14) with a spatial variance $\sigma^2(t) = \sigma^2(0) + (t - \text{Da})/\text{Da}$. Using Eq. (16) for the Gaussian
 441 concentration PDF, it can be verified by direct calculation that Eq. (34) holds identically for all c and
 442 t . As a direct verification of the combined effect of reaction and diffusion on the concentration PDF,
 443 consider the particular case of a linear decay reaction, $r(c) = c$, for which analytical solutions are
 444 available. In this case, the concentration profile remains exactly Gaussian as before, but with a total
 445 mass that evolves in time as $M(t) = \exp(-t)$. The spatial variance remains unchanged with respect to
 446 the conservative case, and Eq. (16) remains valid with $c_M(t)$ given by Eq. (14) as before. Once again,
 447 direct computation of both sides of Eq. (41) shows that they are identical for all values of c and t .

448 Equation (41) quantifies the full evolution of the concentration PDF and sheds light on the fun-
 449 damental governing processes. However, solving it directly is challenging. We will thus focus instead
 450 on extending the weak-coupling approach to directly compute the concentration PDF and associated
 451 quantities based on the evolution of the total mass $M(t)$ and the peak concentration $c_M(t)$. This will
 452 allow us to obtain additional analytical insights into the dynamics. [7] focused on the evolution of
 453 the total mass and spatial variance. For the purpose of determining the concentration PDF, and in
 454 particular the mean concentration above a detection threshold and the associated variability, it is more
 455 convenient to quantify the dynamics in terms of the evolution of total mass and peak concentration,

456 as the latter plays a central role (see Eqs. (12), (19), and (21)). At time $t = \text{Da}$, when we begin
 457 approximating the concentration profile as Gaussian, the mass and peak are approximated as

$$M(\text{Da}) = c_M(\text{Da}) = c_B(\text{Da}) = [1 - (1 - \beta) \text{Da}]^{\frac{1}{1-\beta}}, \quad (42)$$

458 where $c_B(\text{Da})$ is computed according to the batch solution (38). We note that in [7], instead of
 459 matching the peak value to the batch dynamics at $t = \text{Da}$, the spatial variance was set to match that
 460 of the initial square pulse, $\sigma^2(\text{Da}) = 1/12$. This leads to qualitatively similar results and makes no
 461 difference at late times. The present choice enforces continuity of $c_M(t)$ at $t = \text{Da}$, while the previous
 462 choice enforces continuity of $\sigma^2(t)$ instead. Due to Eq. (14), the approximation of a sharp transition
 463 between batch dynamics and a Gaussian profile cannot enforce the continuity of both, and for the
 464 current choice we have $\sigma^2(\text{Da}) = 1/(2\pi)$, roughly double the initial spatial variance.

465 The total mass dynamics are then obtained from the local reaction kinetics. That is, integrating
 466 Eq. (35) in space for fixed time and using Eq. (12) for the Gaussian profile, neglecting mass present
 467 at concentrations below the detection limit c_m , we obtain the mass evolution for $\beta > 0$ as

$$\frac{dM(t)}{dt} = -\frac{M^\beta(t)}{\sqrt{\beta}} [2\pi\sigma^2(t)]^{\frac{1-\beta}{2}}. \quad (43)$$

468 In order to obtain an equation for the peak concentration, we employ Eq. (35) at $x = 0$. This gives

$$\frac{dc_M(t)}{dt} = -\frac{c_M(t)}{2\text{Da}\sigma^2(t)} - c_M^\beta(t). \quad (44)$$

469 Using Eq. (14) to express the spatial variance in terms of the mass and peak concentration, we obtain

$$\frac{dM(t)}{dt} = -\frac{M(t)}{\sqrt{\beta}} c_M^{\beta-1}(t), \quad (45a)$$

470

$$\frac{dc_M(t)}{dt} = -\frac{\pi c_M^3(t)}{\text{Da} M^2(t)} - c_M^\beta(t). \quad (45b)$$

471 Note that Eq. (45a) for the overall reaction rate can also be obtained directly from the concentration
 472 PDF by using Eqs. (18) and (28). The result follows from setting $c_m = 0$ in the lower integration
 473 limit, which, for $\beta > 0$, is equivalent to neglecting the mass present at concentrations lower than c_m ,
 474 as was done for the spatial profile in Eq. (43). This confirms that, as expected, knowledge of the
 475 concentration PDF directly determines overall reaction rates and mass evolution, without need for
 476 additional detailed knowledge about the spatial profile.

477 Equations (45), with initial conditions at time $t = \text{Da}$ according to Eq. (42), fully determine the
 478 evolution of total mass and peak concentration in this regime. Given knowledge of the mass and peak
 479 concentration, the concentration PDF for $t \geq \text{Da}$, based on the Gaussian assumption, is given by
 480 Eq. (16). In the examples considered here, we fix the minimum concentration, corresponding to an
 481 arbitrary lower detection limit, to $c_m = 10^{-6}$. Recall that, in nondimensional units, this refers to a
 482 detection limit six orders of magnitude below the initial concentration characterizing the rectangular
 483 pulse injection. The results are qualitatively similar for different c_m , so long as the peak concentration
 484 $c_M(t)$ remains large compared to c_m for the times of interest. If $c_M(t)$ approaches c_m , an appreciable
 485 amount of mass loss will start occurring as it drops below the detection limit. The system will then
 486 appear completely depleted, with all detectable mass and concentrations reaching zero.

487 In [7], good agreement was shown to hold between the total mass and spatial variance predicted by
 488 the weak-coupling approximation and numerical simulations of Eq. (35). Here, we verify the predictions
 489 of this approach, cast in terms of the total mass and peak concentration, for the full concentration PDF,
 490 as well as the time-evolution of the associated mean concentration and concentration variance. To this
 491 end, we first conduct resolved numerical simulations of the coupled diffusion and reaction problem,
 492 Eq. (35). To compute the quantities associated with model predictions, we employ Eqs. (45), which
 493 constitute ordinary rather than partial differential equations and can be efficiently solved numerically.

494 The numerical methods used for both these computations are detailed in Appendix C. Furthermore,
 495 we obtain analytical predictions for late-time behaviors under the weak-coupling approximation.

496 In order to test the applicability of the Gaussian assumption for predicting concentration variability
 497 at times $t \geq \text{Da}$, we note that the concentration PDF associated with a Gaussian profile, Eq. (16) can
 498 be expressed in terms of concentrations rescaled by their (time-dependent) peak value, $c' = c/c_M(t)$,
 499 as

$$p'(c'; t) = c_M(t)p[c_M(t)c'; t] = f_p(c') \frac{H(1-c')H[c' - c'_m(t)]}{\sqrt{\ln[1/c'_m(t)]}}, \quad (46)$$

500 where $c'_m(t) = c_m/c_M(t)$, and

$$f_p(c') = \frac{1}{2c' \sqrt{\ln(1/c')}}. \quad (47)$$

501 The concentration PDF $p'(c'; t)$ of rescaled concentration is independent of time except through the
 502 lower cutoff $c'_m(t)$ (on which it depends in terms of both its range and normalization). The func-
 503 tional dependency $f_p(c')$ on rescaled concentration under the Gaussian approximation is both time-
 504 independent and independent of the system parameters β and Da . In order to compare this to the
 505 resolved numerical results, below we compute the functional dependency according to Eq. (46), i.e., as
 506 $\sqrt{\ln[1/c'_m(t)]}c_M(t)p[c_M(t)c'; t]$.

507 Similarly, to assess the quality of the Gaussian approximation regarding the scalar dissipation rate,
 508 we consider the rescaled form (see Eq. (40))

$$\chi'(c'; t) = \frac{\text{Da} M^2(t)}{2\pi c_M^4(t)} \chi[c_M(t)c', t] = f_\chi(c') H(1-c') H[c' - c'_m(t)], \quad (48)$$

509 where the functional dependency on rescaled concentration is given by

$$f_\chi(c') = c'^2 \ln(1/c'). \quad (49)$$

510 Below, we employ Eq. (48) to compute the functional dependency from numerical simulations, similarly
 511 to the case above for the concentration PDF. Comparison of the concentration PDF functional forms
 512 provides a metric for the performance of the Gaussian approximation regarding the relative frequency
 513 of occurrence of different concentration values, and comparison of the scalar dissipation rate func-
 514 tional forms provides complementary information about the approximation's performance regarding
 515 the gradient values associated with each concentration value.

516 As they correspond to qualitatively different regimes, we consider the cases $\beta < 1$, $1 < \beta < 3$,
 517 and $\beta > 3$ separately below. In what follows, we also discuss analytical approximations for late-time
 518 behaviors. Before proceeding, we note that the starting point for these results is the fact that, for
 519 $t \geq \text{Da}$, the concentration profile may be approximated as Gaussian with a spatial variance that
 520 increases diffusively as $\sigma^2(t) \approx t/\text{Da}$ [7]. Substituting into Eq. (43) and solving the resulting equation,
 521 we obtain an approximation for the mass evolution for $t \geq \text{Da}$,

$$M(t) \approx \left[M(\text{Da})^{1-\beta} - \frac{2}{\sqrt{\beta}} \frac{1-\beta}{3-\beta} \left(\frac{2\pi}{\text{Da}} \right)^{\frac{1-\beta}{2}} \left[t^{\frac{3-\beta}{2}} - \text{Da}^{\frac{3-\beta}{2}} \right] \right]^{\frac{1}{1-\beta}}, \quad (50)$$

522 valid for $\beta \neq 1, 3$. Recall that the case $\beta = 1$, corresponding to a first-order decay reaction, can be
 523 fully solved analytically. The case $\beta = 3$, which we do not analyze in detail here for brevity, behaves
 524 qualitatively similarly to $\beta > 3$, although extremely slow (logarithmic) decay of mass occurs at late
 525 times [7].

526 4.4 Reaction order $\beta < 1$ — Full-depletion regime

527 For $\beta < 1$, reaction rates increase with decreasing concentration, leading to full depletion in finite
 528 time. Under fully-mixed conditions, the depletion time t_f^B is given by Eq. (39). Recall that for

529 sufficiently large Da full depletion occurs before transport must be taken into account. We thus focus
 530 on Damköhler numbers such that $\text{Da} < t_f^B$.

531 Under the combined effect of reaction and diffusion, mass is still fully depleted in a finite time t_f ,
 532 different from t_f^B . Setting $M(t_f) = 0$ in Eq. (50) and solving for t_f yields [7]

$$t_f \approx \left[\text{Da}^{\frac{3-\beta}{2}} + \frac{\sqrt{\beta} (3-\beta)}{2(1-\beta)} \left(\frac{\text{Da}}{2\pi} \right)^{\frac{1-\beta}{2}} [1 - (1-\beta)\text{Da}] \right]^{\frac{2}{3-\beta}}. \quad (51)$$

533 For sufficiently small detection limit c_m , we expect this prediction to provide a good estimate of the
 534 time at which the peak, mean concentration, and concentration variance reach zero. Interestingly,
 535 the depletion time decreases with decreasing Da. This decrease is due to the fact that, because in
 536 this regime reaction is faster at lower concentrations, stronger diffusion (smaller Da) leads to faster
 537 depletion when compared to a system with the same reaction rate. For this reason, both mass and
 538 peak concentration decay faster than the batch solution. In particular, for small $\text{Da} \ll 1$, we find a
 539 simple power-law scaling with Da,

$$t_f \approx \left(\frac{\sqrt{\beta} (3-\beta)}{2(1-\beta)} \right)^{\frac{2}{3-\beta}} \left(\frac{\text{Da}}{2\pi} \right)^{\frac{1-\beta}{3-\beta}}. \quad (52)$$

540 Note however that t_f/Da increases with decreasing Da, meaning that with increasing diffusion the
 541 depletion time occurs increasingly later than the time $t = \text{Da}$ at which the Gaussian approximation
 542 kicks in.

