PUBLICATION

MUSTANG

A MUltiple Space and Time scale Approach for the quaNtification of deep saline formations for CO_2 storaGe

Project Number:227286

AUTHORS: *Dentz, M.; Tartakovsky, D. M.*

TITLE: *Probability density functions for passive scalars dispersed in random velocity fields*

The research leading to these results has received funding from the European Community's Seventh Framework Programme [FP7/2007/2013) under grant agreement n° [227286]

Status	AUTHOR VERSION
Date	2010
Publisher	Wiley Online Library
Reference	Geophysical Research Letters, 37

Probability Density Functions for Passive Scalars Dispersed in Random Velocity Fields

Marco Dentz,[1] Daniel M. Tartakovsky,[2]

Spatial and temporal heterogeneity of ambient natural environments play a significant role in large scale transport phenomena. Uncertainty about spatio-temporal fluctuations in system parameters (e.g., flow velocity) make deterministic predictions of macroscopic systems states (e.g., solute concentration) elusive. Distributions of system states generally exhibit highly non-Gaussian behavior, which cannot be captured solely by the corresponding mean and variance. Instead, these features of transport are described by the probability density function (PDF) of a system state, e.g., the PDF of concentration at a certain point in space and time. We study the PDF of the distribution of a passive scalar that disperses in a random velocity field. We derive an explicit map between the velocity distribution and the scalar PDF, and obtain approximate solutions for the PDF of the normalized scalar. These solutions allow for the explicit quantification of the impact of dispersion on the evolution of the passive scalar PDF without recurrence to classical closure approximations in terms of mixing models.

Dispersion in random velocity fields plays a central role in a variety of geophysical phenomena. We start from the hypothesis that local scale transport of a passive scalar $c(\mathbf{x}, t)$ can be described by the advection-dispersion equation (ADE)

$$\frac{\partial c(\mathbf{x}, t)}{\partial t} + \nabla \cdot [\mathbf{u}(\mathbf{x}, t) c(\mathbf{x}, t)] - \nabla \cdot \mathbf{D} \nabla c(\mathbf{x}, t) = 0, \qquad (1)$$

where $\mathbf{u}(\mathbf{x}, t)$ is the flow velocity and $\mathbf{D}$ the dispersion tensor, which here is assumed to be constant. Examples of passive scalars $c(\mathbf{x}, t)$ include solute concentration and fluid temperature. In many geophysical applications characterized by large Reynolds numbers Re, randomness of $\mathbf{u}(\mathbf{x}, t)$ is a manifestation of turbulence. In other applications, of which flow and transport in porous media are a prime example, the velocity $\mathbf{u}(\mathbf{x}, t)$ is often treated as random to reflect spatial heterogeneity and related uncertainty about the ambient environment (e.g., uncertainty about the porosity $\phi(\mathbf{x})$ and hydraulic conductivity $K(\mathbf{x})$ of a heterogeneous porous medium) even though Re might be very small and flow is laminar. In the former class of problems, temporal variability of $\mathbf{u}(\mathbf{x}, t)$ is essential, while in the latter class velocity is often considered at steady state.

Regardless of application, randomness in, or uncertainty about, the flow velocity $\mathbf{u}(\mathbf{x}, t)$ render a solution of (1) stochastic, i.e., given in terms of the probability density function (PDF) of $c(\mathbf{x}, t)$. As a practical matter, it is common to focus on the one-point concentration PDF, $p_c(\psi; \mathbf{x}, t)$, which specifies the probability of the random concentration c at a point $\mathbf{x}$ and time t to have a value in $[\psi, \psi + d\psi]$.

The scalar PDF carries information on the mixing state of a system [e.g., *Villermaux and Duplat*, 2006] and as such plays a central role for the quantification of non-linear mixing-driven reaction systems beyond the mean field [e.g., *Pope*, 2000]. Furthermore, the scalar PDF is a key quantity for the assessment of environmental hazards and risks [e.g., *Tartakovsky*, 2007] because it encodes the uncertainty about the mean behavior.

