

# Diffusion in random velocity fields with applications to contaminant transport in groundwater

Nicolae Suciu<sup>a,b</sup>,

<sup>a</sup>*Tiberiu Popoviciu Institute of Numerical Analysis, Romanian Academy, P.O. Box 68, 400110 Cluj-Napoca, Romania.*

<sup>b</sup>*Department of Mathematics, Friedrich-Alexander University of Erlangen-Nuremberg, Cauerstr. 11, 91058 Erlangen, Germany.*

---

## Abstract

The process of diffusion in a random velocity field is the mathematical object underlying currently used stochastic models of transport in groundwater. The essential difference from the normal diffusion is given by the nontrivial correlation of the increments of the process which induces transitory or persistent dependence on initial conditions. Intimately related to these memory effects is the ergodicity issue in subsurface hydrology. These two topics are discussed here from the perspectives of Itô and Fokker-Planck complementary descriptions and of recent Monte Carlo studies. The latter used a global random walk algorithm, stable and free of numerical diffusion. Beyond Monte Carlo simulations, this algorithm and the mathematical frame of the diffusion in random fields allow efficient solutions to evolution equations for the probability density of the random concentration.

**Keywords:** Groundwater, Transport processes, Ergodicity, Random fields, Random walk, PDF methods

---

## 1. Introduction

Stochastic modeling became a leading paradigm in studies of complex systems since several decades. Random media, random environments, or random fields are central topics for thousands of research papers in physics, technology, geophysics, and life sciences. For instance, a search for the topic “random media” in Web of Science (seen online in January 2014) returns 4110 results and 2073 average citations per year in the last two decades, with a strong increasing trend. A similar dynamics (3197 results with 1345 average citations per year) shows for the same period the topic “groundwater contamination”, which is one of the investigation directions where the “randomness” paradigm is intensively used.

Mathematical models of transport in random environments (e.g. continuous diffusion processes with random coefficients or random walks with random jump probabilities [11]) are often used for phenomena which are not reproducible experimentally under macroscopically identical conditions or in cases where the incomplete knowledge of the physical parameters precludes deterministic descriptions. To the first class belongs the turbulence, characterized by an intrinsic

---

*Email addresses:* [suciu@math.fau.de](mailto:suciu@math.fau.de) (Nicolae Suciu), [suciu@math.fau.de](mailto:suciu@math.fau.de) (Nicolae Suciu), [suciu@math.fau.de](mailto:suciu@math.fau.de) (Nicolae Suciu), [suciu@math.fau.de](mailto:suciu@math.fau.de) (Nicolae Suciu)

randomness, which is modeled by random velocity fluctuations [109, 78, 49, 47]. In plasma physics the turbulent state of the system of charged particles is described by random electric potentials and magnetic fields [7, 6]. Transport in groundwater belongs to the second class. The way randomness enters modeling in hydrogeology is through stochastic parameterizations of incompletely known hydraulic conductivity fields which induce random Darcy velocity fields [44, 25].

A common feature of transport processes in random environments is the apparent increase of the diffusion coefficients with the scale of observation. In hydrogeology, the increase from Darcy scale, to laboratory, and to field scale of the diffusion coefficients inferred from measurements through different approaches (by fitting concentrations with solutions of advection-diffusion equations, by computing spatial moments of tracer concentrations, or by analysis of concentration series recorded at different travel distances from the source) has been called “scale effect” [42, 17, 18]. Similar scale dependence characterizes the so called “running diffusion coefficient” in plasma physics [5] and the “turbulent diffusivity” in turbulence [109, 79].

Another characteristic of transport in random media is the presence of various memory effects associated with the departure of the transport process from a genuine Gaussian diffusion. Memory effects manifested by non-Markovian evolution were explicitly associated with the stochastic nature of the environment in plasma physics [6]. In the frame of stochastic subsurface hydrology, the departure from Fickian, linear-time behavior of the second moment of the solute plume may be interpreted as a memory effect [88, 104]. This type of memory effects is usually associated with Markovian diffusion processes and are omnipresent in stochastic models of transport in groundwater. The prototype memory-free process is the Wiener process with independent increments. Therefore, a direct quantification of such memory effects is provided by correlations of increments of the transport process [92].

The groundwater is contained in aquifer systems consisting of spatially heterogeneous hydrogeological formations. The scarcity of direct measurements of their hydraulic conductivity is compensated by spatial interpolations and empirical correlations, further modeled as space random fields [14]. The groundwater flow caused by piezometric pressure gradients is usually modeled by Darcy law for the filtration velocity in porous media and the randomness of the hydraulic conductivity induces the randomness of the flow velocity [25]. Contaminant solutes are transported by advection, diluted by diffusion and hydrodynamic dispersion, and undergo various chemical reactions. Under simplifying assumptions, also supported by experiments, the hydrodynamic dispersion is approximated as a Gaussian diffusion [84] and summing up the molecular diffusion at the pore-scale one arrives at a local scale diffusive model with diffusive flux governed by Fick’s law [8]. Hence, the primary mechanism responsible for the fate of contaminants in groundwater can be described as a diffusion in random velocity fields.

Concentrations and transition probability densities of the diffusion in given realizations of the random velocity field are governed by parabolic partial differential equations local in time and space. However, in case of statistically non-homogeneous fields, theoretical investigations [71] and numerical simulations [72] show that the evolution of the ensemble average concentration is non-Fickian and has to be described by integro-differential equations non-local in both time and space. Non-locality also may occur in modeling the local dispersion. For instance, following the Mori-Zwanzig memory function formalism of the equilibrium statistical mechanics [120, 22, 19], Cushman and Ginn derived space-time nonlocal models for diffusion in porous media with hydraulic parameters displaying fractal character [20, 21]. A model non-local in time but local in space is the “continuous time random walk” process, with uncorrelated polydisperse features consisting of a random walk with waiting times uniformly sampled from a probability distribu-

tion [46], which has been proposed by Berkowitz and Scher [9, 10] to describe the behavior of the ensemble mean concentration. A comparative study of such non-local models is presented in a review paper by Neuman and Tartakovsky [73]. Since non-local and non-Fickian behavior may arise from either normal or anomalous local scale diffusion models, it is difficult to extract information on the true nature of the stochastic transport process from experiments and diffusion in random velocity fields remains competitive with respect to the other models analyzed in [73]. Moreover, if the hydraulic conductivity and the velocity field may be characterized by power-law correlations, the model of diffusion in random fields naturally leads to anomalous diffusive behavior of the transport process [39, 92]. Estimates of the prediction errors [71, 73] and ergodicity assessments [34, 95] also can be obtained by comparing results for fixed realizations of the random field, corresponding to the observed transport process, to their ensemble averages. Last but not the least, the model of diffusion in random velocity fields facilitates the development of methods similar to those used in turbulence studies for the probability density function (PDF) of the random concentration [83, 68].

The process of diffusion in a single realization of the velocity field, is presented in Section 2 below. The spatial variability of the velocity field is found to be the source of both scale effects and memory effects induced by position-velocity correlations, specific to solute transport in groundwater. The relationship between memory effects and the ergodicity issue for the usual setup of passive transport in hydrogeology (Section 3), investigated numerically through Monte Carlo simulations based on the global random walk (GRW) algorithm, is analyzed in Section 4. The findings are consistent with theoretical results on statistical homogeneity properties and ergodicity, derived within the same passive transport setup in Section 5.

The GRW algorithm consists of an arbitrarily large superposition of weak Euler schemes for the Itô equation and is therefore accurate, stable, and free of numerical diffusion (Section 6). Coupling this algorithm with finite element solutions to the flow equations results in considerable speedup over the classical finite element solution to both flow and transport equations. The GRW algorithm is also a key tool in solving evolution equations for the probability density function (PDF) of the random concentrations in reactive transport. PDF evolution equations are derived from models for the local mixing and upscaled processes of diffusion in random fields. The feasibility of the GRW-PDF approach is illustrated in Section 7 for the one-dimensional transport of the cross-section space average concentration in saturated aquifers. Some conclusions and future prospects are presented in Section 8.

## 2. Diffusion with space-variable drift

### 2.1. Fokker-Planck equation

Scale and memory effects are already present in case of diffusion processes with deterministic coefficients if the drift coefficients vary in space.

The density of the transition probability  $g(\mathbf{x}, t \mid \mathbf{x}_0, t_0)$  of a real diffusion process  $\{X_i(t), t \geq 0, X_i \in \mathbb{R}, i = 1, 2, 3\}$  with drift coefficients  $V_i$  and diffusion coefficients  $D_{ij}$  is the solution of the Cauchy problem for the Fokker-Planck equation

$$\frac{\partial g}{\partial t} + \frac{\partial}{\partial x_i}(V_i g) = \frac{\partial^2}{\partial x_i \partial x_j}(D_{ij} g) \quad (2.1)$$

with the initial condition  $g(\mathbf{x}, t_0 \mid \mathbf{x}_0, t_0) = \delta(\mathbf{x} - \mathbf{x}_0)$ . Here and in the rest of the paper summation over repeated indices is implied.

The transition probability  $g$  governs the evolution of the concentration,

$$c(\mathbf{x}, t) = \int g(\mathbf{x}, t \mid \mathbf{x}_0, t_0) c(\mathbf{x}_0, t_0) d\mathbf{x}_0, \quad (2.2)$$

where  $c(\mathbf{x}_0, t_0)$  is the initial concentration. If  $c(\mathbf{x}_0, t_0)$  is normalized to unity, so is  $c(\mathbf{x}, t)$ , and both can be interpreted as one-point probability densities.

By virtue of (2.2), the concentration  $c(\mathbf{x}, t)$  verifies the equation (2.1) with the initial condition  $c(\mathbf{x}, t_0) = c(\mathbf{x}_0, t_0)$ . The equivalence with the concentration balance equation based on Fick's law of diffusion,

$$\frac{\partial c}{\partial t} + \frac{\partial}{\partial x_i} (V_i^* c) = \frac{\partial}{\partial x_i} (D_{ij} \frac{\partial c}{\partial x_j}), \quad (2.3)$$

is established by the relation  $V_i^* = V_i - \partial D_{ij} / \partial x_j$  between velocity components  $V_i^*$  and drift coefficients  $V_i$  [43].

A diffusion process satisfies uniformly in  $\mathbf{x}$  and  $t$ , for all  $\epsilon > 0$  [31, 59],

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}' - \mathbf{x}| \geq \epsilon} g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0, \quad (2.4)$$

$$V_i(\mathbf{x}, t) = \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}' - \mathbf{x}| < \epsilon} (x'_i - x_i) g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}', \quad (2.5)$$

$$D_{ij}(\mathbf{x}, t) = \frac{1}{2} \lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}' - \mathbf{x}| < \epsilon} (x'_i - x_i)(x'_j - x_j) g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}'. \quad (2.6)$$

Condition (2.4) prevents instantaneous jumps and ensures the almost sure continuity of the sample paths  $X(t)$ , (2.5) defines the drift coefficients, and (2.6) the diffusion coefficients [59, 43].