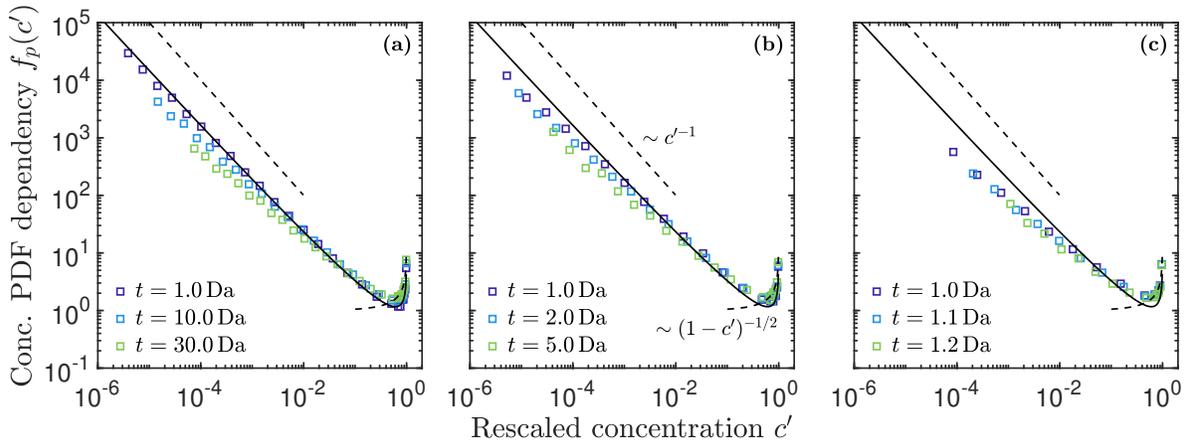


Figure 3: Functional dependency of the concentration PDF in terms of concentration rescaled by peak value, for $\beta = 1/2$ and **(a)**: slow reaction, $\text{Da} = 10^{-2}$, **(b)**: intermediate reaction, $\text{Da} = 10^{-1}$, and **(c)**: fast reaction, $\text{Da} = 1$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (47) under the weak-coupling model. The dashed lines show a pure $1/c'$ scaling for reference at low concentrations and the scaling of the inverse-square-root divergence near the maximum concentration value (see Eqs. (9) and (47)).

543 To illustrate these results, we take $\beta = 1/2$ as a representative example. First, we compare the
 544 functional dependency of the concentration PDF (see Eqs. (46) and (47)) under the weak-coupling
 545 approximation to that obtained from resolved numerical simulations of Eq. (35) (see Appendix A
 546 and Appendix C). We focus on times t such that $\text{Da} \leq t < t_f$ (see Eq. (51)). Results for different
 547 Damköhler numbers and times are shown in Fig. 3. Overall, the Gaussian approximation provides good
 548 estimates of the relative frequency of concentration values. Because, for $\beta < 1$, reaction is faster at
 549 lower concentrations, lower PDF values compared to the Gaussian prediction are observed at low values

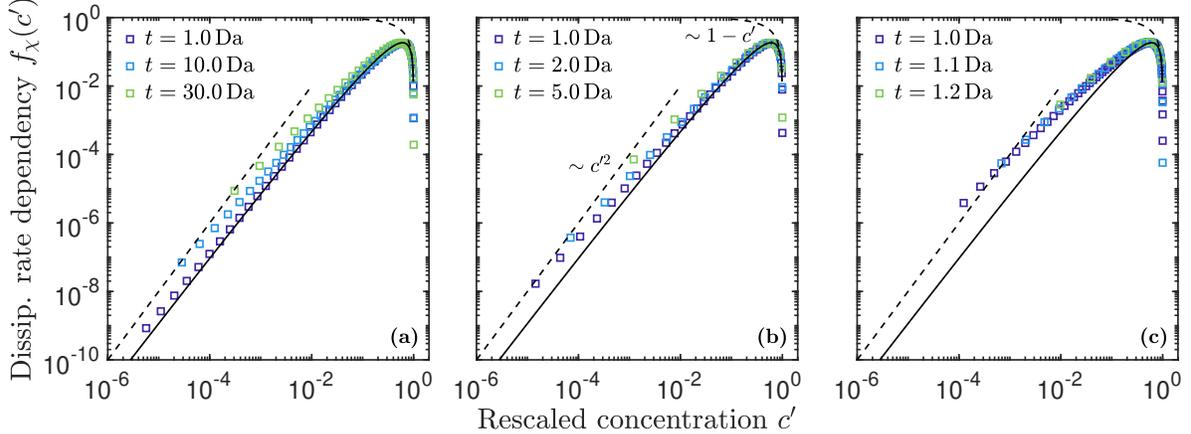


Figure 4: Functional dependency of the scalar dissipation rate in terms of concentration rescaled by peak value, for $\beta = 1/2$ and **(a)**: slow reaction, $Da = 10^{-2}$, **(b)**: intermediate reaction, $Da = 10^{-1}$, and **(c)**: fast reaction, $Da = 1$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (49) under the weak-coupling model. The dashed lines show a pure c'^2 scaling for reference at low concentrations and the linear approach to zero near the peak concentration (see Eqs. (40) and (49)).

550 of concentration. This discrepancy at low concentrations also leads to a corresponding overprediction
 551 of higher concentrations, due to the normalization condition for the PDF. Although the bulk of the
 552 mass distribution is generally well captured, as discussed below, high Da leads to significant depletion
 553 at early times and results in a worse approximation.

554 Similar conclusions are reached from consideration of the functional dependency of the scalar dis-
 555 sipation rate (see Eqs. (48) and (49)), shown in Fig. 4. The Gaussian approximation again provides
 556 good estimates, but higher scalar dissipation rates, corresponding to higher gradients, are observed at
 557 low concentration values. The discrepancy is more pronounced in the same cases and for the same
 558 reasons as discussed regarding the concentration PDF, although in this case normalization does not
 559 play a role and thus no associated discrepancy at higher concentration values is observed.

560 Next, we turn to the evolution of the mass and peak concentration, shown in Fig. 5. As predicted
 561 by the weak-coupling approximation, both quantities reach zero in finite time as complete depletion
 562 occurs. However, due to the nonlinear nature of the reaction and the presence of diffusion, the peak
 563 dynamics differ from the total mass dynamics, as captured by Eqs. (45). Note the onset of a diffusive
 564 scaling of peak decay for low Damköhler, showing that the dynamics are controlled by diffusion at
 565 times $t \sim Da$ (corresponding to dimensional times on the order of the diffusion time). For late times,
 566 as concentration becomes smaller, reaction becomes more efficient. The dynamics depart from the
 567 diffusive scaling and full depletion eventually occurs. The slight underprediction of the depletion time t_f
 568 by the analytical approximation compared to the numerically-computed weak-coupling approximation
 569 results is due mostly to the breakdown of the linear variance growth approximation just before complete
 570 depletion, as observed in [7]. When comparing the predictions of the weak-coupling approximation to
 571 the resolved numerical simulations, we find overall good agreement. Regarding peak concentrations,
 572 the approximation of a sharp transition between batch and Gaussian-profile dynamics at $t = Da$
 573 leads to some discrepancy at times $t \sim Da$, which becomes more pronounced with increasing Da . As
 574 the Damköhler number increases and the depletion time approaches Da from above ($t_f/Da \sim 1$, see
 575 Eq. (51)), stronger discrepancies are observed for both the mean concentration and the total mass,
 576 due to significant depletion before an approximately Gaussian profile is achieved. Nonetheless, the
 577 predictions for t_f still provide a reasonable approximation. Recall that, for higher $Da > t_f^B = 2$
 578 (Eq. (39)), diffusion does not play a role before depletion the dynamics become well described by
 579 simple batch kinetics.

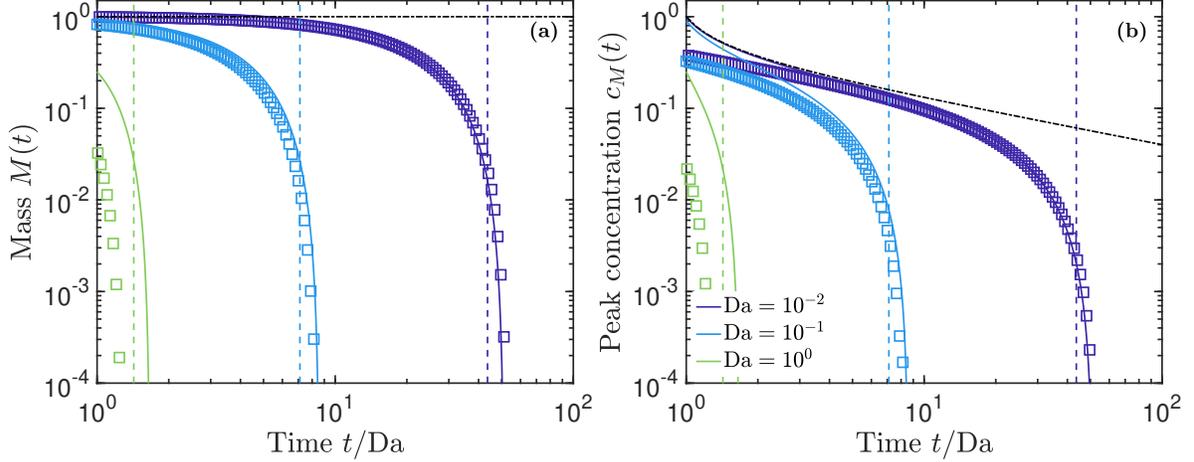


Figure 5: Temporal evolution of **(a)**: total mass and **(b)**: peak concentration for $\beta = 1/2$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), and dash-dotted lines show the purely-diffusive behavior. The vertical dashed lines show approximate analytical results for the depletion time (Eq. (51)).

580 Note that defining a mean concentration in terms of a fixed, reference spatial region, as done
 581 in [7], leads to a mean concentration scaling identical to that of the total mass, since in that case
 582 $\langle C(t) \rangle = M(t)/|\Omega|$ with constant domain size $|\Omega|$. Interestingly, when the mean concentration is
 583 instead defined, as here, in terms of the temporally-variable region where concentration is above a
 584 detection limit, the concentration mean and variance are instead fully controlled by the peak dynamics,
 585 see Eqs. (19) and (21). This leads also to a similar quality of the weak-coupling approximation when
 586 compared to the resolved simulations, as shown in Fig. 6. In particular, for low Damköhler numbers,
 587 our approach accurately predicts a transition from diffusion- to reaction-controlled dynamics, governed
 588 by the peak behavior described above, for both the mean concentration and the concentration variance.

589 4.5 Reaction order $1 < \beta < 3$ — Power-law-decay regime

590 In this regime, the interplay between reaction and diffusion leads to power-law mass decay at late
 591 times. Indeed, for $t \gg \text{Da}$, Eq. (50) reduces to [7]

$$M(t) \approx \sqrt{\frac{2\pi}{\text{Da}}} \left(\frac{\sqrt{\beta} 3 - \beta}{2 \beta - 1} \right)^{\frac{1}{\beta-1}} t^{-\frac{3-\beta}{2(\beta-1)}}. \quad (53)$$

592 Substituting in Eq. (45b), and noting that, for $1 < \beta < 3$, as the peak concentration decreases the
 593 reactive term eventually dominates over the diffusive term, we have for late times

$$\frac{dc_M(t)}{dt} \approx -c_M^\beta(t). \quad (54)$$

594 Solving this equation, we obtain the late time peak decay

$$c_M(t) \approx [(\beta - 1)t]^{-\frac{1}{\beta-1}}. \quad (55)$$

595 This behavior is characteristic of reaction-dominated conditions, and identical to the late-time batch
 596 dynamics, see Eq. (38). However, note that the total mass, Eq. (53), exhibits a different temporal
 597 scaling, as it results from the reactive decay of Gaussian-distributed concentration values undergoing
 598 diffusive spreading. This results, in contrast to the $\beta < 1$ regime, in slower asymptotic mass decay
 599 than predicted by batch dynamics, because in this case reaction is slower at lower concentrations.