While derivation of PDF equations for purely advective transport ($\mathbf{D} \equiv \mathbf{0}$) is mathematically rigorous and relatively straitforward [e.g., *Indelman and Shvidler*, 1985; *Chen et al.*, 1989], the quantification of the role of diffusion in the evolution of the scalar PDF remains a fundamental question. Phenomenologically, diffusion reduces uncertainty by smearing out scalar gradients. It sharpens the scalar PDF, or in other words it reduces scalar variance. These mechanisms have been quantified mainly using phenomenological approaches, so called mixing models. Such approaches include the interaction by exchange with the mean model (IEM) [*Villermaux and Devillon*, 1972; *Dopazo and O'Brien*, 1974], mapping approaches [*Chen et al.*, 1989] and stochastic mixing models [*Valiño and Dopazo*, 1991; *Fox and Yeung*, 2003; *Fedotov et al.*, 2005], see also *Pope* [2000] for an overview. In general, the relaxation, or degradation mechanisms caused by diffusion have been found difficult to account for *Chen et al.* [1989]. An alternative approach is to rely on an assumed form of the PDF, most often by postulating that the concentration PDF is a β-distribution [*Girimaji*, 1991]. This approach has proved to be successful in modeling transport in random porous media in steady-state random velocity fields $\mathbf{u}(\mathbf{x})$ [*Caroni and Fiorotto*, 2005; *Bellin and Tonina*, 2007; *Cirpka et al.*, 2008].

This dichotomy points to the need to develop an approach that is equally applicable to transient and steady-state velocity fields $\mathbf{u}(\mathbf{x}, t)$, posing as few restrictions on its statistics as possible. PDF methods [e.g., *Tartakovsky et al.*, 2009; *Meyer et al.*, 2010] provide a general framework for achieving this goal. In the present analysis we compute the PDF of concentration $c(\mathbf{x}, t)$ in (1) by imposing the following two constraints on $\mathbf{u}(\mathbf{x}, t)$. First, we assume the (steady or transient) velocity to be divergence-free, $\nabla \cdot \mathbf{u}(\mathbf{x}, t) = 0$. Second, we assume that $\mathbf{u}(\mathbf{x}, t)$ is a statistically homogeneous (stationary) multivariate Gaussian random field. The latter assumption is somewhat restrictive, since the spatio-temporally fluctuating random velocity field $\mathbf{u}(\mathbf{x}, t)$ is determined by boundary conditions and, in the case of porous flow, the medium heterogeneity. Yet, experimental evidence strongly suggests that $\mathbf{u}(\mathbf{x}, t)$ is indeed (approximately) Gaussian for turbulent flows [e.g., *Bronski and McLaughlin*, 2000]. The same assumption is routinely made in analyses of transport in random porous media [e.g., *Koch and Shaqfeh*, 1992; *Zhang*, 1995; *Jaekel and Vereecken*, 1997; *Fiori and Dagan*, 2000; *Dentz and Tartakovsky*, 2008]. For non-stationary and non-Gaussian velocity fields, the presented approach can be used to obtain a prior distribution

[1]Spanish National Research Council, IDAEA-CSIC, Barcelona, Spain
[2]Department of Mechanical and Aerospace Engineering, University of California, San Diego (UCSD), La Jolla, USA.

0094-8276/10/$5.00

for the concentration PDF, which can be updated through a Bayesian approach or ensemble Kalman filtering to account for non-stationarity and non-Gaussianity.

With these assumptions in mind the mean flow velocity $\langle \mathbf{u} \rangle$ and variance σ_u^2 are constant,

$$\langle \mathbf{u}(\mathbf{x}, t) \rangle = \overline{\mathbf{u}}, \qquad \sigma_u^2 = \langle \mathbf{u}'(\mathbf{x}, t)^2 \rangle. \tag{2}$$

The two-point correlation correlation function has the form

$$C_{ij}(\mathbf{x} - \mathbf{x}', t - t') = \langle u_i'(\mathbf{x}, t) u_j'(\mathbf{x}', t') \rangle. \tag{3}$$