In applications to transport in groundwater, the class of diffusion processes is restricted by imposing conditions for finite first and second spatial moments of  $g$  at finite times [57, 104]:

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}' - \mathbf{x}| \geq \epsilon} x'_i g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0, \quad (2.7)$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{|\mathbf{x}' - \mathbf{x}| \geq \epsilon} x'_i x'_j g(\mathbf{x}', t + \Delta t \mid \mathbf{x}, t) d\mathbf{x}' = 0. \quad (2.8)$$

With (2.7-2.8), the integrals in (2.5-2.6) extend over the entire  $\mathbb{R}^3$ . In fact, the local averages, over spheres of radius  $\epsilon$ , are used in (2.4-2.6) to avoid the hypothesis that the first two moments exist [31, p. 276]. However, the latter is always true when the drift coefficients are samples of random velocity fields with finite-range correlations, as well as for samples of fractional Gaussian noise velocity fields, the two situations considered in the following.

The conditions (2.7) and (2.8) are fulfilled, for instance, by the one-dimensional Gaussian diffusion with affine mean and linear variance,

$$\begin{aligned} \mu(t) &= \int x c(x, t) dx = x_0 + V(t - t_0), \\ s(t) &= \int [x - \mu(t)]^2 c(x, t) dx = 2D(t - t_0), \end{aligned}$$

constant drift and diffusion coefficients,  $V = d\mu(t)/dt$ ,  $D = \frac{1}{2}ds(t)/dt$ , and transition probability density invariant to spatial translations,

$$g(x, t | x_0, t_0) = (4\pi Dt)^{-1/2} \exp\left(-(x - x_0 - V(t - t_0))^2/4D(t - t_0)\right). \quad (2.9)$$

## 2.2. Dispersion and memory terms

For diffusion processes with variable coefficients, the linear time behavior of the first two moments no longer holds. General relations between moments and coefficients were recently derived in [104, Appendix A]. For a general diffusion process satisfying (2.4-2.6) and the conditions for finite moments (2.7-2.8), the components of the first moment,  $\mu_i$ , and of the covariance,  $s_{ij}$ ,  $i, j = 1, 2, 3$ , are given by:

$$\mu_i(t, t_0) = \int x_i c(\mathbf{x}, t) d\mathbf{x} = \mu_i(t_0) + \int_{t_0}^t \overline{V}_i(t') dt', \quad (2.10)$$

$$\begin{aligned} s_{ij}(t, t_0) &= \int (x_i - \mu_i(t))(x_j - \mu_j(t)) c(\mathbf{x}, t) d\mathbf{x} \\ &= s_{ij}(t_0) + 2 \int_{t_0}^t dt' \int D_{ij}(\mathbf{x}, t') c(\mathbf{x}, t') d\mathbf{x} + s_{u,ij}(t, t_0) + m_{ij}(t, t_0), \end{aligned} \quad (2.11)$$

$$\begin{aligned} s_{u,ij}(t, t_0) &= \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \int c(\mathbf{x}_0, t_0) d\mathbf{x}_0 \int \int (u_i(\mathbf{x}', t'') u_j(\mathbf{x}, t') \\ &+ u_j(\mathbf{x}', t'') u_i(\mathbf{x}, t')) g(\mathbf{x}, t' | \mathbf{x}', t'') g(\mathbf{x}', t'' | \mathbf{x}_0, t_0) d\mathbf{x} d\mathbf{x}', \end{aligned} \quad (2.12)$$

$$\begin{aligned} m_{ij}(t, t_0) &= \int_{t_0}^t dt' \int c(\mathbf{x}_0, t_0) d\mathbf{x}_0 \int ((x_{0j} - \mu_j(t_0)) u_i(\mathbf{x}, t') \\ &+ (x_{0i} - \mu_i(t_0)) u_j(\mathbf{x}, t')) g(\mathbf{x}, t' | \mathbf{x}_0, t_0) d\mathbf{x} \end{aligned} \quad (2.13)$$

where  $\overline{V}_i(t) = \int V_i(\mathbf{x}, t) c(\mathbf{x}, t) d\mathbf{x}$  and  $u_i(\mathbf{x}, t) = V_i(\mathbf{x}, t) - \overline{V}_i(t)$ .

According to (2.11), the covariance  $s_{ij}$  is decomposed in “dispersion terms”  $s_{u,ij}$ , positive definite, expressed through correlations of the drift coefficients, (2.12), and “memory terms”, consisting of correlations between drift coefficients and initial positions (2.13), which are no longer positive definite (see [104, Fig. 1]). The decomposition (2.11) can be viewed as an extension of an earlier result of Kitanidis [57]. Comparing [57, Eq. 25] and [104, Eq. A2] one can readily check that the cross correlations position-velocity occurring in the Kitanidis’ relation are precisely the sum between the dispersion terms (2.12) and the memory terms (2.13).

Modeling motions in random environments often requires relations between spatial moments of probability densities and the statistics of the process trajectories (e.g., [65, p. 287]). A systematical derivation of such relations can be achieved by means of suitably defined consistent finite-dimensional probability distributions (A.1) introduced in Appendix A.1. Using them, in Appendix A.2 it is proved that the decomposition (2.11) for the diagonal components of the variance of the process governed by the Fokker-Planck equation (2.1) with a constant diffusion

coefficient  $D$  can be recast in terms of trajectories as follows,

$$\begin{aligned} s_{ii}(t, t_0) &= s_{ii}(t_0) + 2D(t - t_0) \\ &+ 2 \int_{t_0}^t dt' \int_{t_0}^{t'} \langle u_i(\mathbf{X}(t')) u_i(\mathbf{X}(t'')) \rangle_{DX_0} dt'' \\ &+ 2 \int_{t_0}^t \langle [X_i(t_0) - \langle X_i(t_0) \rangle_{DX_0}] u_i(\mathbf{X}(t')) \rangle_{DX_0} dt', \end{aligned} \quad (2.14)$$

where  $\langle \cdot \rangle_{DX_0}$  denotes the average over the realizations of the diffusion process and over the initial positions  $\mathbf{X}_0$  of the trajectories  $\mathbf{X}(t)$ .

For given coefficients  $V_i$  and  $D$  of the Fokker-Planck equation (2.1) it is possible to construct a process satisfying the Itô equation (e.g. [59, p. 144])

$$X_i(t) = X_{0i} + \int_{t_0}^t V_i(\mathbf{X}(t')) dt' + W_i(t - t_0), \quad (2.15)$$

where  $W_i$  is the standard Wiener process of mean  $E(W_i) = 0$  and variance  $E(W_i^2) = 2D(t - t_0)$ . Equation (2.15) describes the diffusion process in a weak sense, that is, only the coefficients are specified but not the Wiener process [59]. If sufficient conditions for the existence of weak solutions to (2.15) are fulfilled, the process has the same probability distribution as the diffusion process governed by the corresponding Fokker-Planck equation. Doob [31, Chap. VI, Sec. 3] also proved the equivalence of Itô and Fokker-Planck representations in a strong sense. That means, under more restrictive conditions, the path-wise unique solutions of the Itô equation are diffusion processes satisfying (2.4-2.6) and, given a diffusion process with transition probability solving the Fokker-planck equation, the associated Itô equation admits path-wise unique solutions [59, Theorems 4.6.1, and 4.7.1].

When the variance of the process (2.15) is computed for a fixed Wiener process (e.g., by Itô formula, as in [99, p. 5]) one obtains, in addition to the terms of (2.14), a term consisting of correlations between the Wiener process and the velocity fluctuations [99, Eq. 27]. This term is canceled, for instance, when a weak solution to (2.15) is constructed by successive approximations with independent Wiener processes in each iteration [99, p. 9]. However, the representation (2.14) holds for either strong or weak solutions to Itô equation if the diffusion process satisfies the supplementary conditions (2.7) and (2.8) and, as proved in Appendix A.2, it is equivalent to the decomposition (2.11) derived within the Fokker-Planck description of the process. The GRW scheme presented in Section 6 below provides numerical approximations for such diffusion processes.

To emphasize the role of the initial conditions, it is useful to rewrite the variance (2.14) as

$$s_{ii}(t, t_0) = s_{ii}(t_0) + \tilde{s}_{ii}(t, t_0) + m_{ii}(t, t_0), \quad (2.16)$$

where the sum of the second and third term of (2.14) is expressed in terms of displacements  $\tilde{X}_i(t) = X_i(t) - X_i(t_0)$ ,

$$\tilde{s}_{ii}(t, t_0) = \langle (\tilde{X}_i(t) - \langle \tilde{X}_i(t) \rangle_{DX_0})^2 \rangle_{DX_0}$$

The term  $\tilde{s}_{ii}$  describes an enhanced dispersion (with respect to the local dispersion  $2D(t - t_0)$  in (2.14)), which explains the scale effect in modeling subsurface transport processes (e.g. [42]). The last term in (2.16),

$$m_{ii}(t, t_0) = 2 \langle (X_i(t_0) - \langle X_i(t_0) \rangle_{DX_0})(\tilde{X}_i(t) - \langle \tilde{X}_i(t) \rangle_{DX_0}) \rangle_{DX_0}, \quad (2.17)$$

quantifies the memory effects.

### 2.3. Memory effects and transition probabilities

Similarly to (2.16), for any three successive times,  $t_1 < t_2 < t_3$ , the variances of the increments of the process are related by

$$\widetilde{s}_{ii}(t_1, t_3) = \widetilde{s}_{ii}(t_1, t_2) + \widetilde{s}_{ii}(t_2, t_3) + m_{ii}(t_1, t_2, t_3), \quad (2.18)$$

where

$$\begin{aligned} \widetilde{s}_{ii}(t_3, t_1) &= \text{var}\{X_i(t_3) - X_i(t_1)\}, \\ \widetilde{s}_{ii}(t_1, t_2) &= \text{var}\{X_i(t_2) - X_i(t_1)\}, \\ \widetilde{s}_{ii}(t_2, t_2) &= \text{var}\{X_i(t_3) - X_i(t_2)\}, \\ m_{ii}(t_1, t_2, t_3) &= 2\text{cov}\{(X_i(t_2) - X_i(t_1)), (X_i(t_3) - X_i(t_2))\}, \end{aligned}$$

$\text{var}\{\cdot\}$  denotes the variance, and  $\text{cov}\{\cdot\}$  the covariance. In fact, (2.18) is the general binomial rule saying that the variance of the sum of two random variables is the sum of variances plus two times their covariance (e.g., [77, p.213]) and as such it is valid for any stochastic process  $X(t)$ . The relation (2.16) above is retrieved for the increments of the process (2.15) with the expectation  $E\{\cdot\}$  defined as in Appendix A.1 by  $\langle \cdot \rangle_{Dx_0}$ .

The condition of vanishing memory terms,  $m_{ii}(t_1, t_2, t_3) = 0$ , leads to

$$E\{(X_i(t_2) - X_i(t_1))(X_i(t_3) - X_i(t_2))\} = E\{X_i(t_2) - X_i(t_1)\}E\{X_i(t_3) - X_i(t_2)\},$$

which expresses the uncorrelatedness of the increments of the process. As follows from (2.18), vanishing memory terms is equivalent with the additivity of the variance of the increments  $\widetilde{s}_{ii}$  with respect to nonoverlapping time intervals [92, p. 5]. In the particular case of diffusion with constant coefficients the increments are uncorrelated,  $m_{ii}(t_1, t_2, t_3) = 0$ , and (2.18) expresses the linearity of the variance  $\widetilde{s}_{ii}(t_m, t_n) = 2D(t_n - t_m)$ ,  $t_n > t_m$ . It is also easy to see that the uncorrelatedness of the increments is a consequence of the translation invariance of the transition probability density (2.9). Moreover, it has been shown that the only Itô-diffusion process with space-homogeneous transition probabilities are Gaussian diffusion processes with constant drift and diffusion coefficients [1].