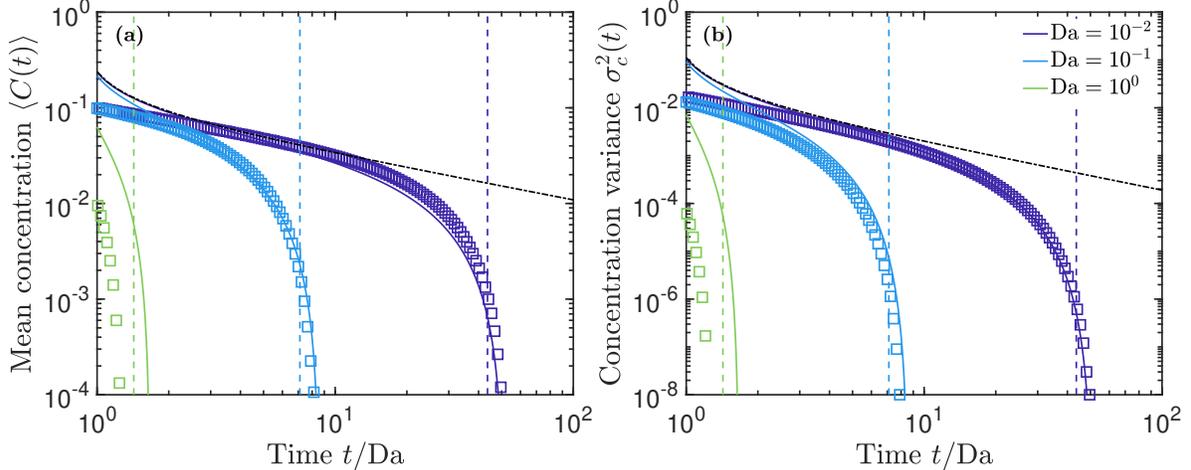


Figure 6: Temporal evolution of (a): mean concentration and (b): concentration variance for $\beta = 1/2$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), and dash-dotted lines show the purely-diffusive behavior. The vertical dashed lines show approximate analytical results for the depletion time (Eq. (51)).

600 We now take $\beta = 2$ as a representative example. Again, we start by assessing the performance
 601 of the Gaussian assumption for the functional dependency of the concentration PDF (Fig. 7). The
 602 approximation provides very good estimates of the frequency of occurrence of different concentrations.
 603 A slight underestimation of low concentrations, and corresponding overestimation of intermediate con-
 604 centrations, occurs at late times for large Damköhler number. When considering the scalar dissipation
 605 rate (Fig. 8), we again observe very good agreement, with a corresponding slight but more discernible
 606 overestimation of concentration gradients at low concentrations. In this case, reaction is less efficient
 607 at low concentrations, so these results are somewhat counter-intuitive. Indeed, reaction is stronger
 608 and therefore has a more pronounced effect compared to diffusion at high concentrations. However,
 609 when the corresponding spatial profile is compared to a Gaussian of the same variance and maximum
 610 concentration, the latter underestimates the intermediate values but overestimates the tails. This is
 611 illustrated in Fig. 9 for the case of $Da = 10^2$ at time $t = 10 Da$. This effect is slight, but it is more
 612 pronounced at the level of concentration gradients.

613 Next, we consider the evolution of total mass and peak concentration, see Fig. 10. The analytical
 614 approximation captures the asymptotic scalings correctly, although it slightly underpredicts the mass
 615 and overpredicts the peak concentration when compared to the numerically-computed weak-coupling
 616 approximation results. These discrepancies result in this case from small corrections to the $\sigma^2(t) \approx$
 617 t/Da diffusive spatial variance growth approximation of [7], implicit in Eq. (50) for the approximate
 618 late-time mass evolution. Again, the onset of a purely-diffusive scaling of peak decay is visible for low
 619 Damköhler before the asymptotic regime is reached. The weak-coupling approximation provides very
 620 good estimates of the resolved dynamics, even for $Da \sim 1$. As expected, the largest discrepancies occur
 621 for times $t \sim Da$, around which the approximation of a sharp transition between batch and Gaussian-
 622 profile dynamics has the most impact. In addition, a sharp depletion of mass can be observed at
 623 late times for the high- Da cases due to the detection limit. As expected, the transition from the
 624 dynamics predicted by the weak-coupling approximation to this sharp depletion occurs when the peak
 625 concentration becomes comparable to c_m .

626 As for the $\beta < 1$ case, the concentration mean and variance (Fig. 11) are controlled by the peak
 627 dynamics, see Eqs. (19) and (21). However, the changes in the size of the domain where concentration is
 628 larger than the detection limit lead to logarithmic corrections to the purely-reactive power-law scaling
 629 observed for the peak concentration. As for the mass and peak, the weak-coupling approximation

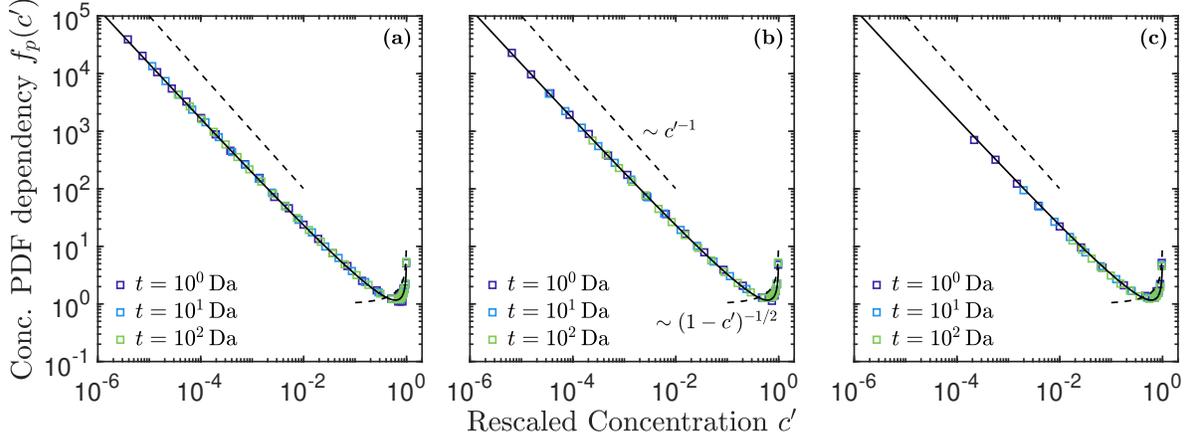


Figure 7: Functional dependency of the concentration PDF in terms of concentration rescaled by peak value, for $\beta = 2$ and **(a)**: slow reaction, $\text{Da} = 10^{-2}$, **(b)**: intermediate reaction, $\text{Da} = 1$, and **(c)**: fast reaction, $\text{Da} = 10^2$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (47) under the weak-coupling model. The dashed lines show a pure $1/c'$ scaling for reference at low concentrations and the scaling of the inverse-square-root divergence near the maximum concentration value (see Eqs. (9) and (47)).

630 provides very good predictions of the full dynamics, with the quality of the approximation improving
 631 for late times $t \gtrsim 10 \text{ Da}$. The discrepancies in the analytical *vs* numerical results for the weak-coupling
 632 approximation result from the discrepancies in the computation of the peak concentration discussed
 633 above.

634 4.6 Reaction order $\beta > 3$ — Incomplete-depletion regime

635 In this case, the substantial reaction slowdown associated with decreasing concentrations, enhanced
 636 by diffusion-induced dilution, prevents the complete depletion of mass by reaction, even for arbitrarily
 637 large times. Taking the limit $t \rightarrow \infty$ in Eq. (50) yields the leftover mass [7]

$$M_\infty \approx \left[1 + \left(1 + \frac{2}{(\beta - 3)\sqrt{(2\pi)^{\beta-1}\beta}} \right) (\beta - 1) \text{Da} \right]^{-\frac{1}{\beta-1}}. \quad (56)$$

638 Substituting in Eq. (45b) as before, we now conclude that the late-time dominant contribution is
 639 diffusive, so that

$$\frac{dc_M(t)}{dt} \approx -\frac{\pi c_M^3(t)}{\text{Da} M_\infty^2}. \quad (57)$$

640 Solving this equation leads, for large times, to

$$c_M(t) \approx M_\infty \sqrt{\frac{\text{Da}}{2\pi t}}. \quad (58)$$

641 As the mass becomes constant at late times, the decay of peak concentration exhibits the signature of
 642 diffusive plume spreading. The mass in a well-mixed batch decreases asymptotically to zero, meaning
 643 the diffusing system leads to less efficient reaction, as expected since the reaction slows down strongly
 644 with decreasing concentration in this case. In contrast, however, the diffusion-governed peak decay is
 645 asymptotically faster than the corresponding batch prediction, Eq. (38).

646 To illustrate this regime, we take $\beta = 4$ as a representative example. As predicted by the weak-
 647 coupling approximation, reaction is sufficiently inefficient at low concentrations for diffusive spreading

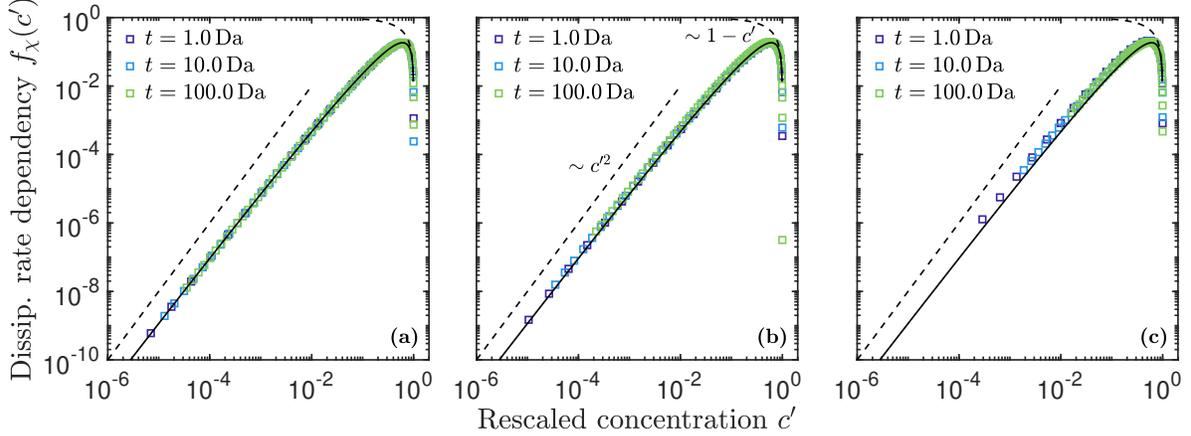


Figure 8: Functional dependency of the scalar dissipation rate in terms of concentration rescaled by peak value, for $\beta = 2$ and **(a)**: slow reaction, $\text{Da} = 10^{-2}$, **(b)**: intermediate reaction, $\text{Da} = 1$, and **(c)**: fast reaction, $\text{Da} = 10^2$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (49) under the weak-coupling model. The dashed lines show a pure c'^2 scaling for reference at low concentrations and the linear approach to zero near the peak concentration (see Eqs. (40) and (49)).