Here $\mathbf{u}'(\mathbf{x}, t)$ denotes zero-mean random fluctuations of the velocity field $\mathbf{u}(\mathbf{x}, t)$ about its ensemble mean $\overline{\mathbf{u}}$, i.e., $\mathbf{u}(\mathbf{x}, t) = \overline{\mathbf{u}} + \mathbf{u}'(\mathbf{x}, t)$. The angular brackets $\langle \cdot \rangle$ denote the ensemble average over the random field $\mathbf{u}(\mathbf{x}, t)$. The components C_{ij} of the correlation matrix $\mathbf{C}$ decay on the correlation scales l_{ij} and τ_{ij}. The advection time $\tau_u = \ell_u / |\overline{\mathbf{u}}|$ measures the time for advective transport over the correlation scale ℓ_u in the direction of the mean velocity. The diffusion scale $\tau_D = \ell_D / D$ denotes the typical diffusion time over a transverse correlation distance ℓ_D. The dimensionless Péclet number is defined as $Pe = \tau_D / \tau_u$. It compares the efficiency of diffusive and advective transport.

The single point PDF of the concentration distribution $c(\mathbf{x}, t)$ is defined as

$$p_c(\psi; \mathbf{x}, t) = \langle \delta[\psi - c(\mathbf{x}, t)] \rangle, \tag{4}$$

where ψ is the sampling variable. The concentration distribution $c(\mathbf{x}, t)$ is a functional of the flow field $\mathbf{u}(\mathbf{x}, t)$, whose concrete form is unknown because there is no closed form solution known for Eq. (1) for general spatially fluctuating velocity fields.

Here we derive a mapping approach to obtain the concentration PDF $p_c(\psi; \mathbf{x}, t)$ that explicitly takes into account the impact of diffusion on the evolution of the concentration PDF. This approach is based on mapping the disorder distribution as quantified in terms of the joint PDF of the (random) centroid and (random) spatial width of $c(\mathbf{x}, t)$ onto the scalar PDF. To this end, we establish an expression for $c(\mathbf{x}, t)$ that depends explicitly on these (random) observables. To obtain such an expression, we consider the Langevin equation for the particle trajectories $\mathbf{x}(t)$ that is equivalent to the ADE (1),

$$\frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t} = \mathbf{u}\left[\mathbf{x}(t), t\right] + \boldsymbol{\xi}(t), \tag{5}$$

where $\boldsymbol{\xi}(t)$ is a Gaussian white noise characterized by zero mean and correlation

$$\left\langle \xi_i(t) \xi_j(t') \right\rangle_\xi = 2 D_{ij} \delta(t - t'). \tag{6}$$

where D_{ij} are the components of the dispersion tensor $\mathbf{D}$. The angular brackets $\langle \cdot \rangle_\xi$ denote the noise average over $\boldsymbol{\xi}(t)$. The Langevin equation (5) contains two stochastic processes: the random velocity field $\mathbf{u}(\mathbf{x}, t)$ and noise $\boldsymbol{\xi}(t)$, which models diffusion. The random processes $\mathbf{u}(\mathbf{x}, t)$ and $\boldsymbol{\xi}(t)$ are statistically independent. The random concentration $c(\mathbf{x}, t)$ in a single disorder realization can be written in terms of the particle trajectories by averaging over the noise $\boldsymbol{\xi}(t)$, i.e., $c(\mathbf{x}, t) = \langle \delta[\mathbf{x} - \mathbf{x}(t)] \rangle_\xi$. The average concentration is obtained by averaging over $\mathbf{u}(\mathbf{x}, t)$.

Mapping Approach: Let us rewrite the Langevin equation (5) as

$$\frac{\mathrm{d}\mathbf{x}(t)}{\mathrm{d}t} = \mathbf{v}(t) + \boldsymbol{\eta}(t), \tag{7}$$

where $\mathbf{v}(t)$, the particle velocity averaged over the noise $\boldsymbol{\xi}(t)$, and $\boldsymbol{\eta}(t)$, the velocity fluctuations about $\mathbf{v}(t)$, are defined as

$$\mathbf{v}(t) = \frac{\mathrm{d}\mathbf{m}(t)}{\mathrm{d}t}, \qquad \boldsymbol{\eta}(t) = \delta\mathbf{u}(t) + \sqrt{2\mathbf{D}} \cdot \boldsymbol{\xi}(t). \tag{8}$$