In general, according to Theorem II.3.2 of Doob [31, p. 74], for any real process with  $E\{|X(t)|^2\} < \infty$  and uncorrelated increments there exists a wide sense version of  $X(t)$  (i.e. with the same first two moments) which is a Gaussian process with independent increments [31, p. 100]. By the definition of the statistical independence, this process has space-homogeneous transition probabilities. Since the converse is clearly true, i.e. processes with homogeneous transition probabilities have uncorrelated increments, we have the following corollary [92, p. 5]:

*If the memory terms of a real process with finite first and second moments vanish for arbitrary successive time increments, then, the transport process is a wide-sense version of a Gaussian processes with spatially homogeneous transition probabilities.*

Thus, memory-free processes have homogeneous transition probabilities. Inhomogeneous transition probabilities as memory effects were also identified in case of rare and extreme events (where the memory-free limit corresponds to independent identically distributed variables) and for non-Markovian processes (generalized Langevin equation, diffusion equations with memory, or fractional diffusion) [92]. It is worth noting that the memory effects quantified by (2.17) are not necessarily an indication of non-Markovian behavior of the processes. They characterize all Itô processes such as (2.15), which are Markovian processes [59, Chap. 4], as far as their increments are correlated.

### 3. Diffusion in random fields model of passive transport in aquifers

Models of transport in highly heterogeneous media such as atmosphere, plasmas, industrial devices, or groundwater are based on stochastic partial differential equations of parabolic type [3, 4, 11, 65, 5, 16, 45, 2]. In case of transport in saturated aquifers, essential features of the transport, such as the scale dependence, may be described by the simple advection-diffusion equation without sources and with constant diffusion coefficients (e.g., [25, 57, 28, 34]),

$$\partial_t c + \mathbf{V} \cdot \nabla c = D \nabla^2 c, \quad (3.1)$$

where  $c(\mathbf{x}, t)$  is the concentration field,  $D$  is a local dispersion coefficient, and  $\mathbf{V}(\mathbf{x})$  is a sample of a random velocity field. The latter is a solution of continuity and Darcy equations

$$\nabla \cdot \mathbf{V} = 0, \quad \mathbf{V} = -K \nabla \psi, \quad (3.2)$$

where  $\psi$  is the piezometric head and  $K$  is the hydraulic conductivity, which is a sample of a space random function. This model reflects the specificity of transport in groundwater, where, unlike in the case of turbulence, the flow is laminar and randomness is introduced by a stochastic parametrization of the flow equations (3.2).

Equation (3.1) is the particular case of the concentration balance equation (2.3) for constant diffusion coefficient  $D$ . Since in this case the velocity components coincide with the drift coefficients, (3.1) is identical to the Fokker-Planck equation. Thus, the concentration  $c(\mathbf{x}, t)$  normalized to unity may be interpreted as the probability density function of the diffusion process described by the Itô equation (2.15).

For a given realization of the velocity field, corresponding to a realization of the hydraulic conductivity, (3.1) describes the diffusion with space variable drift analyzed in Section 2. To model diffusion in random velocity fields, the space of events from Appendix A.2 is enlarged to the Cartesian product  $\Omega = \mathbb{R}^3 \times \Omega_D \times \Omega_V$ , where  $\Omega_V$  is the space of realizations of the random velocity field. Accordingly, the expectation will be formally written as  $\langle \cdot \rangle = \langle \langle \cdot \rangle_D \rangle_{x_0} \rangle_V = \langle \cdot \rangle_{Dx_0V}$ . With these, we define three centered processes of mean zero,  $X_i^{eff}(t)$ ,  $X_i^{ens}(t)$ ,  $X_i^{cm}(t)$ ,  $i = 1, 2, 3$ , so that their variance describes the “effective” and the “ensemble” dispersion,  $S_{ii}(t)$  and  $\Sigma_{ii}(t)$ , and the fluctuations of the center of mass,  $R_{ii}(t)$  [105]:

$$\begin{aligned} X_i^{eff}(t) &= X_i(t) - \langle X_i(t) \rangle_{Dx_0}, & S_{ii}(t) &= \langle (X_i^{eff}(t))^2 \rangle \\ X_i^{ens}(t) &= X_i(t) - \langle X_i(t) \rangle_{Dx_0V}, & \Sigma_{ii}(t) &= \langle (X_i^{ens}(t))^2 \rangle \\ X_i^{cm}(t) &= \langle X_i(t) \rangle_{Dx_0} - \langle X_i(t) \rangle_{Dx_0V}, & R_{ii}(t) &= \langle (X_i^{cm}(t))^2 \rangle \end{aligned} \quad (3.3)$$

Using the relations between spatial moments of probability densities and trajectories’ statistics presented in Appendix A, it can easily be seen that the variances  $S_{ii}(t)$ ,  $\Sigma_{ii}(t)$ , and  $R_{ii}(t)$  of the three processes defined in (3.3) correspond respectively to the expectation (average over velocity realizations) of the second spatial moment of the single-realization concentration  $c(\mathbf{x}, t)$ , to the second moment of the ensemble average concentration  $\langle c(\mathbf{x}, t) \rangle_V$ , and to the variance of the first spatial moment of  $c(\mathbf{x}, t)$ . These quantities are related by

$$S_{ii} = \Sigma_{ii} - R_{ii}. \quad (3.4)$$

This identity was used by Le Doussal and Machta [62], in the context of measurements methods for diffusion coefficients, to define “quenched” and “annealed” coefficients,  $S_{ii}/(2t)$  and  $\Sigma_{ii}/(2t)$



respectively. Attinger et al. [2] considered the same quantities to define effective and ensemble dispersion coefficients,  $\frac{1}{2}dS_{ii}/dt$  and  $\frac{1}{2}d\Sigma_{ii}/dt$  respectively. Kitanidis [57] also obtained the identity (3.4) after computing  $S_{ii}(t)$  and  $\Sigma_{ii}(t)$  by averaging an advection-diffusion equation with random coefficients.

If the necessary joint measurability conditions which allow permutations of averages are fulfilled (e.g. [119]) the second moment of the mean concentration can be expressed as (see [100] and, for the case  $D = 0$ , [98])

$$\Sigma_{ii} = S_{ii}(0) + \langle X_{ii} \rangle_{x_0} + M_{ii} + Q_{ii}, \quad (3.5)$$

where where  $S_{ii}(0) = \langle (X_{0i} - \langle X_{0i} \rangle_{x_0})^2 \rangle_{x_0}$ ,  $X_{ii} = \langle (\tilde{X}_i - \langle \tilde{X}_i \rangle_{DV})^2 \rangle_{DV}$  is the “one-particle dispersion” (defined by averaging with respect to  $D$  and  $V$  for a fixed initial position),  $M_{ii} = \langle m_{ii} \rangle_v$  is the ensemble mean of the memory term (2.17), and  $Q_{ii} = \langle (\langle \tilde{X}_i \rangle_{DV} - \langle \tilde{X}_i \rangle_{DX_0V})^2 \rangle_{x_0}$  is the spatial variance of the one-particle center of mass  $\langle \tilde{X}_i \rangle_{DV}$ , computed by averages over  $X_0$ .

As follows from (2.15), the trajectory  $\mathbf{X}(t)$  depends on the Lagrangian velocity field  $V_i(\mathbf{X}(t))$ , which consists of observations at random locations on the trajectory of the random Eulerian velocity (which is defined in a fixed reference frame) [119]. If the Lagrangian field is statistically homogeneous the one-particle center of mass  $\langle \tilde{X}_i \rangle_{DV}$  and dispersion  $X_{ii}$  are independent of  $X_0$ . Then  $M_{ii}$  and  $Q_{ii}$  vanish and from (3.4) and (3.5) one obtains

$$S_{ii} = S_{ii}(0) + X_{ii} - R_{ii}. \quad (3.6)$$

The validity of the Lagrangian homogeneity hypothesis and of the relation (3.6), first derived by Dagan [26], is crucial for the interpretation of the field measurements and for the inference of the upscaled diffusion coefficients.

#### 4. Monte Carlo results

An ideal tracer experiment, consisting of passive transport of substance under different deterministic initial conditions, was simulated numerically with the method presented in Section 6 below. A two-dimensional advection-diffusion problem was solved by simultaneously tracking large collections of computational particles (ten billions in most cases, see e.g. [95, 96, 98, 100, 101]) by a GRW approach equivalent to a superposition of weak Euler schemes for the Itô equation (implementation details are given in [95, Appendix A]).

For a given statistically homogeneous log-normal random hydraulic conductivity  $K$  with exponential correlation and finite correlation length  $\lambda$ , the velocity field was approximated to the first order in the variance of  $\ln K$ . This approximation, obtained by a formal asymptotic expansion of the flow equations (3.2) [45, 25], was computed numerically by the Kraichnan’s approach [61] as sum between a constant mean  $(U, 0)$  and a superposition of random periodic fluctuations (e.g. [96, Eq. 8]). In this way one obtains fast estimations of samples of random velocity fields which permit the computation of thousands of transport simulations at moderate computational costs. For finite numbers of random periodic modes the fluctuations of the estimated dispersion quantities may be affected by an artificial logarithmic increase [35, Appendix A]. As an empirical recipe, the number of modes was chosen to be of the order of the total computation time [35]. The convergence of the Monte Carlo estimates was ensured by using several hundreds of simulations [102, Fig. 4].

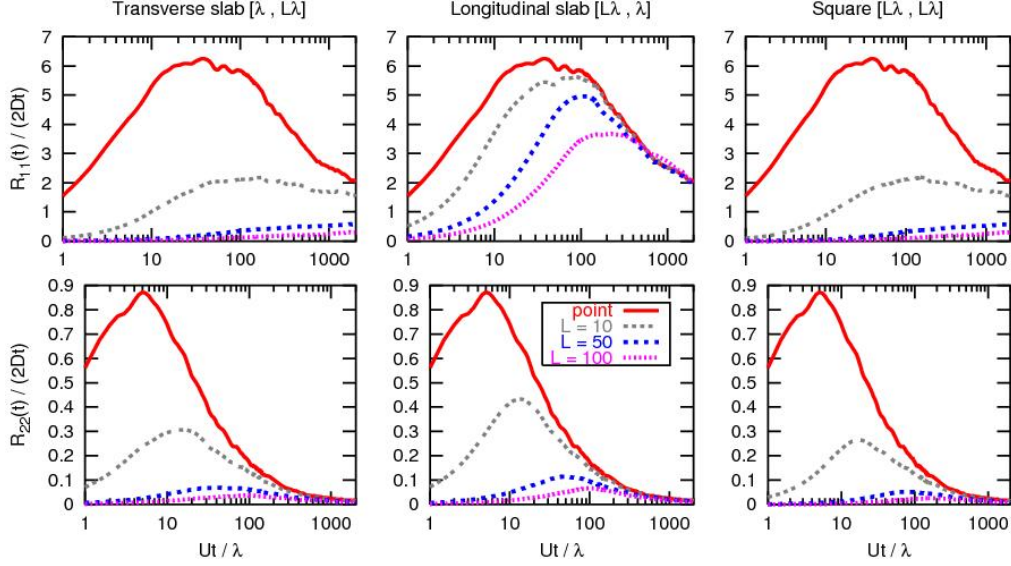


Figure 1: The variance of the center of mass  $R_{ii}/(2Dt)$ ,  $i = 1, 2$ , decreases uniformly with increasing source dimension and goes to zero for large times.