648 to completely arrest mass decay. This means that the system dynamics are essentially dominated by
 649 diffusion. Correspondingly, both the concentration PDF and the scalar dissipation rate show excellent
 650 agreement with the Gaussian prediction, as shown in Figs. 12 and 13, respectively.

651 Next, we consider the evolution of total mass and peak concentration, see Fig. 14. In this case, the
 652 analytical asymptotic predictions provide very accurate estimates of the weak-coupling dynamics. As
 653 expected from the analytical discussion, the results become indistinguishable from a purely diffusive
 654 system for sufficiently low Da . However, when comparing to the resolved numerical simulations, we
 655 find that the weak-coupling approximation underpredicts the asymptotic mass at higher Da . The main
 656 reason for the discrepancy is that, because the reaction is particularly inefficient at low concentrations,
 657 the system transitions to the Gaussian regime earlier in this case. Indeed, as shown by the dash-dotted
 658 lines in Fig. 14, assuming the transition occurs at $t = \text{Da}/10$ rather than at $t = \text{Da}$ leads to improved
 659 estimates of the asymptotic mass. To obtain this prediction, we proceed as for Eq. (56) but set the
 660 initial condition of the weak-coupling Gaussian regime at $t = \text{Da}/10$ (see Eq. (42)), leading to

$$M_\infty \approx \left[1 + \left(1 + \frac{2 \cdot 10^{\frac{\beta-1}{2}}}{(\beta-3)\sqrt{(2\pi)^{\beta-1}\beta}} \right) (\beta-1) \frac{\text{Da}}{10} \right]^{-\frac{1}{\beta-1}}. \quad (59)$$

661 Note that the scaling of asymptotic mass with Da , and the relationship between asymptotic peak
 662 dynamics and asymptotic mass, Eq. (58), remain unchanged.

663 The concentration mean and variance for this case are shown in Fig. 15. The considerations
 664 pertaining to the $1 < \beta < 3$ case regarding the scaling of concentration mean and variance in terms of
 665 the peak concentration remain valid here, but in this case we observe logarithmically-corrected diffusive
 666 rather than reactive scalings. Once again, the low- Da case is indistinguishable from purely-diffusive
 667 dynamics. In addition, due to the low efficiency of reaction at low concentrations, the scaling behavior
 668 of both mean concentration and concentration variance remains purely diffusive, even for large Da .
 669 Overall, as for the total mass and peak concentration, the analytical approximation provides very good
 670 asymptotic estimates of the weak-coupling approximation, but better predictions of the fully-resolved
 671 dynamics are obtained by assuming the transition to the Gaussian regime occurs at time $t = \text{Da}/10$
 672 rather than at $t = \text{Da}$.

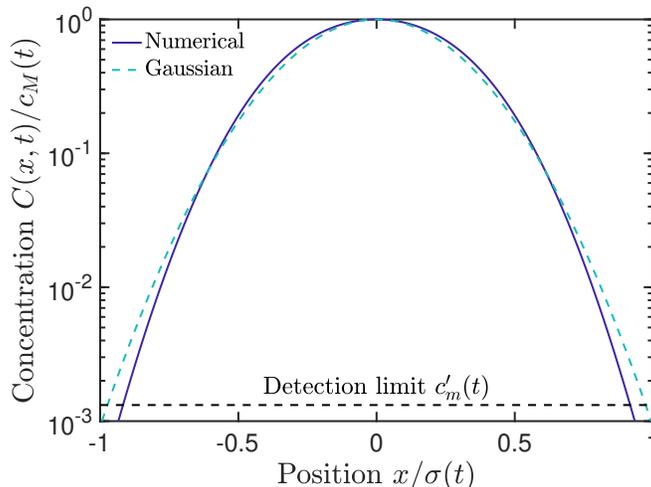


Figure 9: Concentration profile for $\beta = 2$ and $\text{Da} = 10^2$, at time $t = 10 \text{ Da}$. The solid line shows the profile computed from resolved numerical simulations of Eq. (35), and the dashed colored line shows a Gaussian profile with the same variance $\sigma^2(t)$ and maximum concentration $c_M(t)$. The horizontal dashed line shows the lower detection limit.

5 Discussion and conclusions

673

674 We have presented a detailed discussion of the theoretical and numerical properties of the concentra-
 675 tion PDF of a reactive plume evolving under the coupled action of dilution and nonlinear reaction. The
 676 concentration PDF encodes the full point statistical variability of concentration values found through-
 677 out a spatial domain, and is therefore of central interest to both fundamental and applied reactive
 678 transport and risk assessment problems.

679 As a first step towards solving the full advection–diffusion–reaction system, we have conducted a
 680 detailed analysis of nonlinear decay of a single solute undergoing one-dimensional diffusion. We have
 681 shown that the weak-coupling approximation developed in [7] to quantify the evolution of total mass
 682 and mean concentration in a fixed reference domain can be extended to quantify the evolution of
 683 mean concentrations above a lower detection limit, along with the associated variability. In particular,
 684 we have found that the late-time Gaussian profile approximation leads to good predictions of the
 685 concentration PDF. Even for this simple one-dimensional diffusive system, the effective reaction kinetics
 686 governing these quantities exhibit rich dynamics. In contrast to well-mixed batch kinetics, the decay
 687 of concentrations at different Damköhler numbers can be dominated by diffusive or reactive effects
 688 at different times. Late-time concentrations can exhibit complete extinction, power-law decay, or
 689 complete arrest of reaction depending on the reaction order. The Gaussian approximation underlying
 690 the weak-coupling approach allows us to predict the associated concentration variance. Remarkably,
 691 the dynamics of the maximum concentration value, which provide the key control on the mean and
 692 variance of concentrations above a given detection threshold, differ qualitatively from the dynamics of
 693 total mass. In particular, for low Damköhler numbers, both the mean concentration and associated
 694 variability exhibit diffusion-controlled decay for times on the order of the diffusion time, for any reaction
 695 order. This diffusive control persists across all times and Damköhler numbers for strongly superlinear
 696 decay reactions (of order $\beta > 3$), whereas reaction is the fundamental mechanism controlling late-time
 697 and/or large-Da dynamics for lower reaction orders.

698 We have also derived a dynamical equation for the evolution of the concentration PDF in the
 699 nonlinear reaction–diffusion problem, showing that the impact of transport is encoded in the scalar
 700 dissipation rate seen as a function of concentration. It is important to note that the generalization of
 701 this equation to multiple dimensions, variable advection and/or diffusion tensor, and arbitrary reaction
 702 rates, for which concentration is no longer necessarily monotonically decreasing, is not straightforward.

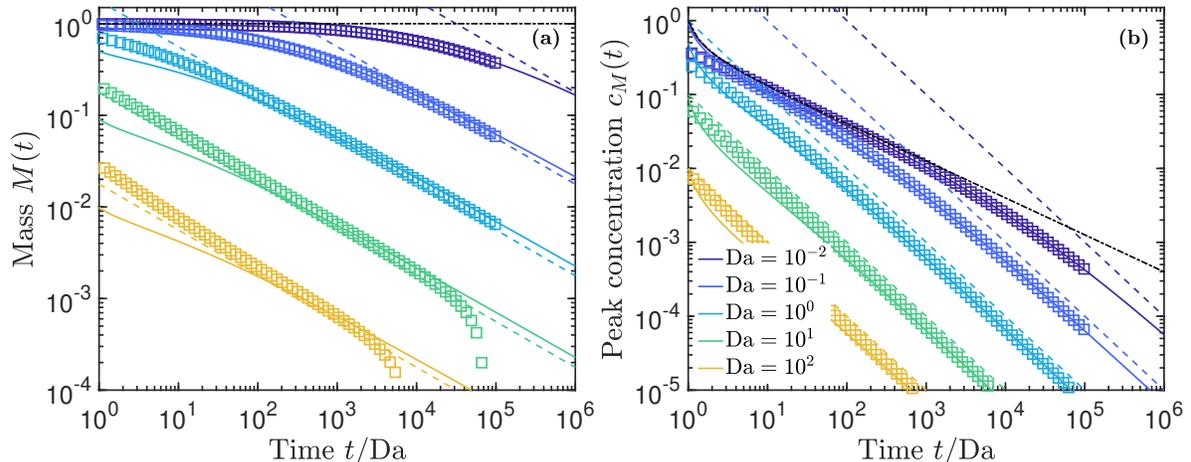


Figure 10: Temporal evolution of **(a)**: total mass and **(b)**: peak concentration for $\beta = 2$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), dashed lines show approximate asymptotic analytical results (Eqs. (53) and (55)), and dash-dotted lines show the purely-diffusive behavior.

703 Nonetheless, we believe the approach developed here, highlighting the role of the scalar dissipation rate,
 704 has the potential to form the basis for upscaling procedures in more complex systems. In particular, as
 705 discussed in Section 3, the dynamics of reaction under advection–diffusion in heterogeneous flows, in
 706 both two- and three-dimensional porous media, can be reduced to one-dimensional reaction–diffusion
 707 equations along the principal direction of compression on a collection of lamellar structures. With this
 708 in mind, further work will focus on the generalization of the approach developed here to the dynamics
 709 of Gaussian profiles subject to stretching-enhanced diffusion over an ensemble of lamellae.

710 Declarations

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715 **Conflicts of interest/Competing interests:** The authors declare that they have no conflict of
 716 interest.

717 **Availability of data and material:** This work did not make use of or generate any datasets.

718 **Code availability** Numerical simulations used the `py-pde` open-source Python package for solving
 719 partial differential equations [79]. Please contact the authors for any additional information or requests.

720 A Discretization

721 When computing the concentration PDF numerically, discretizations are typically employed both spa-
 722 tially and for the concentration values. As a simple example that highlights the central concepts,
 723 consider a regular spatial discretization into a grid with constant cell volume V_g , with each grid cell
 724 associated with the average concentration within it. According to the argument for constant concen-
 725 tration regions developed in the previous section, for each fixed time t , the concentration PDF is then

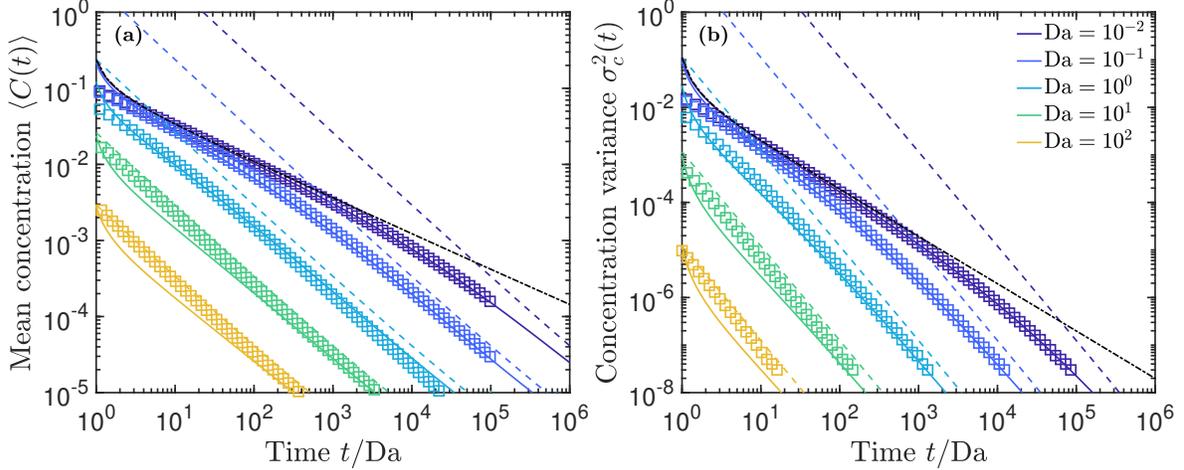


Figure 11: Temporal evolution of **(a)**: mean concentration and **(b)**: concentration variance for $\beta = 2$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), dashed lines show approximate asymptotic analytical results (Eqs. (19) and (21), using Eq. (55) for the peak concentration), and dash-dotted lines show the purely-diffusive behavior.