Here, $\mathbf{m}(t) = \langle \mathbf{x}(t) \rangle_\xi$ is the centroid of the scalar field $c(\mathbf{x}, t)$, and $\delta\mathbf{u}(t) = \mathbf{u}[\mathbf{x}(t), t] - \langle \mathbf{u}[\mathbf{x}(t), t] \rangle_\xi$ the Lagrangian velocity fluctuation. The random processes $\boldsymbol{\eta}(t)$ and $\mathbf{u}(\mathbf{x}, t)$ are not independent. The distribution of $\boldsymbol{\eta}(t)$ is conditional to the specific realization of $\mathbf{u}(\mathbf{x}, t)$, $p_{\eta|u}(\mathbf{h}; t) = \langle \delta[\mathbf{h} - \boldsymbol{\eta}(t)] \rangle_\xi$.

These definitions imply that $\boldsymbol{\eta}(t)$ has zero conditional mean, $\langle \boldsymbol{\eta}(t) \rangle_\xi = \mathbf{0}$, and its conditional correlation function $C_{ij}^\eta(t, t') = \langle \eta_i(t) \eta_j(t') \rangle_\xi$ is given by

$$C_{ij}^\eta(t, t') = 2 D_{ij} \delta_{ij} \delta(t - t') + \langle \delta u_i(t) \delta u_j(t') \rangle_\xi. \tag{9}$$

Note that $\mathbf{C}^\eta(t, t')$ is a random matrix since its definition does not involve averaging over $\mathbf{u}(\mathbf{x}, t)$.

The approach of modeling the Lagrangian velocity increment in order to infer concentration statistics has been employed by, e.g., *Fiori and Dagan* [2000] and *Meyer et al.* [2010]. *Fiori and Dagan* [2000] derived the velocity statistics based on a perturbation approach and determine the mean concentration and concentration variance. Similar results were obtained by, e.g., *Graham and McLaughlin* [1989], *Kapoor and Gelhar* [1994], and *Kapoor and Kitanidis* [1998].

Both $\mathbf{u}(\mathbf{x}, t)$ and $\boldsymbol{\xi}(t)$ are Gaussian processes. We assume that the conditional PDF of $\boldsymbol{\eta}(t)$ in (8) is Gaussian,

$$p_{\eta|u}(\mathbf{h}; t) = \frac{\exp\left\{-\mathbf{h}[2\mathbf{C}^\eta(t, 0)]^{-1}\mathbf{h}\right\}}{\sqrt{(2\pi)^d \det[\mathbf{C}^\eta(t, 0)]}}. \tag{10}$$

To confirm the validity of this assumption we conducted random walk simulations conditioned on a realization of a steady random velocity field $\mathbf{u}(\mathbf{x})$[1]. The increment statistics of $\boldsymbol{\eta}(t)$ as well as the correlation matrix $\mathbf{C}^\eta(t, 0)$ were determined numerically from 10^6 realizations of $\boldsymbol{\xi}(t)$. In Figure 1 we compare the results of these simulations for $\eta_1(t)$ with the conditional PDF (10). One can see that (10) is indeed a good representation of the conditional PDF of $\boldsymbol{\eta}(t)$. We therefore conclude that $\boldsymbol{\eta}(t)$ can be modeled as a correlated Gaussian noise in a single realization of $\mathbf{u}(\mathbf{x}, t)$.

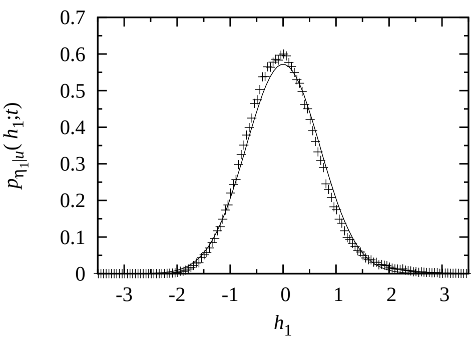

Figure 1. Conditional PDF of the random increment $\eta_1(t)$ at time $t = 10\tau_u$ for $\sigma_u^2 = 1$ and $Pe = 10^2$ in a single realization of $\mathbf{u}(\mathbf{x})$ given by (10) (solid line) and the random walk simulations (+).