#### 4.1. Ergodic properties of the center of mass process

Figure 1 shows the long-time decay of the variance  $R_{ii}$  of the center of mass process  $X_i^{cm}(t)$ . This implies, according to (3.4), that at large times the expectation of the second moment of the concentration may be approximated by the second moment of the mean concentration,  $S_{ii} \approx \Sigma_{ii}$ . Figure 1 also shows the decrease of  $R_{ii}$  with increasing supports of the initial concentration. One expects therefore that, for sufficiently large contaminant sources, the approximation  $S_{ii} \approx \Sigma_{ii}$  also holds at finite times. Following the terminology introduced by Dagan [26], large plumes, for which the expected second moment can be approximated by the second moment of the ensemble mean concentration, are usually called “ergodic plumes” in the hydrogeological literature. One hypothesizes also that the mean second moment  $S_{ii}$  as well as the un-averaged moment  $s_{ii}$  of an ergodic plume can be approximated, according to (3.6), by the one-particle dispersion  $X_{ii}$  [98, 101].

Another ergodic property was formulated by Sposito et al. [89]. The transport in groundwater is called *asymptotically ergodic* if the solution to (3.1) for a given realization of the velocity field approaches that of the “macrodispersion” model, an upscaled advection-diffusion equation supposed to describe the transport in random velocity fields with finite correlation scales [25]. Various meanings of ergodicity in hydrogeological literature are particular cases of the general formulation proposed in [95]: an observable of the transport process is *ergodic with respect to a stochastic model* if the root mean square distance from the model prediction is smaller than a given threshold. The squared distance can be decomposed as sum between the squared deviation of the ensemble mean of the observable from the reference stochastic model and the variance of the observable about its mean [95, definition 5]. The usual statistical inference for ergodic estimators of the mean [118] is retrieved in this formulation when the observable is an average over the parameter range (time or space) and the stochastic model is the ensemble mean

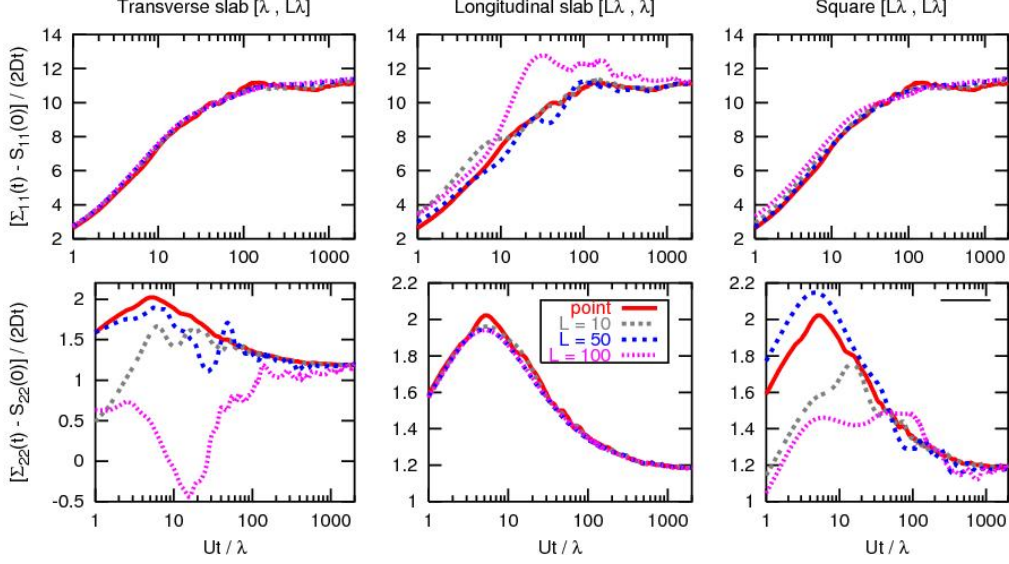


Figure 2: For sources with large dimensions on the  $i$ -direction the ensemble dispersion  $\Sigma_{ii}$  depends on the initial conditions.

of the random function (see also [98]). The *self-averaging property* from statistical physics [11] corresponds to the particular case when the observable is the (un-averaged) process itself and the stochastic model is the ensemble mean of the process. The self-averaging property is thus ensured by a vanishing variance in the long time limit, and, obviously, it is implied by the asymptotic ergodicity.

The decay with time of the variance  $R_{ii}$  indicates the self-averaging of the center of mass process  $X_i^{cm}(t)$ . The self-averaging of the center of mass corresponds to a self-averaging property of the mean Lagrangian velocity  $\langle u_i(\mathbf{X}(t')) \rangle_{DX_0}$  [104, Fig. 2]. The variance of  $(X_i^{cm})^2(t)$  also was found to decrease in time and with increasing source size [100, Fig. 1]. This implies the self-averaging of the quantity  $(X_i^{cm})^2/(2t)$ , which is the single-realization dispersion coefficient of the center of mass [99, Eq. 23]. Since, according to Slutsky's theorem [118] a vanishing variance is a sufficient condition for ergodicity, the self-averaging implies the “usual” ergodicity, that is, the convergence of the time and space averages of the observables  $X_i^{cm}(t)$ ,  $\langle u_i(\mathbf{X}(t')) \rangle_{DX_0}$ , and  $(X_i^{cm})^2/(2t)$ .

#### 4.2. Dependence on initial conditions

The variance of the process  $X_i^{ens}(t)$ , i.e. the second moment  $\Sigma_{ii}$  of the mean concentration, computed for different shapes and sizes of the source is shown in Fig. 2. Significant dependence on initial conditions of the ensemble dispersion corrected for the initial second moment,  $\Sigma_{ii} - S_{ii}(0)$ , manifests in case of asymmetric sources with large extension on the  $i$ -axis while the initial conditions have negligible influence for sources with direction of largest extension perpendicular to the  $i$ -axis. This behavior was attributed to the mean memory terms, which may be significantly large in the first case and negligible in the second case (according to relation (3.5), where the influence of the  $Q_{ii}$  term was found to be negligible, see [104, 100, 98]).

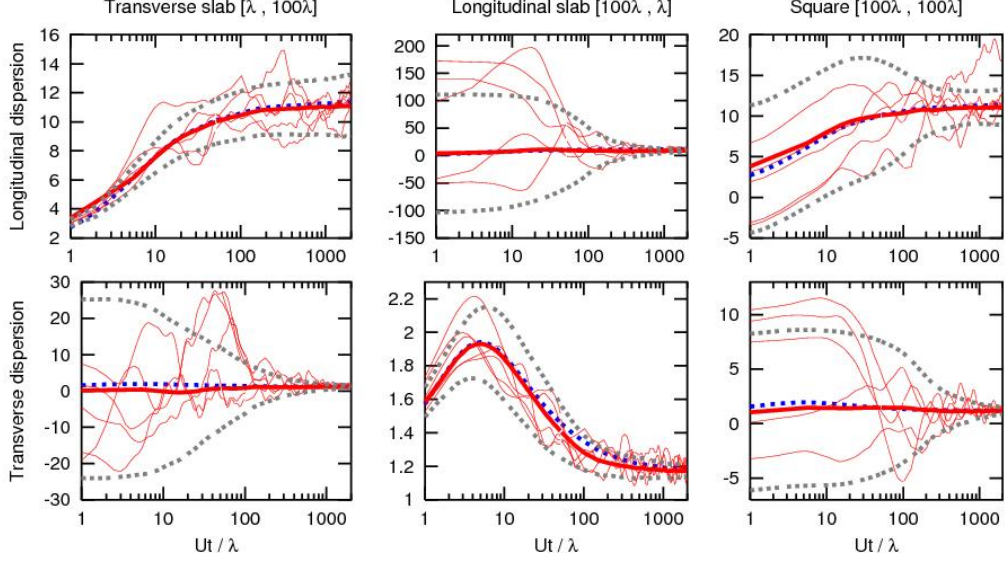


Figure 3: Single-realization dispersion  $(s_{ii} - S_{ii}(0))/(2Dt)$  (thin lines), one-particle dispersion  $X_{ii}/(2Dt)$  (dots), ensemble averages  $(S_{ii} - S_{ii}(0))/(2Dt)$  (solid lines), and  $(S_{ii} - S_{ii}(0) \pm SD(s_{ii}))/ (2Dt)$  (grey dots) [101].

From Fig. 2 we conclude that the second moments of the mean concentration depend on the size, geometry, and orientation of the source. They approximate the one-particle dispersion only in special cases of narrow sources with small extension on  $i$ -th direction and small memory terms (2.17). Otherwise,  $\Sigma_{ii} \neq S_{ii}(0) + X_{ii}$ . This indicates that *the Lagrangian homogeneity, which would imply (3.6), fails even though the velocity field considered in simulations is statistically homogeneous.*

#### 4.3. Non-ergodic effective dispersion at finite times

The variance (2.16) of the effective process  $X_i^{eff}(t)$  computed for fixed realizations of the velocity field shows large sample to sample fluctuations in cases where  $\Sigma_{ii}$  is also strongly influenced by the initial conditions (Fig. 3). The one-particle dispersion  $X_{ii}$  shown in Fig. 3 was approximated by  $\Sigma_{ii} - S_{ii}(0)$  in ergodic situations consisting of large slab sources perpendicular to the  $i$ -axis. The deviation  $S_{ii} - X_{ii}$  of the mean of  $s_{ii}$  from the one-particle dispersion is one to two orders of magnitude smaller than its standard deviation  $SD(s_{ii})$ . These are the two quantities which determine the deviation from ergodic behavior in the general formulation presented in Section 4.1. Thus, the results from Fig. 3 indicate that the single realization dispersion  $s_{ii}$  is in general non-ergodic with respect to the one-particle dispersion  $X_{ii}$  at finite times.

Ergodicity may be expected, within acceptable small root mean square distances, for longitudinal dispersion in case of large transverse slab sources and for transverse dispersion in case of longitudinal slab sources. However, the Monte Carlo results contradict a common belief on ergodic plumes: *large transverse plumes do not necessarily imply the ergodicity of both longitudinal and transverse dispersion.* On the contrary, increasing the plume dimensions might result in dramatic non-ergodic behavior, mainly for the transverse dispersion.

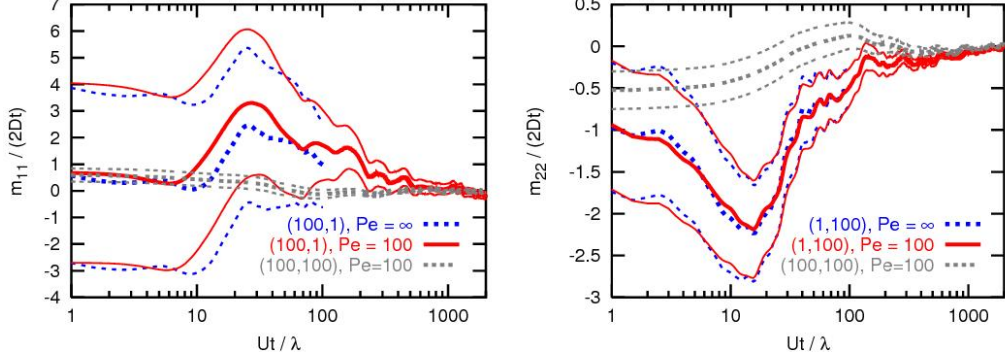


Figure 4: Longitudinal (left) and transverse (right) memory terms in non-ergodic cases, for finite and infinite Peclet numbers. Solid lines correspond to  $M_{ii}$  and thin lines correspond to  $(M_{ii} \pm SD(m_{ii})/R^{1/2})/(2Dt)$ , where  $R = 1024$  is the number of Monte Carlo simulations [99].