726 estimated as

$$p(c; t; N_g) = \frac{1}{N_g} \sum_{i=1}^{N_g} \delta[c - c_i(t)], \quad (60)$$

727 where $N_g = |\Omega|/V_g$ is the number of grid points and c_i is the average concentration in cell i . Note that
728 the c_i associated with different cells are not necessarily all different.

729 Further discretizing concentration into bins leads to a probability mass function with values for the
730 probability of concentration in each bin $B_k = [c^{(k)}, c^{(k+1)}[$, $k \geq 0$:

$$p_k(t; N_g) = \frac{1}{N_g} \sum_{i=1}^{N_g} H[c_i(t) - c^{(k)}] H[c^{(k+1)} - c_i(t)], \quad (61)$$

731 where $H(\cdot)$ is the Heaviside step function. This means that the probability of finding a concentration
732 value in bin k is the fraction of cells where the concentration falls within bin k . If we take concentration
733 bin widths Δc to be constant, $c^{(k)} = k\Delta c$ for $k \geq 0$, and approximate the PDF of concentration by
734 dividing probabilities by Δc (as in Fig. 2), we obtain

$$p(c; t; N_g, \Delta c) = \frac{1}{N_g \Delta c} \sum_{i=1}^{N_g} H[c_i(t) - k\Delta c] H[(k+1)\Delta c - c_i(t)]. \quad (62)$$

735 These discretization procedures generalize directly to a multispecies system. In that case, concentration
736 bins refer to the simultaneous attainment of concentration values of each species. The associated
737 probabilities are computed as above by counting spatial cells where these values occur simultaneously.
738 The procedure also generalizes directly to non-uniform and/or time-dependent spatial cell sizes and/or
739 concentration bins. More involved techniques employing kernel reconstructions of the concentration
740 field may be formalized in a similar manner [80–82].

741 The maximum resolution of the discretized concentration PDF described above is given by $1/(N_g \Delta c)$,
742 and the maximum PDF value is $1/\Delta c$. We now discuss the impact of local spatial extrema, which
743 can be associated with divergences of the continuous PDF as discussed in Section 2.3, on the dis-
744 cretized computation. It is also important to note that sources of error typically come into play in the

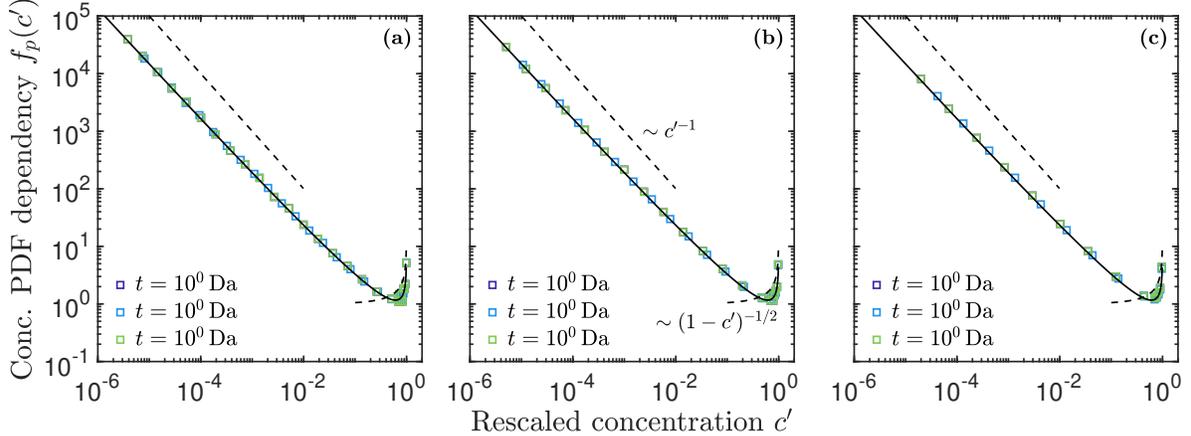


Figure 12: Functional dependency of the concentration PDF in terms of concentration rescaled by peak value, for $\beta = 2$ and **(a)**: slow reaction, $\text{Da} = 10^{-2}$, **(b)**: intermediate reaction, $\text{Da} = 1$, and **(c)**: fast reaction, $\text{Da} = 10^2$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (47) under the weak-coupling model. The dashed lines show a pure $1/c'$ scaling for reference at low concentrations and the scaling of the inverse-square-root divergence near the maximum concentration value (see Eqs. (9) and (47)).

745 determination of the spatial concentration field. For example, if the latter is computed based on a par-
 746 ticle tracking simulation of some transport and reaction dynamics, fluctuations arise due to the finite
 747 number of particles, whereas in a standard Eulerian simulation the spatial discretization impacts the
 748 determination of the true concentration field. We focus here on the error resulting from concentration
 749 discretization Δc , which is dominant given a sufficiently-resolved spatial concentration field.

750 Consider first a region of constant concentration. A delta peak $\delta(c - c_0)|\Omega_0|/|\Omega|$ in the concentration
 751 PDF, associated as discussed above to a subdomain Ω_0 of volume $|\Omega_0|$ where $C(\mathbf{x}; t) = c_0$, corresponds
 752 under sufficiently fine spatial discretization to a discretized contribution $|\Omega_0|/(|\Omega|\Delta c)$. Thus, halving
 753 the concentration discretization Δc leads to a doubling of the numerically-computed peak. More
 754 generally, refining the discretization as $\Delta c \rightarrow a\Delta c$, $a < 1$, yields $p(c_0; t; N_g, a\Delta c) = ap(c_0; t; \Delta c)$.
 755 On the other hand, smooth extrema correspond to divergences only for spatial dimension $d = 1$, for
 756 which they lead to an inverse-square-root divergence, as shown in Section 2.3. In this case, averaging
 757 the concentration over a range Δc near the spatial extreme value c_0 yields $p(c_0; t; \Delta c) \propto 1/\sqrt{\Delta c}$,
 758 so that $p(c_0; t; a\Delta c) \approx \sqrt{a}p(c_0; t; \Delta c)$. Thus, observing these behaviors in a numerical computation
 759 is a signature of the presence of a spatial extremum, and the scaling behavior with concentration
 760 discretization refinement indicates its type.

761 B Dynamical equation for the concentration PDF

762 In this appendix, we provide a detailed derivation of the dynamical equation for the concentration PDF
 763 discussed in the main text, Eq. (34), by explicitly determining the diffusive transport and reaction
 764 contributions in Eq. (29). We first consider the effect of diffusion, $\Delta p_D(c; t)$. For one-dimensional
 765 diffusion and nonlinear concentration decay, assuming a symmetric initial condition about the origin
 766 and monotonically decreasing with distance from the latter, the spatial concentration profile retains
 767 these properties for all times. Therefore, we have $|\Lambda(c; t)| = 2$ for all concentrations within the range
 768 observed at time t , corresponding to the two points $x = \pm x_c(c; t)$ where $C(x; t) = c$. Furthermore, the
 769 concentration gradient magnitude is the same at $\pm x_c$, so that its harmonic average is simply $g_h(c; t) =$
 770 $\nabla C[-x_c(c; t), t] = -\nabla C[x_c(c; t), t]$. Using Eq. (8) and the fact that $|\Lambda(c; t)|$ is time-independent within

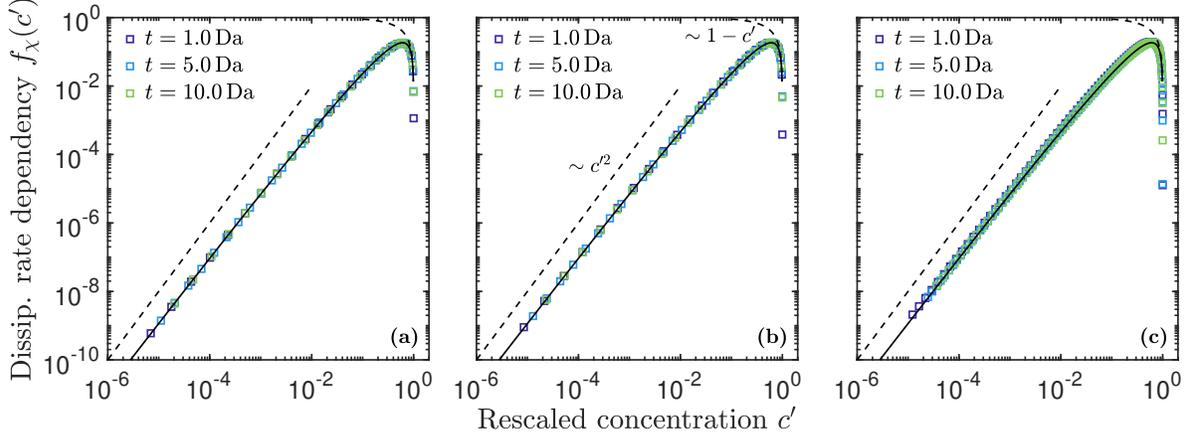


Figure 13: Functional dependency of the scalar dissipation rate in terms of concentration rescaled by peak value, for $\beta = 2$ and **(a)**: slow reaction, $\text{Da} = 10^{-2}$, **(b)**: intermediate reaction, $\text{Da} = 1$, and **(c)**: fast reaction, $\text{Da} = 10^2$. Colors stand for different times, with markers showing the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35). Solid lines represent the analytical solution (49) under the weak-coupling model. The dashed lines show a pure c'^2 scaling for reference at low concentrations and the linear approach to zero near the peak concentration (see Eqs. (40) and (49)).

771 the concentration range observed, we can write the change in the concentration PDF as

$$\frac{\partial p(c; t)}{\partial t} = -p(c; t) \left[\frac{\partial \ln |\Omega(t)|}{\partial t} + \frac{\partial \ln g_h(c; t)}{\partial t} \right]. \quad (63)$$

772 If a fixed reference volume is considered, the term corresponding to the change of $|\Omega(t)|$ in time is
 773 zero. As discussed in the main text, we focus here on the case of a minimum detection limit c_m and a
 774 time-varying domain $\Omega(t)$ where $c > c_m$.