Next, we express the random concentration in a single disorder realization as a conditional average over the correlated noise $\boldsymbol{\eta}(t)$

$$c(\mathbf{x},t) = \langle \delta[\mathbf{x} - \mathbf{x}(t)] \rangle_\eta. \qquad (11)$$

The random particle trajectories $\mathbf{x}(t)$ are obtained by integrating (7) over time,

$$\mathbf{x}(t) = \mathbf{m}(t) + \int_0^t \mathrm{d}t' \boldsymbol{\eta}(t'). \qquad (12)$$

Substituting the resulting $\mathbf{x}(t)$ into (11) and taking the conditional average over $\boldsymbol{\eta}(t)$ using (10) gives

$$c(\mathbf{x},t) = \frac{\exp\left\{-\frac{1}{2}[\mathbf{x} - \mathbf{m}(t)]\boldsymbol{\kappa}(t)^{-1}[\mathbf{x} - \mathbf{m}(t)]\right\}}{\sqrt{(2\pi)^d \det \boldsymbol{\kappa}(t)}}, \qquad (13)$$

where the random matrix $\boldsymbol{\kappa}(t)$ is

$$\kappa_{ij}(t) = \int_0^t \mathrm{d}t' \int_0^t \mathrm{d}t'' C^\eta_{ij}(t', t''). \qquad (14)$$

Solution (13) implicitly assumes that the flow domain is infinite and the initial condition is a point source at $\mathbf{x} = \mathbf{0}$. Distributed sources can be accounted for by treating $c(\mathbf{x},t)$ in (13) as a Green function and integrating it over the source distribution.

Expression (13) maps $[\mathbf{m}(t), \boldsymbol{\kappa}(t)]$ onto $c(\mathbf{x},t)$, that is, $c(\mathbf{x},t) = f[\mathbf{x}, t; \mathbf{m}(t), \boldsymbol{\kappa}(t)]$. The concentration PDF then is given by

$$p_c(\psi; \mathbf{x}, t) = \int \mathrm{d}\boldsymbol{\mu} \int \mathrm{d}\mathbf{k}\, \delta\{\psi - f[\mathbf{x}, t; \boldsymbol{\mu}, \mathbf{k}]\} \times p_{m,\kappa}(\boldsymbol{\mu}, \mathbf{k}; t), \qquad (15)$$

where $p_{m,\kappa}(\boldsymbol{\mu}, \mathbf{k}; t)$ is the joint PDF of $\mathbf{m}(t)$ and $\boldsymbol{\kappa}(t)$.

In the following, we focus on the impact of fluctuations in the centroid $\mathbf{m}(t)$. Thus, we assume that the fluctuations of $\boldsymbol{\kappa}(t)$ about its ensemble mean value $\boldsymbol{\kappa}^e(t) = \langle \boldsymbol{\kappa}(t) \rangle$ are small compared to the fluctuations of $\mathbf{m}(t)$, so that $\boldsymbol{\kappa}(t)$ can be approximated by its mean value $\boldsymbol{\kappa}^e(t)$, which describes the effective width of $c(\mathbf{x},t)$ [e.g., *Kitanidis*, 1988]. This assumption allows us to simplify (15) as

$$p_c(\psi; \mathbf{x}, t) = \int \mathrm{d}\boldsymbol{\mu}\, \delta\{\psi - f[\mathbf{x}, t; \boldsymbol{\mu}, \boldsymbol{\kappa}^e(t)]\} p_m(\boldsymbol{\mu}; t), \qquad (16)$$

where $p_m(\boldsymbol{\mu}; t) = \langle \delta[\boldsymbol{\mu} - \mathbf{m}(t)] \rangle$ is the centroid PDF.