#### 4.4. Loss of memory and asymptotic ergodicity

In ergodic cases shown in Fig. 3 (slab sources perpendicular to  $i$ -axis) the relation  $s_{ii} - S_{ii}(0) \approx X_{ii}$  is an acceptable approximation of (2.16). In non-ergodic cases, the memory terms (2.17) are no longer negligible and (2.16) is approximated by  $s_{ii} - S_{ii}(0) \approx X_{ii} + m_{ii}$ , which allows estimations of means and standard deviations of the memory terms  $m_{ii}$  [104]. Since the deviation of the mean  $S_{ii} - S_{ii}(0) - X_{ii}$  is negligible as compared with the standard deviation  $SD(s_{ii})$  (see Fig. 3),  $SD(m_{ii}) \approx SD(s_{ii})$  also quantifies the non-ergodicity of  $s_{ii}$  with respect to  $X_{ii}$  (see definition in Section 4.1).

The Monte Carlo results presented in Fig. 4 show strong memory effects at finite times for asymmetric sources. The memory terms for  $Pe = 100$  are almost identical with those for pure advection ( $Pe = \infty$ ). The mean-square convergence of  $m_{ii}$  to zero indicates the asymptotic ergodicity of the actual dispersion  $s_{ii}$ .

Asymptotic ergodicity, and implicitly self-averaging behavior, is also indicated by Monte Carlo results on means and standard deviations of the cross-section space average concentration at the plume center of mass [95, Figs. 1 and 2].

## 5. Theoretical results

### 5.1. Statistical homogeneity properties

The failure of Lagrangian homogeneity (Section 4.2) means that the mean  $\langle \tilde{X}_i \rangle_{DV}$  and the variance  $X_{ii}$  of the increment  $\tilde{X}_i(t) = X_i(t) - X_i(t_0)$  depend on the deterministic initial position  $X_i(t_0)$ . Since the transition density  $g(\mathbf{x}, t | \mathbf{x}_0, t_0)$  is the probability density of  $\tilde{X}_i$ , the statistical homogeneity of  $\tilde{X}_i$  is equivalent to the invariance to space translations of the ensemble averaged transition density  $\langle g \rangle_V$ .

The usual set-up for statistical homogeneity is as follows. Let  $V(\omega, \mathbf{x}) = \omega(\mathbf{x})$ ,  $\omega \in \Omega$ , be a homogeneous random function defined on the canonical probability space  $(\Omega, \mathcal{A}, P)$ , where  $\mathcal{A}$  is a  $\sigma$ -algebra on  $\Omega$ . Measure-preserving shifts on  $\Omega$  are defined through  $(\tau_{\mathbf{x}_0} \omega)(\mathbf{x}) = \omega(\mathbf{x} + \mathbf{x}_0)$ ,  $P \circ \tau_{\mathbf{x}_0}^{-1} = P$ . A composed function  $F(V)$  is also homogeneous if it depends on  $\omega$  and  $\mathbf{x}_0$  only through measure preserving shifts  $F = F(\tau_{\mathbf{x}_0} \omega)$  [119].



Let us consider the transition density solving (3.1) in a translated reference system,  $\tilde{\mathbf{x}} = \mathbf{x} - \mathbf{x}_0$ ,

$$\frac{\partial g(\tilde{\mathbf{x}}, t \mid \mathbf{0}, t_0)}{\partial t} + \nabla \cdot (\mathbf{V}(\tilde{\mathbf{x}} + \mathbf{x}_0)g(\tilde{\mathbf{x}}, t \mid \mathbf{0}, t_0)) = D\nabla^2 g(\tilde{\mathbf{x}}, t \mid \mathbf{0}, t_0). \quad (5.1)$$

As follows from (5.1),  $g$  depends on velocity statistics only through  $\tau_{\mathbf{x}_0} \omega = \mathbf{V}(\tilde{\mathbf{x}} + \mathbf{x}_0)$ , hence, it is statistically homogeneous if the Eulerian velocity field  $\mathbf{V}(\mathbf{x}, \omega)$  is homogeneous. If, in addition, the solutions of (3.1) are unique in a classical sense, then  $g(\mathbf{x}, t \mid \mathbf{x}_0, t_0, \omega) = g(\mathbf{x} - \mathbf{x}_0, t \mid \mathbf{0}, t_0, \tau_{\mathbf{x}_0} \omega)$  and the measure-preserving property of  $\tau_{\mathbf{x}_0}$  implies the translation invariance of the mean transition density, that is,  $\langle g \rangle_v(\mathbf{x}, t \mid \mathbf{x}_0, t_0) = \langle g \rangle_v(\mathbf{x} - \mathbf{x}_0, t \mid \mathbf{0}, t_0)$ .

According to (2.15), to Fokker-Plank equation (5.1) one associates an Itô equation solving for displacements  $\tilde{X}_i(t) = X_i(t) - x_{0i}$  from the deterministic initial position  $X_i(t_0) = x_{0i}$ ,

$$\tilde{X}_i(t) = \int_0^t V_i(\tilde{\mathbf{X}}(t') + \mathbf{x}_0) dt' + W_i(t). \quad (5.2)$$

If the solutions to (5.2) are pathwise unique, then the displacement field  $\tilde{\mathbf{X}}(t; \mathbf{x}_0, \omega) = \tilde{\mathbf{X}}(t; \mathbf{0}, \tau_{\mathbf{x}_0} \omega)$  is homogeneous [119, Remark 6.7 and Proposition 6.1]. Homogeneity of  $\tilde{\mathbf{X}}(t)$  implies homogeneity of the Lagrangian velocity field,  $V_i^L(\mathbf{x}_0, t) = V_i(\mathbf{X}(t)) = V_i(\tilde{\mathbf{X}}(t) + \mathbf{x}_0)$ , which depends on statistics of  $\tilde{\mathbf{X}}$  through measure-preserving shifts. Conversely, assuming the homogeneity of  $V_i(\mathbf{x}_0, t)$ , (5.2) implies the homogeneity of  $\tilde{\mathbf{X}}$  (see also [92, p. 2]).

We have thus the following result which summarizes the homogeneity properties of the process of diffusion in random velocity fields:

*If (1) the Eulerian velocity field  $\mathbf{V}(\mathbf{x}, \omega)$  is statistically homogeneous and (2) the Fokker-Plank equation (3.1) admits unique classical solutions for (3) deterministic initial conditions, then (a) The mean transition density  $\langle g \rangle_v$  is invariant to spatial translations,  $\langle g \rangle_v(\mathbf{x}, t \mid \mathbf{x}_0, t_0) = \langle g \rangle_v(\mathbf{x} - \mathbf{x}_0, t \mid \mathbf{0}, t_0)$ .*

*If, in addition, (4) the associated Itô equation (2.15) admits pathwise unique solutions, then (b) the following statements are equivalent:*

- (b1) The displacement field  $\tilde{\mathbf{X}} = X_i(t) - x_{0i}$  is statistically homogeneous.*
- (b2) The Lagrangian velocity field  $V_i^L(\mathbf{x}_0, t)$  is statistically homogeneous.*
- (b3) The ensemble mean transition density  $\langle g \rangle_v$  is translation-invariant.*

The statements (b1) and (b2) in can be proved independently, without requiring the existence of a density  $g$  for the transition probability. The first proof of homogeneity property (b2) and of the equality between Lagrangian and Eulerian means was given by Lumley [64] for purely advective transport, under the implicit assumption of analytical velocity realizations. Port and Stone [80] extended this result by considering diffusion in random advection fields and provided a rigorous proof for the equality of the Lagrangian and Eulerian one-point probability distributions under milder conditions, i.e continuity of the first-order spatial derivatives of the velocity samples. Zirbel [119] extended previous homogeneity results to statistical stationarity in case of space-time velocity fields and generalized the results of Port and Stone by replacing the Wiener process by a family of martingales which allow including the diffusion in the random environment.

The results obtained so far do not go beyond the equality of the one-dimensional probability distributions of the Lagrangian and Eulerian velocity fields. Since the higher-order distributions do not coincide, the probability laws of the Lagrangian and Eulerian fields are in general different [119]. The invariance to spatial translations of the mean density  $\langle g \rangle_v$  (statement (a)) is also a one-point statistical property, which implies the homogeneity of  $\langle \tilde{X}_i \rangle_{dv}$  and  $X_{ii}$ , cancels the mean of the memory terms (2.17), and ensures the validity of the expression (3.6) for the second moment.

These homogeneity properties hold true for unique solutions of the transport equations. The irregularity of the velocity samples for the exponentially correlated  $\ln K$  field used in Monte Carlo simulations (see [92, Fig. 1]), which do not ensure the uniqueness of the solutions, may explain the non-vanishing mean memory terms indicated by Fig. 2 and Fig. 4.

Also essential is the assumption of deterministic initial conditions. In case of random initial conditions, the velocity with the spatial argument translated by  $\mathbf{x}_0(\omega)$  in equations (5.1) and (5.2) is not a measure-preserving shift and we are no longer in the frame of the usual homogeneity setup. Since the mean memory terms are time integrals of the Lagrangian velocity covariance [92, Eq. 15], they are non-vanishing as long as the velocity is correlated. This implies that translation-invariance of the mean transition probabilities associated to successive increments of the process may be expected only in case of un-correlated velocity fields or asymptotically in the long time limit, for velocity fields with finite correlation scales. In such cases, by the Corollary formulated in Section 2.3, the transport process is a wide-sense version of a Gaussian diffusion.

### 5.2. First-order approximations

Theoretical investigations in subsurface hydrology are often based on first-order approximations for the variance of the effective, ensemble, and center of mass processes defined in (3.3) [45, 23, 2, 28, 34]. Such approximations are essentially asymptotic expansions truncated at the first order in the variance of the velocity field. Approximations obtained by Eulerian approaches, based on Fourier representations of solutions to partial differential equations similar to (3.1) [45, 2, 28, 15, 34], are in very good agreement with those derived from trajectory equations of type (2.15) [12, 34, 96, 35]. Moreover, if the same conventions in defining Fourier transform are used, the mathematical expressions of the first order approximations obtained by Eulerian and Lagrangian approaches are identical [105, Remark 4.2]. This is just as we would expect from the Itô - Fokker-Planck equivalence (e.g. Appendix A.2). Itô representation is to be preferred here since it renders the computations easier and leads to simpler physical interpretations [92].