775 In order to compute the terms in square brackets, we consider the time evolution of quantities on
 776 a given concentration surface (in one dimension, at the points $\pm x_c(c; t)$). By definition, the change in
 777 time of concentration over such a surface is zero, so that

$$\frac{\partial C[x_c(c; t); t]}{\partial t} = \left[\frac{\partial x_c(c; t)}{\partial t} \frac{\partial C(x; t)}{\partial x} + \frac{\partial C(x; t)}{\partial t} \right]_{x=x_c(c; t)} = 0 \quad (64)$$

778 Taking into account that, at $x = x_c$, $\partial/\partial x = -g_h(c; t)\partial/\partial c$, the changes associated with transport lead
 779 to

$$\frac{\partial x_c(c; t)}{\partial t} = \frac{1}{2g_h(c; t)} \frac{\partial \chi(c; t)}{\partial c}, \quad (65)$$

780 where $\chi(c; t) = \chi_x[\pm x_c(c; t); t] = Dg_h^2(c; t)$ is the concentration-dependent scalar dissipation rate. The
 781 same approach for the variation of the concentration gradient leads to

$$\frac{\partial g_h(c; t)}{\partial t} = - \left[\frac{\partial x_c(c; t)}{\partial t} \frac{\partial^2 C(x; t)}{\partial x^2} + \frac{\partial}{\partial t} \frac{\partial C(x; t)}{\partial x} \right]_{x=x_c(c; t)}, \quad (66)$$

782 and we find

$$\frac{\partial \ln g_h(c; t)}{\partial t} = \frac{1}{2} \frac{\partial^2 \chi(c; t)}{\partial c^2} - \frac{1}{4} \frac{\partial \ln \chi(c; t)}{\partial c} \frac{\partial \chi(c; t)}{\partial c}. \quad (67)$$

783 The change in domain volume $\Omega(t) = 2x_c(c_m; t)$ due to dilution of concentration below the detection
 784 limit c_m obeys

$$\frac{\partial |\Omega(t)|}{\partial t} = 2 \frac{\partial x_c(c_m; t)}{\partial t}, \quad (68)$$

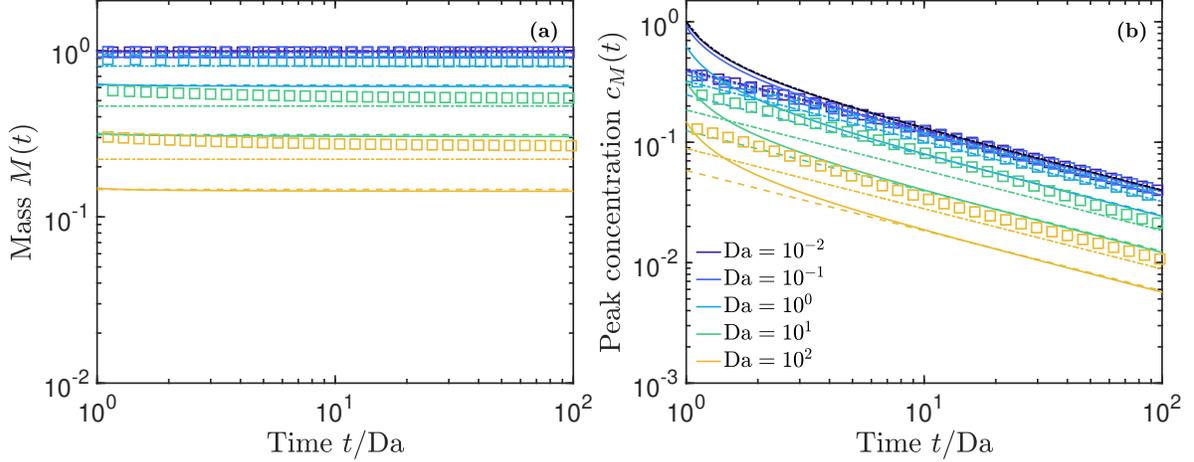


Figure 14: Temporal evolution of **(a)**: total mass and **(b)**: peak concentration for $\beta = 4$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), and dashed lines show approximate asymptotic analytical results (Eqs. (56) and (58)). Dash-dotted lines show analytical results assuming the transition to the Gaussian regime occurs at time $t = Da/10$ rather than at $t = Da$ (Eq. (59)).

785 Using Eq. (65), this leads to

$$\frac{\partial |\Omega(t)|}{\partial t} = \frac{1}{g_h(c_m; t)} \frac{\partial \chi(c; t)}{\partial c} \Bigg|_{c=c_m}, \quad (69)$$

786 so that, dividing through by $|\Omega(t)|$ and using Eq. (8),

$$\frac{\partial \ln |\Omega(t)|}{\partial t} = \frac{p(c_m; t)}{2} \frac{\partial \chi(c; t)}{\partial c} \Bigg|_{c=c_m}. \quad (70)$$

787 Using Eq. (63) for the transport contribution, these results lead to

$$\Delta p_D(c; t) = p(c; t) \left[\frac{1}{4} \frac{\partial \ln \chi(c; t)}{\partial c} \frac{\partial \chi(c; t)}{\partial c} - \frac{1}{2} \frac{\partial^2 \chi(c; t)}{\partial c^2} - \frac{p(c_m; t)}{2} \frac{\partial \chi(c; t)}{\partial c} \Bigg|_{c=c_m} \right]. \quad (71)$$

788 We now turn to the reaction term, Δp_R . Consider a small change dc in the concentrations due to
 789 reaction only, over a small time interval dt . The probability $p(c; t + dt) dc$ of finding concentrations in
 790 the infinitesimal vicinity dc of c decreases due to reaction at rate $r(c)$ away from c , and increases due
 791 to decrease in nearby concentrations towards c . Thus,

$$[p(c; t + dt) - p(c; t)] dc = \sum_{j=1}^{n_s} [r(c + dc)p(c + dc; t) - r(c)p(c; t)] dt. \quad (72)$$

792 Expanding the first term on each side in Taylor series, and dividing through by dt and dc , we obtain

$$\frac{\partial p(c; t)}{\partial t} = \frac{\partial r(c)p(c; t)}{\partial c}. \quad (73)$$

793 When a fixed minimum concentration detection limit is considered, as discussed above, it is necessary
 794 to take the change in volume (in one dimension, length) $|\Omega(t)|$ due to reactive decay of the minimum

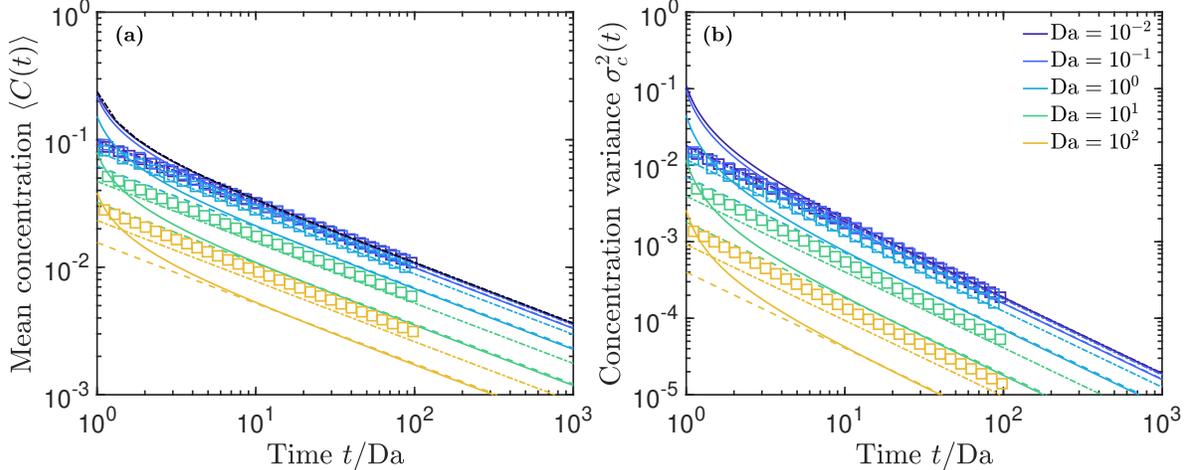


Figure 15: Temporal evolution of **(a)**: mean concentration and **(b)**: concentration variance for $\beta = 4$. Colors stand for different Damköhler numbers, markers show the results of resolved numerical simulations of the fully-coupled reaction–diffusion problem (35), solid lines are numerical results based on the weak-coupling model (Eqs. (45)), and dashed lines show approximate asymptotic analytical results (Eqs. (19) and (21), using Eqs. (56) and (58) for the peak concentration). Dash-dotted lines show analytical results assuming the transition to the Gaussian regime occurs at time $t = Da/10$ rather than at $t = Da$ (Eqs. (19) and (21), using Eqs. (58) and (59) for the peak concentration).

795 concentration into account. Using the same techniques as before, we obtain for the change in the
 796 domain size due to reaction:

$$\frac{\partial \ln |\Omega(t)|}{\partial t} = -p(c_m; t)r(c_m). \quad (74)$$

797 Thus, the complete effect of reaction is

$$\Delta p_R(c; t) = \frac{\partial r(c)p(c; t)}{\partial c} + p(c; t)p(c_m; t)r(c_m). \quad (75)$$

798 Note that integration of the right-hand side from $c = c_m$ to $c = \infty$ yields zero, which ensures the
 799 reactive contribution conserves probability for arbitrary $r(c)$. Substituting the effects of transport
 800 and reaction, Eqs. (33) and (33), in Eq. (29) leads to the dynamical Eq. (34) for the evolution of the
 801 concentration PDF under one-dimensional diffusion and nonlinear decay.

802 C Numerical methods

803 In this appendix, we provide details on the numerical methods used to integrate the weak-coupling
 804 equations (45) and the reaction–diffusion equation (35). Regarding Eqs. (45), which are ordinary differ-
 805 ential equations, we implemented a standard fourth-order Runge–Kutta method in the C++ language.
 806 This method was chosen for its simplicity of implementation and high accuracy, and also because, as
 807 an explicit method, it provides a convenient approach to integrate these nonlinear equations without
 808 requiring numerical root-finding methods. We employed a time step $\Delta t = 10^{-2} \min\{Da, 1/Da\}$ for
 809 the temporal discretization, which we verified led to consistently converged results.

810 For the fully-coupled reaction–diffusion problem, Eq. (35), we employed the `py-pde` open-source
 811 Python package for solving partial differential equations [79]. We used a regular finite difference
 812 discretization of a one-dimensional domain of half-width L and second-order centered differences for
 813 the spatial derivative approximations. For the time integration, we employed an explicit Forward
 814 Euler scheme. We set reflecting boundary conditions at the edges of the computational domain, but
 815 we verified that the latter was sufficiently large that no appreciable mass reached the edges, rendering

Table 1: Discretization parameters used in computing solutions of Eq. (35) to determine the mass and concentration peak, mean, and variance. For these computations, we employed a temporal discretization $\Delta t = a \min\{\text{Da}, 1/\text{Da}\}$ and a spatial discretization $\Delta x = b\sqrt{\Delta t/\text{Da}}$. The corresponding values of (a, b) for different reaction orders β and Damköhler numbers Da are given in the table.

$\beta \setminus \text{Da}$	10^{-2}	10^{-1}	10^0	10^1	10^2
1/2	$(10^{-4}, 1)$	$(10^{-4}, 1)$	$(5 \cdot 10^{-7}, 1)$	–	–
2	$(10^{-2}, 1)$	$(10^{-2}, 1)$	$(10^{-2}, 1)$	$(10^{-1}, 2)$	$(10, 4)$
4	$(10^{-3}, 1)$	$(10^{-2}, 1)$	$(10^{-2}, 1)$	$(10^{-1}, 1)$	$(10^{-1}, 1)$

Table 2: Discretization parameters used in computing solutions of Eq. (35) to determine the concentration PDF and scalar dissipation rate. For these computations, we employed a temporal discretization $\Delta t = a \min\{\text{Da}, 1/\text{Da}\}$ and a spatial discretization $\Delta x = \sqrt{\Delta t/\text{Da}}$. The corresponding values of a for different reaction orders β and Damköhler numbers Da are given in the table.

$\beta \setminus \text{Da}$	10^{-2}	10^{-1}	10^0	10^1	10^2
1/2	10^{-4}	10^{-4}	$5 \cdot 10^{-6}$	–	–
2	10^{-3}	–	10^{-4}	–	10^{-2}
4	10^{-4}	–	10^{-4}	–	10^{-1}

816 the choice of boundary conditions irrelevant. Since the late-time variance growth is approximately
817 diffusive, $L = 10\sqrt{t_m/\text{Da}}$, where t_m is the maximum simulation time, may be used as a simple
818 estimate of necessary domain size. However, because of the lower detection limit $c_m = 10^{-6}$ used in
819 the computation of the quantities of interest, we found that in practice it was never necessary to use
820 $L > 1500$ for the simulations conducted here. We note that, for $\beta < 1$, where complete depletion of
821 concentrations can happen in finite time, the increase of reaction rates with decreasing concentration
822 values can lead to numerical issues, because very low concentrations can drop below zero within a time
823 step. We avoid this issue by setting negative concentrations to zero before computing reaction rates.
824 We chose the spatial and temporal discretizations so as to ensure good accuracy while maintaining
825 reasonable simulation times. The discretization parameters for different system parameters β and Da
826 are summarized in Table 1 for the mass and concentration peak, mean, and variance calculations, and
827 in Table 2 for the concentration PDF and scalar dissipation rate.