Centroid PDF: The random dynamics of centroid $\mathbf{m}(t)$ are described by averaging (5) over $\boldsymbol{\xi}(t)$, $d\mathbf{m}(t)/dt = \langle \mathbf{u}[\mathbf{x}(t), t] \rangle_\xi$. Since $\mathbf{u}(\mathbf{x}, t)$ is Gaussian, we assume that $\mathbf{m}(t)$ is Gaussian as well. It is then completely defined by its mean $\langle \mathbf{m}(t) \rangle = \overline{\mathbf{u}} t$ and variance

$$\kappa^c_{ij}(t) = \langle [m_i(t) - \langle m_i(t) \rangle][m_j(t) - \langle m_j(t) \rangle] \rangle. \qquad (17)$$

The centroid PDF then takes the form

$$p_m(\boldsymbol{\mu}; t) = \frac{\exp\left[-\frac{1}{2}(\boldsymbol{\mu} - \overline{\mathbf{u}}t) \cdot \boldsymbol{\kappa}^c(t)^{-1}(\boldsymbol{\mu} - \overline{\mathbf{u}}t)\right]}{\sqrt{(2\pi)^d \det[\boldsymbol{\kappa}^c(t)]}}. \qquad (18)$$

To test the assumption that the centroid PDF is Gaussian, we conducted Monte Carlo simulations (MCS) of dispersion in a Gaussian random velocity field $\mathbf{u}(\mathbf{x})$. The results of 10^4 realizations of $\mathbf{u}(\mathbf{x})$ were used to compute the PDF of $\mathbf{m}(t)$, its mean $\langle \mathbf{m}(t) \rangle$ and variance $\boldsymbol{\kappa}^c(t)$. Figure 2 compares the centroid PDF obtained via MCS with the Gaussian model (18). This comparison indicates that $\mathbf{m}(t)$ may be modeled as a Gaussian stochastic process for the times and disorder strengths under consideration.

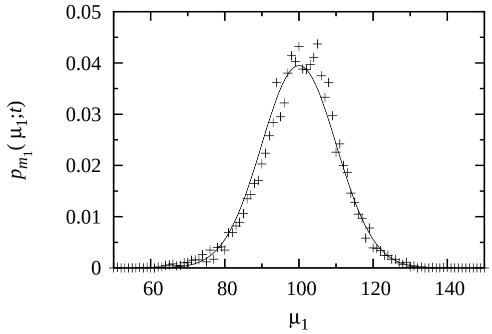

Figure 2. Centroid PDF at time $t = 10^2 \tau_u$ for $\sigma_u^2 = 1$ and $Pe = 10^2$, computed with MCS (+) and the Gaussian model (18).

Concentration PDF: To illustrate the presented mapping approach, we consider the PDF of concentration integrated over the directions transverse to the mean flow and normalized by the maximum concentration,

$$\hat{c}(x_1, t) = \exp\left\{-\frac{[x_1 - m_1(t)]^2}{2\kappa^e_{11}(t)}\right\}, \qquad (19)$$

which varies between 0 and 1. Its PDF is given by $p_{\hat{c}}(\hat{\psi}; x_1, t) = \langle \delta[\hat{\psi} - \hat{c}(x_1, t)] \rangle$. Using (16) to map the centroid PDF (18) onto the concentration PDF we obtain

$$p_{\hat{c}}(\hat{\psi}; x_1, t) = \sqrt{\frac{\alpha_{11}(t)}{\pi}}\, \hat{\psi}^{\alpha_{11}(t)-1} [\ln(1/\hat{\psi})]^{-1/2} \times \cosh\left[\sqrt{2\alpha_{11}(t)\ln(1/\hat{\psi})}\, \frac{x_1 - \overline{u}t}{\sqrt{\kappa^c_{11}(t)}}\right] \exp\left[-\frac{(x_1 - \overline{u}t)^2}{2\kappa^c_{11}(t)}\right], \qquad (20)$$

with $\alpha_{11}(t) = \kappa^e_{11}(t)/\kappa^c_{11}(t)$. Thus, $p_{\hat{c}}(\hat{\psi}; x_1, t)$ is completely parametrized by the centroid variance $\kappa^c_{11}(t)$ and the effective spatial width $\kappa^e_{11}(t)$ of $c(\mathbf{x}, t)$.