In the following, the first-order approximation approach is illustrated for the ensemble process  $X_i^{ens}$ . Approximations for the effective,  $X_i^{eff}$ , and center of mass,  $X_i^{cm}$ , processes can be obtained similarly ([99, Sec. 4]). The Itô process starting from  $\mathbf{x}_0 = \mathbf{0}$ , in non-dimensional form, reads

$$X_i(t) = \delta_{i,1}t + \epsilon \int_0^t u_i(\mathbf{X}(t'))dt' + Pe^{-1/2}W_i(t), \quad (5.3)$$

where  $Pe = U\lambda/D$  is the Péclet number with respect to the correlation length in the mean flow direction  $\lambda = \lambda_{11}$ ,  $U = \langle V_1 \rangle_v$ ,  $u_i = V_i - \delta_{i,1}U$ ,  $\langle u_i \rangle_v = 0$ ,  $\langle u_i^2 \rangle_v = \sigma^2$ , and  $\epsilon = \sigma/U$  are velocity fluctuations. Within the order of magnitude hypothesis  $Pe^{-1/2} = O(\epsilon^\alpha)$ ,  $\alpha > 0$ , the ensemble process  $X_i^{ens}(t) = X_i(t) - \langle X_i(t) \rangle_{DV}$  is described, according to (5.3), by

$$X_i^{ens}(t) = \epsilon \int_0^t u_i(\mathbf{X}(t'))dt' + \epsilon^\alpha W_i(t).$$

The half time derivative of the variance of  $X_i^{ens}$  (see (3.3)), which defines ensemble dispersion coefficients  $D_{ii}^{ens}(t) = \frac{1}{2}d\Sigma_{ii}(t)/dt$  [2, 28], yields a Taylor-Green-Kubo formula [92]:

$$D_{ii}^{ens}(t) = \epsilon^{2\alpha} + \epsilon^2 \int_0^t \langle u_i(\mathbf{X}(t))u_i(\mathbf{X}(t')) \rangle_{DV} dt'. \quad (5.4)$$

The convergence of the integral in (5.4) for  $t \rightarrow \infty$  ensures finite correlation times  $\tau_{ii}$  of the Lagrangian velocity. Finite  $\tau_{ii}$  is a criterion for diffusive limit, formulated for instance by Fanjiang and Komorowski [38]. If this criterion is fulfilled, then the long time limit of (5.4) defines asymptotic dispersion coefficients of the process  $X_i^{ens}$ .

The Kubo relation (5.4) has been derived in [92] in case of homogeneous Lagrangian velocity fields. In absence of Lagrangian homogeneity, (5.4) is still valid if  $u_i(\mathbf{X}(t))$  is replaced by  $v_i(\mathbf{X}(t)) = u_i(\mathbf{X}(t)) - \langle u_i(\mathbf{X}(t)) \rangle_v$ . In the derivation of (5.4), cross-correlations between the Wiener process  $W_i$  and the velocity fluctuations  $v_i$  cancel (see Section 2.2) because the diffusion process fulfils the supplementary conditions (2.7) and (2.8). If we are only interested in a first order of approximation, there is no distinction between the two situations, because the approximated Lagrangian velocity is statistically homogeneous [99, Sec. 4].

A consistent formal asymptotical expansion of the dispersion coefficients (5.4) can be obtained as follows. Consider the asymptotic series of the trajectory (5.3),  $\mathbf{X}(t) = \mathbf{X}^{(0)}(t) + \epsilon \Delta \mathbf{X}(t) + \dots$ , where  $\mathbf{X}^{(0)}(t) = (t, 0, 0)$  is the trajectory of the mean flow, and the formal Taylor expansion of  $u_i$ ,

$$u_i(\mathbf{X}) = u_i(\mathbf{X}^{(0)}) + \epsilon u'_i(\mathbf{X}^{(0)}) \Delta \mathbf{X} + \dots, \quad (5.5)$$

where  $u'_i$  denotes the Fréchet derivative. Then, assuming  $\alpha \geq 1$ , from (5.4) and (5.5) one obtains

$$D_{ii}^{ens} \sim \epsilon^{2\alpha} + \epsilon^2 I_{ii}^{(0)} + \epsilon^4 F(u_i(\mathbf{X}^{(0)}), u'_i(\mathbf{X}^{(0)})) + \dots, \quad (5.6)$$

where  $I_{ii}^{(0)}$  is the integral in (5.4) evaluated on the mean trajectory  $\mathbf{X}^{(0)}(t)$  and  $F$  is a functional of the Lagrangian velocity  $u_i$  and of its Fréchet derivative  $u'_i$ . In the long time limit, the truncation to the first-order in  $\epsilon^2$  yields  $D_{ii}^{ens} \sim \epsilon^{2\alpha} + \epsilon^2 \tau_{ii}^{(0)}$ , where  $\tau_{ii}^{(0)} = \lim_{t \rightarrow \infty} I_{ii}^{(0)}(t)$  are the Lagrangian correlation times. In case of velocity fields with finite correlation range, finite correlation times are ensured by the finiteness of the correlation lengths  $\lambda_{ii}$ . Reverting to dimensional variables, one obtains the asymptotic long time behavior of the approximated dispersion coefficient [92],

$$D_{ii}^{ens} \sim D + \sigma^2 \lambda_{ii} / U. \quad (5.7)$$

Hence, consistent first-order expansions of the dispersion coefficients may be obtained from the first iteration of the Itô equation (5.3) about the reference solution  $\mathbf{X}^{(0)}(t)$  [96, 99]. Formally, this consists of replacing  $u_i(\mathbf{X}(t))$  in (5.4) by  $u_i(t)$  [23].

Assuming Gaussian velocity fluctuations  $u_i(t)$  (corresponding to log-normal hydraulic conductivity of small variance), Dagan [23] derived an advection-dispersion equation for the mean concentration, with constant velocity equal to the mean flow velocity and time-dependent dispersion coefficient given by (5.6) truncated at the first-order in  $\epsilon^2$ . Equations for the mean concentration were also derived from stochastic concentration balance equations by truncated cumulant expansions [90], with approximation errors of the order  $(\sigma \tau_c)^2$  [116, Sect. 12], where  $\tau_c$  is a characteristic time scale on which the randomness of the velocity fluctuations appears as uncorrelated [90, 52], hence of the order of the Lagrangian correlation times  $\tau_{ii}$ . The method, applied initially to passive transport in incompressible, statistically homogeneous random velocity fields, was successively generalized by considering reactive transport in incompressible homogeneous fields [51], passive transport in compressible non-stationary and non-homogeneous time-space random fields [52], and, for the latter case, by adding non-equilibrium sorption [87] and forcing terms [86]. For passive transport in incompressible and statistically homogeneous fields, Dagan's equation is retrieved by sampling velocity fluctuations on the mean flow trajectory [51, 87], similarly to the consistent first-order expansion presented above.



Rigorous proofs of existence for upscaled processes with constant coefficients similar to (5.7) (limit theorems) can be found in a series of papers by Kesten, Papanicolaou, Fannjiang, Komorowski [56, 38, 60], among others.

The first iteration of the Itô equation about the process of diffusion taking place in the mean flow field,  $\mathbf{Z}^{(0)}(t) = \mathbf{X}^{(0)}(t) + \epsilon^\alpha \mathbf{W}(t)$  leads to

$$D_{ii}^{ens}(t) = D + \int_0^t dt' \int \int \langle u_i(\mathbf{x}) u_i(\mathbf{x}') \rangle_{DV} p(\mathbf{x}, t; \mathbf{x}', t') d\mathbf{x} d\mathbf{x}'. \quad (5.8)$$

where  $p(\mathbf{x}, t; \mathbf{x}', t')$  is the Gaussian joint probability density of the diffusion process  $\mathbf{Z}^{(0)}(t)$  (see [92, Eq. 11] and [99, Eq. 34]). This approximation is an inconsistent asymptotic expansion, because it mixes the orders of magnitude, by including the contribution  $\epsilon^\alpha$  in the zero-th order  $\mathbf{Z}^{(0)}$ . However, (5.8) leads to the same asymptotic behavior (5.7) as the consistent expansion [96, Fig. 2]. In addition, the inconsistent approximation, unlike the consistent one, accounts for enhanced diffusion (i.e. scale effect) in single realizations of the velocity field [96]. Eulerian perturbation methods [28] and Lagrangian approaches [24] yield the same explicit expressions for both ensemble and effective dispersion coefficients [105, Remark 7]. Moreover, Sposito and Barry have shown that Dagan's expression of the ensemble coefficients [24] is equivalent to that obtained by the method of cumulant expansion [90]. Such approximations also allow the computation of the dispersion coefficients in case of power-law correlated velocity fields as linear combinations of scale-dependent coefficients for diffusion in velocity fields with short-range correlations [105, Eq. 42].

### 5.3. Anomalous diffusion, ergodicity, and self-averaging

Anomalous diffusion behavior is commonly characterized by the time dependence of the variance. If it grows like  $t^\alpha$  with  $\alpha < 1$ ,  $\alpha = 1$ , or  $\alpha > 1$  one considers that the process is subdiffusive, diffusive, or superdiffusive, respectively. There are however cases where this classification scheme might be misleading, as for instance the apparently diffusive behavior with  $\alpha = 1$  resulted from the competition between subdiffusion and Lévi flights [33]. To overcome such situations, O'Malley and Cushman proposed a renormalization-group classification of diffusive processes, which generalizes the notion of self-similarity [75, 76]. The new scheme performs better in case of processes with infinite variance and/or non-stationary increments and yields the same classification as the variance scheme for processes with stationary increments, as those considered in the following. Another special case is that of the process made up of the sum of a subdiffusion and a normal diffusion, with linear long time behavior of the variance, which is, however, not a normal diffusion because of the indefinite persistence of the memory terms [92]. Though it cannot classify different types of diffusive behavior, the criterion of vanishing memory terms allows unambiguous identification of normal diffusion processes (see Section 2.3).

The ergodicity of the center of mass process  $X_i^{cm}(t)$  (shown, for instance in Fig. 1) has been associated with that of the space-random fields with finite correlation range and with the normal diffusive behavior of the process at large times [26]. In the more general case of space-time random fields, arguments have been put forward that temporally ergodic flows satisfy the diffusion limit criterion of convergent integral in (5.4) and that the violation of this criterion may lead to anomalous diffusion [38]. For time-independent fields and small velocity fluctuations, some relations between the ergodicity of the random fields, the ergodicity of the dispersion coefficients, and the type of diffusive behavior are readily available in the frame of the consistent first-order approximation.

Consider first velocity fields with short-range correlations. In such cases the integral range is finite and the space-random velocity is necessarily ergodic [14]. Typical examples are exponential and Gaussian short-range correlations, for which, according to Section 5.2, the first-order approximation of the Lagrangian correlation behaves like  $\text{cov}_{\mathbf{u}}(t) \sim e^{-t}$  and  $\text{cov}_{\mathbf{u}}(t) \sim e^{-t^2}$ , respectively. The corresponding correlation times  $\tau_{ii}$  are finite and define constant dispersion coefficients, given by (5.6) truncated at the order  $\epsilon^2$ .

An ergodic estimator in the first-order of approximation of the dispersion coefficient for the “reduced” process  $Y_i = X_i^{\text{ens}} - W_i$  can be obtained by replacing in (5.4) the Lagrangian covariance  $\text{cov}_{\mathbf{u}}(t - t') = \langle u_i(t)u_i(t') \rangle_v$  by a time average of the product  $u_i(t)u_i(t')$ ,

$$D_{Y,ii}^*(t) = \int_0^t dt' \frac{1}{T-t} \int_0^{T-t'} u_i(t+s)u_i(t'+s)ds = \int_0^t \text{cov}_{\mathbf{u}}^T(t, t') dt'. \quad (5.9)$$

Since to the first-order the velocity fields are Gaussian of mean zero (e.g., [45, 26]), the forth moments are completely determined by the correlation function (e.g., [118, equation (3.29)]). The limit, in the mean square sense,  $\langle [\text{cov}_{\mathbf{u}}^T(t, t') - \text{cov}_{\mathbf{u}}(t - t')]^2 \rangle_v \rightarrow 0$  as  $T \rightarrow \infty$  exists if and only if the condition of Slutsky’s theorem for ergodic variance is fulfilled [118, p. 234], i.e.

$$\frac{1}{T} \int_0^T (\text{cov}_{\mathbf{u}}(s))^2 ds \xrightarrow{T \rightarrow \infty} 0. \quad (5.10)$$

The validity of (5.10) for short-range correlation fields implies the mean square convergence of the estimator  $D_{Y,ii}^*$  towards the ensemble coefficient  $D_{Y,ii}^{\text{ens}}$ .