828 The concentration PDF was obtained by counting discretized spatial locations where the concen-
829 tration value fell within prescribed bins (see also Section A). In order to accurately resolve both low
830 and high concentrations, we employed n_ℓ logarithmically-spaced concentration bins for concentrations
831 between the lower detection limit c_m and $2c_M(t)/3$, where the time-dependent peak value $c_M(t)$ was
832 determined from the numerical concentration profiles, and n_h linearly-space bins for the remaining
833 concentrations between $2c_M(t)/3$ and $c_M(t)$. For the lower, intermediate, and higher time examined
834 in each case, we employed $(n_\ell, n_h) = (20, 10)$, $(15, 8)$, and $(10, 6)$, respectively. The scalar dissipation
835 rate was calculated according to Eq. (77b) by numerically computing the spatial derivative at each dis-
836 cretized spatial location (in the rising limb of the symmetric concentration profile), using second-order
837 central differences. The corresponding concentration values at each spatial location were recorded and
838 used to obtain the scalar dissipation rate as a function of concentration.

D Problem setup and nondimensionalization

This appendix provides additional details on the nondimensionalization used in Section 4. Denoting nondimensionalized quantities by an asterisk, we have

$$C_*(x_*; t_*) = \frac{C(s_0 x_*, \tau_R t_*)}{c_0}, \quad r_*(c_*) = \frac{\tau_R}{c_0} r(c_0 c_*) = c_*^\beta, \quad (76)$$

where the characteristic reaction time $\tau_R = \kappa^{-1} c_0^{1-\beta}$. The minimum and maximum concentrations $c_M(t)$ and $c_m(t)$ are normalized in the same manner. Similarly, the nondimensional spatial variance $\sigma_*^2(t_*) = \sigma^2(\tau_R t_*)/s_0^2$. The concentration PDF and scalar dissipation are then nondimensionalized accordingly as

$$p_*(c_*; t_*) = c_0 p(c_0 c_*; \tau_R t_*), \quad (77a)$$

$$\chi_*(c_*; t_*) = \frac{\tau_R}{c_0^2} \chi(c_0 c_*; \tau_R t_*) = \frac{1}{2 \text{Da}} \left(\frac{\partial C_*(x_*, t_*)}{\partial x_*} \right)_{x_* = x_c(c)/s_0}^2, \quad (77b)$$

with the Damköhler number $\text{Da} = \tau_D/\tau_R$.

Note that, in nondimensional units, the pulse initial condition is given by a unit-width rectangle centered at the origin,

$$C_*(x_*; 0) = H(1/2 - x_*) H(1/2 + x_*), \quad (78)$$

which implies $p_*(c_*; 0) = \delta(c_* - 1)$. The batch concentration $c_B(t)$ for the well-mixed problem is nondimensionalized as above, and $c_{B*}(0) = 1$.

E Batch dynamics

Here, we provide some details on the equations governing the well-mixed batch problem discussed in Section 4 and its relation to the concentration PDF. Noting that $p(c; t) = \delta[c - c_B(t)]$ for the batch problem, where $c_B(t) = C(x; t)$ is the homogeneous concentration over the domain, and assuming $c_B(t) > c_m$, Eq. (34) becomes

$$\frac{\partial p(c; t)}{\partial t} = \frac{\partial r(c)p(c; t)}{\partial c}. \quad (79)$$

Multiplying through by c and integrating over c (using integration by parts on the right hand side), we recover the standard well-mixed rate law for the batch concentration as a function of time,

$$\frac{dc_B(t)}{dt} = -r[c_B(t)]. \quad (80)$$

Substituting Eq. (76) for the rate yields Eq. (37).

Once $c_B(t)$ drops below c_m , at some time t_m , the domain $\Omega(t)$ where concentrations are above this detection limit becomes empty, and the concentration PDF becomes ill-defined. By convention, we can set $c_B(t > t_m) = 0$ and $p(c; t > t_m) = \delta(c)$, which conveys the meaning that concentrations are zero everywhere (below the detection limit).

References

- [1] Carl I Steefel, Donald J DePaolo, and Peter C Lichtner. Reactive transport modeling: An essential tool and a new research approach for the earth sciences. *Earth Planet. Sci. Lett.*, 240(3-4):539–558, 2005.
- [2] Laura Guadagnini, Alessandra Menafoglio, X Sanchez-Vila, and Alberto Guadagnini. Probabilistic assessment of spatial heterogeneity of natural background concentrations in large-scale groundwater bodies through functional geostatistics. *Sci. Total Environ.*, 740:140139, 2020.

- 870 [3] Erica R Siirila and Reed M Maxwell. Evaluating effective reaction rates of kinetically driven
871 solutes in large-scale, statistically anisotropic media: Human health risk implications. *Water*
872 *Resour. Res.*, 48(4), 2012.
- 873 [4] Ilenia Battiato, Daniel M Tartakovsky, Alexandre M Tartakovsky, and T Scheibe. On breakdown
874 of macroscopic models of mixing-controlled heterogeneous reactions in porous media. *Adv. Water*
875 *Resour.*, 32(11):1664–1673, 2009.
- 876 [5] I Battiato and DM Tartakovsky. Applicability regimes for macroscopic models of reactive trans-
877 port in porous media. *J. Contam. Hydrol.*, 120:18–26, 2011.
- 878 [6] A. Hubert, T. Aquino, H. Tabuteau, Y. Méheust, and T. Le Borgne. Enhanced and non-monotonic
879 effective kinetics of solute pulses under michaelis–menten reactions. *Adv. Water Resour.*, 146:
880 103739, 2020.
- 881 [7] Charlotte Le Traon, Tomás Aquino, Camille Bouchez, Kate Maher, and Tanguy Le Borgne.
882 Effective kinetics driven by dynamic concentration gradients under coupled transport and reaction.
883 *Geochim. Cosmochim. Acta*, 306:189–209, 2021. ISSN 0016-7037. doi: [https://doi.org/10.1016/j.](https://doi.org/10.1016/j.gca.2021.04.033)
884 [gca.2021.04.033](https://doi.org/10.1016/j.gca.2021.04.033).
- 885 [8] EE O’Brien. The probability density function (pdf) approach to reacting turbulent flows. In
886 *Turbulent reacting flows*, pages 185–218. Springer, 1980.
- 887 [9] Stephen B Pope. Pdf methods for turbulent reactive flows. *Prog. Energy Combust. Sci.*, 11(2):
888 119–192, 1985.
- 889 [10] Stephen B Pope. Lagrangian pdf methods for turbulent flows. *Annu. Rev. Fluid Mech.*, 26(1):
890 23–63, 1994.
- 891 [11] PR Van Slooten, Jayesh, and SB Pope. Advances in pdf modeling for inhomogeneous turbulent
892 flows. *Phys. Fluids*, 10(1):246–265, 1998.
- 893 [12] Steven R Hanna. The exponential probability density function and concentration fluctuations in
894 smoke plumes. *Bound.-Layer Meteorol.*, 29(4):361–375, 1984.
- 895 [13] Eugene Yee. The shape of the probability density function of short-term concentration fluctuations
896 of plumes in the atmospheric boundary layer. *Bound.-Layer Meteorol.*, 51(3):269–298, 1990.
- 897 [14] Eugene Yee and R Chan. A simple model for the probability density function of concentration
898 fluctuations in atmospheric plumes. *Atmos. Environ.*, 31(7):991–1002, 1997.
- 899 [15] Jean-Rémi Alisse and Claude Sidi. Experimental probability density functions of small-scale
900 fluctuations in the stably stratified atmosphere. *J. Fluid Mech.*, 402:137–162, 2000.
- 901 [16] RJ Munro, PC Chatwin, and N Mole. The high concentration tails of the probability density
902 function of a dispersing scalar in the atmosphere. *Bound.-Layer Meteorol.*, 98(2):315–339, 2001.
- 903 [17] József Bakosi, Pasquale Franzese, and Zafer Boybeyi. Probability density function modeling of
904 scalar mixing from concentrated sources in turbulent channel flow. *Phys. Fluids*, 19(11):115106,
905 2007.
- 906 [18] César Dopazo and Edward E O’Brien. An approach to the autoignition of a turbulent mixture.
907 *Acta Astronaut.*, 1(9-10):1239–1266, 1974.
- 908 [19] P. Givi, J. I. Ramos, and W. A. Sirignano. Probability density function calculations in turbu-
909 lent chemically reacting round jets, mixing layers and one-dimensional reactors. *J. Non-Equilib.*
910 *Thermodyn.*, 10(2):75–104, 1985.

- 911 [20] MS Anand and SB Pope. Calculations of premixed turbulent flames by pdf methods. *Combust.*
912 *Flame*, 67(2):127–142, 1987.
- 913 [21] Rodney O Fox. Computation of turbulent reactive flows: first-principles macro/micromixing
914 models using probability density function methods. *Chem. Eng. Sci.*, 47(9-11):2853–2858, 1992.
- 915 [22] Daniel Connell Haworth. Progress in probability density function methods for turbulent reacting
916 flows. *Prog. Energy Combust. Sci.*, 36(2):168–259, 2010.
- 917 [23] S Broyda, Marco Dentz, and DM Tartakovsky. Probability density functions for advective–reactive
918 transport in radial flow. *Stoch. Environ. Res. Risk. Assess.*, 24(7):985–992, 2010.
- 919 [24] Vivek Kapoor and Peter K Kitanidis. Concentration fluctuations and dilution in aquifers. *Water*
920 *Resour. Res.*, 34(5):1181–1193, 1998.
- 921 [25] Aldo Fiori and Gedeon Dagan. Concentration fluctuations in transport by groundwater: Com-
922 parison between theory and field experiments. *Water Resour. Res.*, 35(1):105–112, 1999.
- 923 [26] Aldo Fiori and Gedeon Dagan. Concentration fluctuations in aquifer transport: A rigorous first-
924 order solution and applications. *J. Contam. Hydrol.*, 45(1-2):139–163, 2000.
- 925 [27] Mark Shvidler and Kenzi Karasaki. Probability density functions for solute transport in random
926 field. *Transp. Porous Media*, 50(3):243–266, 2003.
- 927 [28] M. Dentz, D. Bolster, and T. Le Borgne. Concentration statistics for transport in random media.
928 *Phys. Rev. E*, 80:010101(R), 2009.
- 929 [29] Marco Dentz and Daniel M Tartakovsky. Probability density functions for passive scalars dispersed
930 in random velocity fields. *Geophys. Res. Lett.*, 37(24), 2010.
- 931 [30] Tanguy Le Borgne, Marco Dentz, and Emmanuel Villiermaux. The lamellar description of mixing
932 in porous media. *J. Fluid Mech.*, 770:458–498, 2015.
- 933 [31] Emmanuel Villiermaux. Mixing versus stirring. *Annu. Rev. Fluid Mech.*, 51:245–273, 2019.
- 934 [32] Matteo Icardi and Marco Dentz. Probability density function (pdf) models for particle transport
935 in porous media. *GEM - Int. J. Geomath.*, 11(1):1–17, 2020.
- 936 [33] Mayumi Hamada, Luis Cueto-Felgueroso, and Pietro de Anna. Diffusion limited mixing in confined
937 media. *Phys. Rev. Fluids*, 5(12):124502, 2020.
- 938 [34] Olaf A Cirpka, Ronnie L Schwede, Jian Luo, and Marco Dentz. Concentration statistics for
939 mixing-controlled reactive transport in random heterogeneous media. *J. of Contam. Hydrol.*, 98
940 (1-2):61–74, 2008.
- 941 [35] Xavier Sánchez-Vila, Alberto Guadagnini, and Daniel Fernández-García. Conditional probabil-
942 ity density functions of concentrations for mixing-controlled reactive transport in heterogeneous
943 aquifers. *Mathematical geosciences*, 41(3):323–351, 2009.
- 944 [36] Pietro De Anna, Tanguy Le Borgne, Marco Dentz, Diogo Bolster, and Philippe Davy. Anomalous
945 kinetics in diffusion limited reactions linked to non-Gaussian concentration probability distribution
946 function. *J. Chem. Phys.*, 135(17):174104, 2011.
- 947 [37] A. Bellin, G. Severino, and A. Fiori. On the local concentration probability density function of
948 solutes reacting upon mixing. *Water Resour. Res.*, 47(1), 2011.
- 949 [38] Olaf A Cirpka, Felipe P J de Barros, Gabriele Chiogna, and Wolfgang Nowak. Probability density
950 function of steady state concentration in two-dimensional heterogeneous porous media. *Water*
951 *Resour. Res.*, 47(11), 2011.