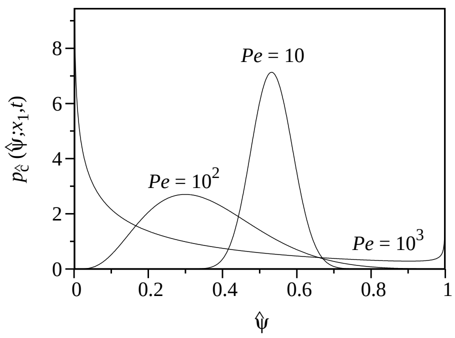

Figure 3. Concentration PDFs at $x_1 = 10^3 l$ and $t = 1025\, \tau_u$, for $\sigma_u^2 = 10^{-1}$ and different Péclet numbers.

We evaluate this expression for transport in a steady three-dimensional divergence-free random velocity field $\mathbf{u}(\mathbf{x})$. For $\sigma_u^2 < 1$, the effective width $\kappa_{11}^e(t)$ and the centroid variance $\kappa_{11}^c(t)$ can be obtained through a first-order perturbation expansion in σ_u^2 as [e.g., *Dentz et al.*, 2000]

$$\kappa_{11}^e(t) = \sigma_{uu}^2 \overline{u} l \sqrt{2\pi}\, t - \kappa_{11}^c(t). \tag{21}$$

$$\kappa_{11}^c(t) = \sigma_{uu}^2 \overline{u} l \sqrt{\pi/8}\, \tau_D \ln\left(1 + 4t/\tau_D\right). \tag{22}$$

Alternatively, one can obtain these observables either by measurements or MCS.

Figure 3 illustrates the impact of dispersion on the concentration PDF. As Pe increases, i.e., as the dispersion coefficient decreases, $p_{\hat{c}}(\hat{\psi}; x_1, t)$ becomes broader. In other words, increasing dispersion decreases concentration uncertainty. In the limit as $Pe \to \infty$ ($\alpha_{11} \to 0$) the PDF in (20) reduces to a sum of two delta-functions peaked at $\hat{\psi} = 0$ and 1. Typically, the impact of dispersion on the concentration PDF is modeled in terms of closures such as the IEM model. Here we derived a mapping approach to obtain the concentration PDF taking explicitly into account mixing due to dispersion and spatial disorder.

In summary we derived an explicit map between the scalar PDF and the distribution of the random velocity field as quantified in terms of the joint PDF of the (random) centroid and (random) spatial variance of the passive scalar. The explicit analytical expressions for the scalar PDF shed new light on the role of dispersion in the evolution of the concentration PDF.

Acknowledgments. This research was partially supported by the DOE Office of Science Advanced Scientific Computing Research (ASCR) program in Applied Mathematical Sciences, and by the Office of Science (BER), Cooperative Agreement No. DE-FC02-07ER64324. MD acknowledges the financial support of project 200930I188 of the Spanish National Research Council (CSIC) and the EU funded project MUSTANG (Grant Agreement 227286).

Notes

1. Numerical simulations correspond to isotropic three-dimensional divergence-free steady Gaussian random velocity fields $\mathbf{u}(\mathbf{x})$ with $\ell_u = \ell_D = l$; all theoretical derivations remain valid for anisotropic velocity fields.

References

Bellin, A., and D. Tonina (2007), Probability density function of non-reactive solute concentration in heterogeneous porous formations, *J. Contam. Hydrol.*, *94*, 109–125.

Bronski, J. C., and R. M. McLaughlin (2000), Rigorous estimates of the tails of the probability distribution function for the random linear shear model, *J. Stat. Phys.*, *98*(3), 897–915, doi: 10.1023/A:1018639928526.

Caroni, E., and V. Fiorotto (2005), Analysis of concentration as sampled in natural aquifers, *Transp. Porous Media*, *59*(1), 19–45.

Chen, H. D., S. Y. Chen, and R. H. Kraichnan (1989), Probability distribution of a stochastically advected scalar field, *Phys. Rev. Lett.*, *63*(24), 2657–2660.

Cirpka, O. A., R. L. Schwede, J. Luo, and M. Dentz (2008), Concentration statistics for mixing-controlled reactive transport in random heterogeneous media, *J. Contam. Hydrol.*, *98*(1-2), 61–74.