Power-law velocity correlations also may occur in hydrological modeling if the analysis of the field data shows a dependence on the observation scale of the log-hydraulic conductivity. A discussion on this topic and explicit relations of the longitudinal dispersion coefficients for two important classes of long-range correlated  $\ln K$  fields, namely fractional Gaussian noise and fractional Brownian motion correlation types, can be found in [39].

Consider in the following *fractional Gaussian noise* velocities with power-law correlations  $\text{cov}_{\mathbf{u}}(t) \sim t^{-\beta}$ ,  $0 < \beta < 2$ . According to (5.4), the variance of the process  $Y_i$  behaves like  $\Sigma_{ii} = \langle Y_i^2 \rangle \sim t^{2-\beta}$ . If  $\beta \neq 1$ ,  $Y_i$  is a *fractional Brownian motion* with *Hurst exponent*  $H = 1 - \beta/2$ ,  $0 < H < 1$ ,  $H \neq 1/2$  (*superdiffusion* if  $0 < \beta < 1$  and *subdiffusion* if  $1 < \beta < 2$ ). If  $\beta = 1$  (the case of “ $1/x$ ” noise), then  $\Sigma_{ii} \sim t \ln t - t$ . In all these cases of anomalous diffusion, the increments of the process are correlated and the memory terms  $M_{ii} \sim t^{2-\beta}$  persist indefinitely [92].

For the case of fractional Brownian motion, Deng and Barkai [27] proved the ergodicity of the variance by a direct analytical computation of the variance of its ergodic estimator. Since the condition (5.10) holds for all  $\beta > 0$ , the ergodicity of  $\Sigma_{ii}$  and  $D_{ii}^{\text{ens}}$  is also a corollary of Slutsky’s theorem.

Summarizing, we have the following result: *Ensemble dispersion coefficients for diffusion in velocity fields with short-range correlations as well as in fractional Gaussian noise random fields with correlations  $\text{cov}_{\mathbf{u}} \sim t^{-\beta}$ ,  $0 < \beta < 2$ , are ergodic within the precision of the consistent first-order approximation.*

The normal diffusion is retrieved as a particular case of fractional Brownian motion, together with the super- and subdiffusive cases, if one considers correlations of fractional Gaussian noise of the form  $\text{cov}_{\mathbf{u}} \sim c_1(1 - \beta)t^{-\beta} + c_2 t^{1-\beta} \delta(t)$ , where  $t = t_1 - t_2$ ,  $t_1 > t_2 > 0$  (see e.g. [50]). With Hurst exponent defined as above by  $H = 1 - \beta/2$ , normal diffusion corresponds to  $\beta = 1$  and  $H = 1/2$ .

It is worth noting that anomalous diffusion is generated, through (5.4), by the power-law correlation of the Lagrangian velocity without necessarily requiring a power-law correlation of the Eulerian velocity field. This is illustrated by the famous model of Matheron and de Marsily [67] where the interplay between the local dispersion and the longitudinal Eulerian velocity with finite correlation length along the transverse direction produces a Lagrangian velocity with longitudinal correlation scaling as  $\sim t^{-1/2}$  [67, 12]. This results in superdiffusive behavior with Hurst exponent  $H = 3/4$  in two-dimensions [92]. The same model also shows subdiffusive behavior in three-dimensions, and a  $\sim t \ln t - t$  behavior when extended to higher dimensions [66].

To check whether the variance of the process  $Y_i = X_i^{ens} - W_i$  is also *self-averaging*, consider the single-trajectory quantity

$$\Sigma_{ii}^*(t) = 2 \int_0^t (t - \tau) d\tau \left( \frac{1}{t - \tau} \int_0^{t-\tau} u_i(s) u_i(s + \tau) ds \right).$$

The expression in the brackets is an ergodic estimator of the velocity covariance  $\text{cov}_{\mathbf{u}}(t)$ . If this estimator is accurate enough at finite times, then

$$\Sigma_{ii}^*(t) = 2 \int_0^t d\tau \int_0^{t-\tau} u_i(s) u_i(s + \tau) ds \approx 2 \int_0^t (t - \tau) \text{cov}_{\mathbf{u}}(\tau) d\tau. \quad (5.11)$$

Since the right hand side of the approximate equality in (5.11) is the Taylor's formula valid for a stationary ensemble variance  $\Sigma_{ii}$  [70, equation (9.30')],  $\Sigma_{ii}^*$  is a self-averaging estimator of  $\Sigma_{ii}$ . The self-averaging property (5.11) has been demonstrated numerically and used to estimate ensemble dispersion coefficients  $D_{ii}^{ens} \approx \Sigma_{ii}^*/(2t)$  on a single trajectory of *diffusion in short-range correlated velocity fields* [102]. Such self-averaging estimates are useful as input parameters in models for the evolution of the probability density of the random concentration [108] (see also Section 7).

First-order consistent approximations of effective dispersion coefficients  $S_{ii}/(2t)$  are computed according to (3.4) by subtracting from the ensemble coefficients the coefficients of the center of mass  $R_{ii}/(2t)$  evaluated by spatial integrals of two-particle velocity covariances over the support of the initial plume [26, 99]. For singular point-like sources,  $\Sigma_{ii} - 2Dt = R_{ii}$  and the consistent first-order effective coefficient equals the local dispersion coefficient  $D$  [96]. Useful first-order approximations for point sources can be obtained in an Eulerian frame by computing small perturbations around the process of diffusion in the constant mean velocity field [2, 28]. Even though a recent study, considering two-dimensional transport in velocity fields with short-range correlations and point sources, reports non-vanishing variance of the longitudinal effective coefficients in the long time limit [30, Fig. 1], direct numerical estimations, using ensembles of single-realization effective coefficients computed by the same perturbation approach [34], clearly show the decay of the variance at large times [96, Fig. 3]. This self-averaging property, demonstrated numerically for both two- and three-dimensional cases [35], is also consistent with the results on asymptotic ergodicity presented in Section 4.4. On the other side, in case of anomalous diffusion with  $H = 3/4$ , generated by the model of Matheron and de Marsily, the sample-to-sample fluctuations calculated analytically do not converge to zero and the longitudinal effective dispersion coefficient is not self-averaging [15, Fig. 4].

## 6. Global random walk

### 6.1. Global random walk algorithm

The GRW algorithm used in the Monte Carlo simulations presented in Section 4 solves diffusion problems by moving large collections of computational particles on regular lattices. Instead of moving particles sequentially, GRW redistributes all particles from a lattice site, through advective displacements and diffusion jumps, in a single numerical procedure. GRW can thus be thought as a superposition of weak solutions to Itô equation projected on the lattice: instead of computing individual trajectories, it approximates the evolution of the probability distribution of the Itô diffusion by that of the number of particles at lattice sites [110].

In a one-dimensional GRW algorithm, the number of particles  $n$  at lattice sites  $i$  and successive time steps  $k$  and  $k + 1$  is given by the relations

$$n(j, k) = \delta n(j + v_j, j, k) + \delta n(j + v_j - d, j, k) + \delta n(j + v_j + d, j, k), \quad (6.1)$$

$$n(i, k + 1) = \delta n(i, i, k) + \sum_{j \neq i} \delta n(i, j, k), \quad (6.2)$$

where  $v_j = [V_j \delta t / \delta x]$  are discrete displacements due to advection by the local velocity field, computed as the integer part  $[\cdot]$  of the non-dimensional velocity,  $\delta t$  and  $\delta x$  are the time and the space steps,  $j + v_j$  are new positions after advective displacements, and  $d$  are natural numbers describing discrete diffusive jumps  $d\delta x$ . The number of particles undergoing diffusion jumps,  $\delta n(j + v_j \pm d, j, k)$ , and the number of particles waiting at  $j + v_j$  over the  $k$ -time step,  $\delta n(j + v_j, j, k)$ , are binomial random variables. The space and time steps,  $\delta x$  and  $\delta t$ , are related to the diffusion coefficient  $D$  through

$$D = r \frac{(d\delta x)^2}{2\delta t}, \quad (6.3)$$

where  $r$  is a rational number,  $0 \leq r \leq 1$ .

The relation (6.3) is the Kolmogorov's definition of the diffusion coefficient (2.6) projected on the lattice, where the parameter  $r$  plays the role of the transition probability. Indeed, according to (6.1), the trajectory of each particle is governed by

$$\hat{X}_{k+1} = \hat{X}_k + v\delta x + \xi, \quad (6.4)$$

where  $\hat{X}_k = j\delta x$ ,  $v = v_j$ , and the discrete process  $\xi$  is an *unbiased random walk* with amplitude  $|\xi| = d\delta x$  and transition probabilities

$$P\{\xi = \pm \sqrt{2D\delta t}\} = \frac{r}{2}, \quad P\{\xi = 0\} = 1 - r. \quad (6.5)$$

In Appendix B.1 it is proved that the GRW algorithm (6.1-6.3) fulfills the requirements for an exact decomposition of the spatial second moment of the concentration as sum of dispersion and memory terms (see Section 2.2). As shown by (6.3) and (B.2), the algorithm is *free of numerical diffusion* by construction. The main source of errors is the truncation of the advective displacement from the last term in (B.1). A priori error estimates are not available for the GRW algorithm. However, a posteriori error estimates obtained by comparisons with a biased-GRW (see Section 6.3), indicate the decrease of the truncation errors with refining the lattice [94].

The resolution of the velocity field in GRW simulations is controlled by the parameter  $p = U\delta t / \delta x$ , where  $U$  is the mean velocity [93]. An empirical recipe to reduce the truncation errors

in case of variable velocity is to chose a value of the mean Courant number  $U\delta t/d\delta x = p/d$  smaller than one [107].

As shown in [Appendix B.2](#), for a constant drift  $V$  the GRW algorithm is strictly equivalent to a superposition of weak Euler schemes, with convergence order  $O(\delta t^2)$ , which approximates the one-point probability density of the Itô process by the particle density at lattice sites.

The mean of the binomial random variables  $\delta n(j + v_j \pm d, j, k)$  with parameters  $n(j, k)$  and  $r/2$  (see (6.5)), i.e. the mean number of unbiased right/left jumps from the lattice site  $j$  at time  $t$ , equals  $\frac{1}{2}rn(j, k)$  [77, p. 156]. Taking the mean over an ensemble of GRW runs (denoted in the following by an overline) and using (6.1) one obtains

$$\overline{\delta n(j + v_j \pm d, j, k)} = \frac{1}{2}r \overline{n(j, k)}, \quad \overline{\delta n(j, j + v_j, k)} = (1 - r) \overline{n(j, k)}. \quad (6.6)$$

In case of constant  $D$  and  $V = 0$ , according to (6.1-6.2), the evolution of the mean number of particles is described by an explicit finite difference scheme for the diffusion equation  $\partial_t c = D\partial_x^2 c$ ,

$$\overline{n(i, k + 1)} = \frac{r}{2}\overline{n(i + d, k)} + (1 - r)\overline{n(i, k)} + \frac{r}{2}\overline{n(i - d, k)}. \quad (6.7)$$

The continuous solution can be approximated by  $c(x_i, t_k) = \overline{n(i, k)}/\delta x$  [110]. In weak formulations,  $c(x_i, t_k)$  is usually approximated by a sum of Dirac measures [63, 37]. Since the initial value problem is well-posed (as consequence of conservation of the number of particles) and the scheme (6.7) is stable ( $r \leq 1$  fulfils the von Neumann's criterion), it is also convergent, according to Lax-Richtmyer Equivalence Theorem [91]. The convergence order is  $O(\delta t)$  in time and  $O(\delta x^2)$  in space.