- 952 [39] Gabriele Chiogna and Alberto Bellin. Analytical solution for reactive solute transport considering
953 incomplete mixing within a reference elementary volume. *Water Resour. Res.*, 49(5):2589–2600,
954 2013.
- 955 [40] Nicolae Suciuc, Florin A Radu, Sabine Attinger, L Schüler, and Peter Knabner. A fokker–planck
956 approach for probability distributions of species concentrations transported in heterogeneous me-
957 dia. *J. Comput. Appl. Math.*, 289:241–252, 2015.
- 958 [41] Nicole Sund, Tomás Aquino, and Diogo Bolster. Effective models for transport in complex het-
959 erogeneous hydrologic systems. In Patricia Maurice, editor, *Encyclopedia of Water: Science,*
960 *Technology, and Society*. John Wiley & Sons, 2019. ISBN 9781119300762.
- 961 [42] Peter C Lichtner and DM Tartakovsky. Stochastic analysis of effective rate constant for hetero-
962 geneous reactions. *Stoch. Env. Res. Risk. A.*, 17(6):419–429, 2003.
- 963 [43] D. M. Tartakovsky, M. Dentz, and P. C. Lichtner. Probability density functions for advective-
964 reactive transport with uncertain reaction rates. *Water Resour. Res.*, 45(7), 2009.
- 965 [44] Daniel M Tartakovsky and Svetlana Broyda. Pdf equations for advective–reactive transport in
966 heterogeneous porous media with uncertain properties. *J. Contam. Hydrol.*, 120:129–140, 2011.
- 967 [45] Daniele Venturi, Daniel M Tartakovsky, Alexandre M Tartakovsky, and George E Karniadakis.
968 Exact pdf equations and closure approximations for advective-reactive transport. *J. Comput.*
969 *Phys.*, 243:323–343, 2013.
- 970 [46] T. Le Borgne, P. D. Huck, M. Dentz, and E. Villermaux. Scalar gradients in stirred mixtures and
971 the deconstruction of random fields. *J. Fluid Mech.*, 812:578–610, 2017. doi: 10.1017/jfm.2016.799.
- 972 [47] Emilie Guilbert, Christophe Almarcha, and Emmanuel Villermaux. Chemical reaction for mixing
973 studies. *Phys. Rev. Fluids*, 6(11):114501, 2021.
- 974 [48] Pietro De Anna, Marco Dentz, Alexandre Tartakovsky, and Tanguy Le Borgne. The filamentary
975 structure of mixing fronts and its control on reaction kinetics in porous media flows. *Geophys.*
976 *Res. Lett.*, 41(13):4586–4593, 2014.
- 977 [49] Tanguy Le Borgne, Timothy R Ginn, and Marco Dentz. Impact of fluid deformation on mixing-
978 induced chemical reactions in heterogeneous flows. *Geophys. Res. Lett.*, 41(22):7898–7906, 2014.
- 979 [50] Joaquín Jiménez-Martínez, Pietro de Anna, Hervé Tabuteau, Régis Turuban, Tanguy Le Borgne,
980 and Yves Méheust. Pore-scale mechanisms for the enhancement of mixing in unsaturated porous
981 media and implications for chemical reactions. *Geophys. Res. Lett.*, 42(13):5316–5324, 2015.
- 982 [51] Aditya Bandopadhyay, Tanguy Le Borgne, Yves Méheust, and Marco Dentz. Enhanced reac-
983 tion kinetics and reactive mixing scale dynamics in mixing fronts under shear flow for arbitrary
984 damköhler numbers. *Adv. Water Resour.*, 100:78–95, 2017.
- 985 [52] YB Zeldovich. The asymptotic law of heat transfer at small velocities in the finite domain problem.
986 *Zh. Eksp. Teoret. Fiz*, 7(12):1466–1468, 1937.
- 987 [53] Julio M Ottino and JM Ottino. *The kinematics of mixing: stretching, chaos, and transport*,
988 volume 3. Cambridge university press, 1989.
- 989 [54] Tanguy Le Borgne, Marco Dentz, Diogo Bolster, Jesus Carrera, Jean-Raynald De Dreuzy, and
990 Philippe Davy. Non-Fickian mixing: Temporal evolution of the scalar dissipation rate in hetero-
991 geneous porous media. *Adv. Water Resour.*, 33(12):1468–1475, 2010.
- 992 [55] Felipe PJ De Barros, Marco Dentz, Jonas Koch, and Wolfgang Nowak. Flow topology and scalar
993 mixing in spatially heterogeneous flow fields. *Geophys. Res. Lett.*, 39(8), 2012.

- 994 [56] Nicholas B Engdahl, Timothy R Ginn, and Graham E Fogg. Scalar dissipation rates in non-
995 conservative transport systems. *J. Contam. Hydrol.*, 149:46–60, 2013.
- 996 [57] Deepashree S Rajee and Vivek Kapoor. Experimental study of bimolecular reaction kinetics in
997 porous media. *Environ. Sci. Technol.*, 34(7):1234–1239, 2000.
- 998 [58] Carolyn M Gramling, Charles F Harvey, and Lucy C Meigs. Reactive transport in porous media:
999 A comparison of model prediction with laboratory visualization. *Environ. Sci. Technol.*, 36(11):
1000 2508–2514, 2002.
- 1001 [59] FJ Valdes-Parada and J Alvarez-Ramirez. On the effective diffusivity under chemical reaction in
1002 porous media. *Chem. Eng. Sci.*, 65(13):4100–4104, 2010.
- 1003 [60] FJ Valdés-Parada, CG Aguilar-Madera, and J Alvarez-Ramirez. On diffusion, dispersion and
1004 reaction in porous media. *Chem. Eng. Sci.*, 66(10):2177–2190, 2011.
- 1005 [61] JMC Pereira, JEP Navalho, ACG Amador, and JCF Pereira. Multi-scale modeling of diffusion
1006 and reaction–diffusion phenomena in catalytic porous layers: comparison with the 1d approach.
1007 *Chem. Eng. Sci.*, 117:364–375, 2014.
- 1008 [62] William E Ranz. Applications of a stretch model to mixing, diffusion, and reaction in laminar
1009 and turbulent flows. *AIChE J.*, 25(1):41–47, 1979.
- 1010 [63] Tomás Aquino and Tanguy Le Borgne. The diffusing-velocity random walk: a spatial-Markov
1011 formulation of heterogeneous advection and diffusion. *J. Fluid Mech.*, 910:A12, 2021.
- 1012 [64] William Feller. *An introduction to probability theory and its applications*, volume 2. John Wiley
1013 & Sons, 2008.
- 1014 [65] Lars Hörmander. *The analysis of linear partial differential operators I: Distribution theory and
1015 Fourier analysis*. Springer, 2015.
- 1016 [66] Frank E Marble and James E Broadwell. The coherent flame model for turbulent chemical reac-
1017 tions. Technical Report TRW-9-PU, Project SQUID, Purdue Univ., West Lafayette, IN, 1977.
- 1018 [67] Emmanuel Villiermaux. Mixing by porous media. *C. R. Mécanique*, 340(11-12):933–943, 2012.
- 1019 [68] Tanguy Le Borgne, Marco Dentz, and Emmanuel Villiermaux. Stretching, coalescence, and mixing
1020 in porous media. *Phys. Rev. Lett.*, 110(20):204501, 2013.
- 1021 [69] George Keith Batchelor. The effect of homogeneous turbulence on material lines and surfaces.
1022 *Proc. R. Soc. A*, 213(1114):349–366, 1952.
- 1023 [70] R Betchov. An inequality concerning the production of vorticity in isotropic turbulence. *J. Fluid
1024 Mech.*, 1(5):497–504, 1956.
- 1025 [71] WJ Cocke. Turbulent hydrodynamic line stretching: consequences of isotropy. *Phys. Fluids*, 12
1026 (12):2488–2492, 1969.
- 1027 [72] Wm T Ashurst, AR Kerstein, RM Kerr, and CH Gibson. Alignment of vorticity and scalar
1028 gradient with strain rate in simulated navier–stokes turbulence. *Phys. Fluids*, 30(8):2343–2353,
1029 1987.
- 1030 [73] SS Girimaji and SB Pope. Material-element deformation in isotropic turbulence. *J. Fluid Mech.*,
1031 220:427–458, 1990.
- 1032 [74] D Martínez-Ruiz, P Meunier, B Favier, L Duchemin, and E Villiermaux. The diffusive sheet
1033 method for scalar mixing. *J. Fluid Mech.*, 837:230–257, 2018.

- 1034 [75] Patrice Meunier and Emmanuel Villermaux. The diffusive strip method for scalar mixing in two
1035 dimensions. *J. Fluid Mech.*, 662:134–172, 2010.
- 1036 [76] J. Heyman, D. R. Lester, R. Turuban, Y. Méheust, and T. Le Borgne. Stretching and folding
1037 sustain microscale chemical gradients in porous media. *Proc. Natl. Acad. Sci. U.S.A.*, 2020.
- 1038 [77] Jérôme Duplat and Emmanuel Villermaux. Mixing by random stirring in confined mixtures. *J.*
1039 *Fluid Mech.*, 617:51–86, 2008.
- 1040 [78] Daniel R Lester, Marco Dentz, and Tanguy Le Borgne. Chaotic mixing in three-dimensional
1041 porous media. *J. Fluid Mech.*, 803:144–174, 2016.
- 1042 [79] David Zwicker. py-pde: A python package for solving partial differential equations. *J. Open*
1043 *Source Softw.*, 5(48):2158, 2020. doi: 10.21105/joss.02158. URL [https://doi.org/10.21105/
1044 joss.02158](https://doi.org/10.21105/joss.02158).
- 1045 [80] Vlad I Morariu, Balaji Vasan Srinivasan, Vikas C Raykar, Ramani Duraiswami, and Larry S
1046 Davis. Automatic online tuning for fast gaussian summation. In *Advances in Neural Information*
1047 *Processing Systems*, volume 21, pages 1113–1120, Vancouver, 2008. Citeseer.
- 1048 [81] Daniel Fernández-García and Xavier Sánchez-Vila. Optimal reconstruction of concentrations,
1049 gradients and reaction rates from particle distributions. *J. Contam. Hydrol.*, 120:99–114, 2011.
- 1050 [82] Guillem Sole-Mari, Diogo Bolster, Daniel Fernández-García, and Xavier Sanchez-Vila. Particle
1051 density estimation with grid-projected and boundary-corrected adaptive kernels. *Adv. Water*
1052 *Resour.*, 131:103382, 2019.