Dentz, M., and D. M. Tartakovsky (2008), Self-consistent four-point closure for transport in steady random flows, *Phys. Rev. E*, *77*(6), 066307, doi:10.1103/PhysRevE.77.066307.

Dentz, M., H. Kinzelbach, S. Attinger, and W. Kinzelbach (2000), Temporal behavior of a solute cloud in a heterogeneous porous medium, 1, point-like injection, *Water Resour. Res.*, *36*(12), 3591–3604.

Dopazo, C., and E. E. O'Brien (1974), An approach to the autoignition of a turbulent mixtures, *Acta Astronaut.*, *1*, 1239–1266.

Fedotov, S., M. Ihme, and H. Pitsch (2005), Stochastic mixing model with power law decay of variance, *Phys. Rev. E*, *71*(1), 016310, doi:10.1103/PhysRevE.71.016310.

Fiori, A., and G. Dagan (2000), Concentration fluctuations in aquifer transport: a rigorous first-order solution and applications, *J. of Cont. Hydrol.*, *45*(1-2), 139–163.

Fox, R. O., and P. K. Yeung (2003), Improved Lagrangian mixing models for passive scalars in isotropic turbulence, *Phys. Fluids*, *15*, 961–985.

Girimaji, S. S. (1991), Assumed β-pdf model for turbulent mixing: validation and extension to multiple scalar mixing, *Combust. Sci. Technol.*, *78*, 177–196.

Graham, W., and D. McLaughlin (1989), Stochastic analysis of nonstationary subsurface solute transport,1, Unconditional moments, *Water Resour. Res*, *25*, 215–232.

Indelman, P. V., and M. I. Shvidler (1985), Averaging of stochastic evolution equations of transport in porous media, *Fluid Dyn.*, *20*(5), 775–784.

Jaekel, U., and H. Vereecken (1997), Renormalization group analysis of macrodispersion in a directed random flow, *Water Resour. Res.*, *33*(10), 2287–2299.

Kapoor, V., and L. W. Gelhar (1994), Transport in three-dimensionally heterogeneous aquifers: 1. dynamics of concentration fluctuations, *Water Resour. Res.*, *30*, 1775–1788.

Kapoor, V., and P. K. Kitanidis (1998), Concentration fluctuations and dilution in aquifers, *Water Resour. Res.*, *34*, 1181–1193.

Kitanidis, P. K. (1988), Prediction by the method of moments of transport in heterogeneous formations, *J. Hydrol.*, *102*, 453–473.

Koch, D. L., and E. S. G. Shaqfeh (1992), Averaged equation and diagrammatic approximations to the average concentration of a tracer dispersed by a Gaussian random velocity field, *Phys. Fluids A*, *4*, 887–894.

Meyer, D. W., H. A. Tchelepi, and P. Jenny (2010), A joint velocity-concentration pdf method for tracer dispersion in heterogeneous porous media, *Water Resour. Res.*, in press.

Pope, S. B. (2000), *Turbulent Flows*, Cambridge Univ. Press, Cambridge, UK.

Tartakovsky, D. M. (2007), Probabilistic risk analysis in subsurface hydrology, *Geophys. Res. Lett.*, *34*, L05404, doi: 10.1029/2007GL029245.

Tartakovsky, D. M., M. Dentz, and P. C. Lichtner (2009), Probability density functions for advective-reactive transport in porous media with uncertain reaction rates, *Water Resour. Res.*, *45*, W07414, doi:10.1029/2008WR007383.

Valiño, L., and C. Dopazo (1991), A binomial Langevin model for turbulent mixing, *Phys. Fluids*, *3*, 3034–3037.

Villermaux, E., and J. Duplat (2006), Coarse grained scale of turbulent mixtures, *Phys. Rev. Lett.*, *97*, 144,506.

Villermaux, J., and J. C. Devillon (1972), Représentation de la coalescence et de la redispersion des domaines de ségrégation dans un fluide par un modèle d'interaction phénoménologique, in *Proc. of 2nd International Symposium Chem. React. Engng.*, Elsevier, New York.

Zhang, Q. (1995), Transient behavior of mixing induced by a random velocity field, *Water Resour. Res.*, *31*, 2955–2963.