## 6.2. Implementation and numerical convergence

The exact GRW algorithm is implemented by extracting the random variables  $\delta n(j + v_j \pm d, j, k)$  from the cumulative binomial distribution function (see [110, pp. 532-533]). Several other implementations were also proposed in [110], for instance, the “deterministic GRW”, where one gives up the particle indivisibility and  $n$  are arbitrary positive real numbers evolving according to (6.7), approximations of the binomial distributions by *erf*-functions for large  $n$ , or the reduced fluctuations GRW algorithm. The latter proved its efficiency in large scale simulations of transport in groundwater [96, 100].

In the reduced fluctuations GRW, the number of left jumps is given by

$$\delta n(j + v_j - d, j, k) = \begin{cases} n/2 & \text{if } n \text{ is even} \\ [n/2] + \theta & \text{if } n \text{ is odd,} \end{cases} \quad (6.8)$$

where  $n = n(j, k) - \delta n(j + v_j, j, k)$ ,  $[n/2]$  is the integer part of  $n/2$ , and  $\theta$  is a random variable taking the values 0 and 1 with probability 1/2. The number of right jumps is given by the difference  $n - \delta n(j + v_j - d, j, k)$ .

In practice, (6.8) is implemented by summing up reminders of division by 2 and multiplication by  $r$  of  $n(j, k)$  and by assigning a particle to the lattice site where the sum of reminders reaches the unity. In this way, one avoids the need to use random number generators [107].

The GRW solution to the initial value problem for a Gaussian diffusion is illustrated in Fig. 5. By increasing the number of particles the un-averaged GRW solution approaches the solution of the finite difference scheme (6.7). It was found that the GRW algorithm is *self-averaging*, in the sense that if the total number of particles  $N$  is large enough, no ensemble averaging over GRW

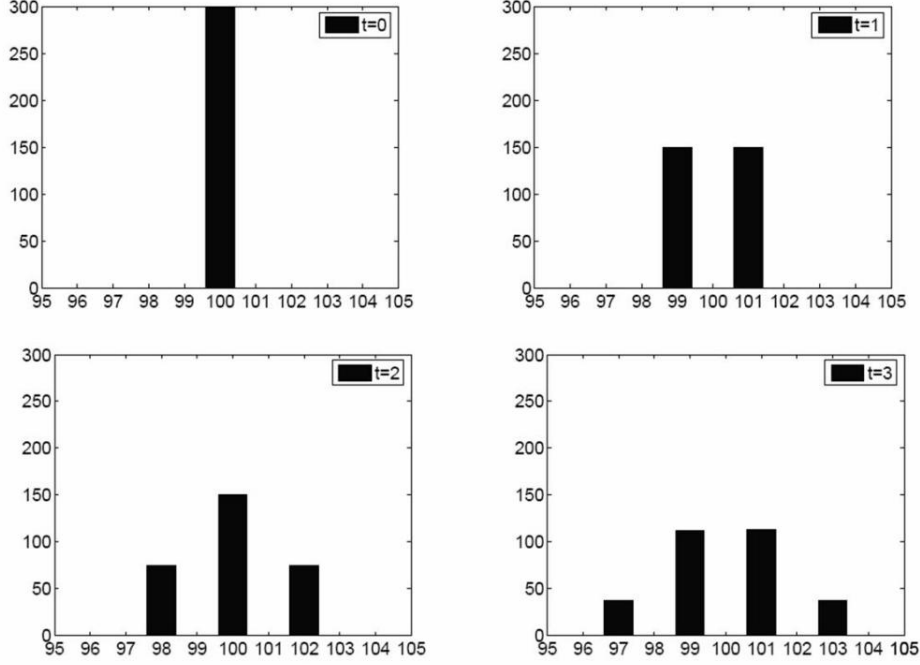


Figure 5: Distribution of  $N = 300$  particles starting from  $x = 100$  after the first three GRW time steps for  $D = 1$  and fixed parameters  $r = 1$  and  $d = 1$ .

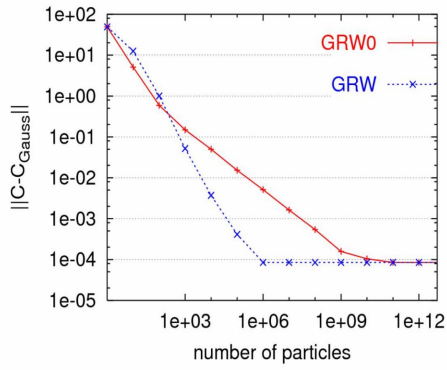


Figure 6: Convergence with the number of particles of the exact GRW algorithm (GRW0) and of the reduced fluctuations algorithm (GRW), for a one-dimensional Gaussian diffusion problem.

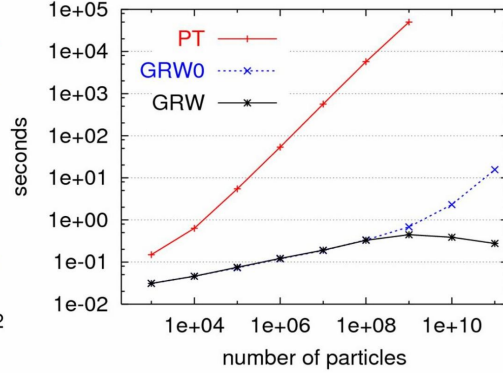


Figure 7: Comparison of CPU times for simulations carried out with GRW, GRW0, and PT of a three-dimensional Gaussian diffusion problem over ten dimensionless time steps.

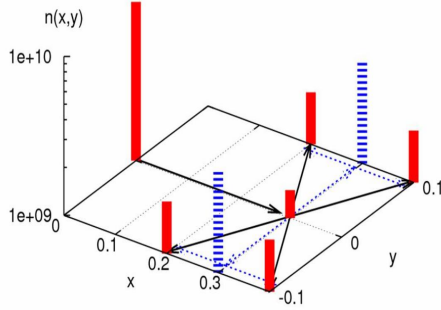


Figure 8: Two-dimensional GRW for constant diffusion coefficient, built as a superposition of two one-dimensional GRW procedures.

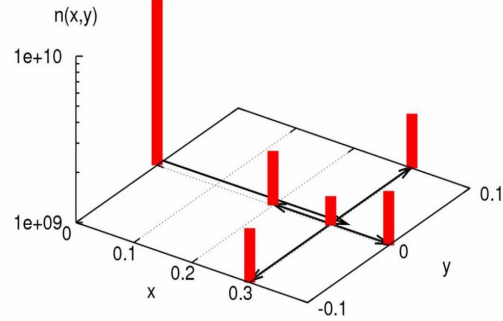


Figure 9: Two-dimensional GRW for variable diffusion coefficients, based on two independent random walks on  $x$ - and  $y$ -directions (right).

runs is necessary to obtain smooth solutions [110, Fig. 5]. Thus, the GRW solution converges like  $O(\delta x^2) + O(1/\sqrt{N})$ . The decay with  $N$  of the error norm is a bit faster in case of reduced fluctuations GRW (Fig. 6). The number of particles required for self-averaging increases with the simulation time and with the dimension of the spatial domain. In case of large scale simulations in groundwater it was found to be  $N \sim 10^{10}$  [93].

Compared with sequential particle tracking procedures (PT), usually consisting of ensembles of strong solutions to Itô equation, GRW has the advantage of providing smooth solutions by using huge numbers of particles, at low computational costs. This is shown by a comparison of CPU time used to solve the same problem given in Fig. 7. While for PT the CPU time increases linearly with  $N$  and requires increasing numbers of processors (up to 256 for  $N = 10^9$  on a Cray T3E parallel computer), the computing time increases significantly only for  $N > 10^8$  in case of exact GRW algorithm (GRW0) and is practically constant in case of reduced fluctuations GRW.

Two- and three-dimensional GRW algorithms are designed by repeating the one-dimensional procedure for each spatial direction, in case of constant diffusion coefficients (Fig. 8), or by using independent random walks, in case of variable diffusion coefficients (Fig. 9). In the latter case, a two-dimensional GRW is constructed with space-time variable  $r_x$  and  $r_y$ ,  $r_x + r_y \leq 1$ . For given  $d_x, d_y, \delta x$  and  $\delta y$ , the time step is chosen to satisfy

$$\delta t \leq \left( \frac{2D_x^{\max}}{(d_x \delta x)^2} + \frac{2D_y^{\max}}{(d_y \delta y)^2} \right)^{-1}.$$

where  $D_x^{\max} = \max\{D_x(x, y, t)\}$  and  $D_y^{\max} = \max\{D_y(x, y, t)\}$ . This implementation yields accurate solutions even if the diffusion coefficients are highly variable and random (for instance, in simulations of diffusion in human skin, modeled as a three-layer two-dimensional model with Gaussian distributed diffusion coefficients [103]).

### 6.3. Biased-GRW algorithm

If the velocity and the diffusion coefficients vary in space, overshooting errors may occur when the particles jump over more than one lattice site (see Fig. 10). This is mainly the case of diffusion in space-variable velocity fields, when velocity values at sites lying between the initial



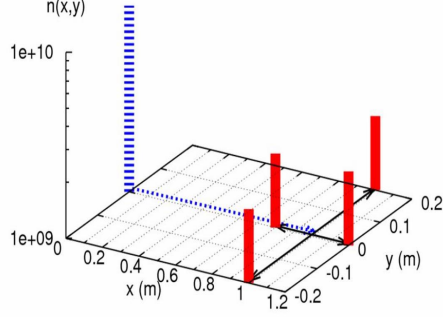


Figure 10: The state of the unbiased GRW at  $t = \delta t = 0.5$ .

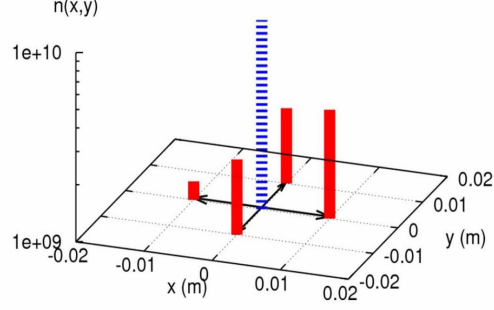


Figure 11: BGRW state at  $t = \delta t = 0.0025$ , for the same problem as in Fig. 10.

and final position of the group of particles during the advection step may have sharp variations. Overshooting can be avoided if advection is simulated by a bias in the random walk probability and only jumps to the nearest sites are allowed, as shown in Fig. 11. This results in a biased global random walk (BGRW) algorithm [94]. Since BGRW moves all the particles lying at a lattice site in a single numerical procedure,  $N$  can be as large as necessary to ensure the self-averaging, which is the main difference with respect to the biased-random walks on lattices which move particles sequentially [55, 36]).

The two-dimensional BGRW is defined by the relation

$$\begin{aligned} n(i, j, k) &= \delta n(i, j | i, j, k) \\ &+ \delta n(i + 1, j | i, j, k) + \delta n(i - 1, j | i, j, k) \\ &+ \delta n(i, j + 1 | i, j, k) + \delta n(i, j - 1 | i, j, k), \end{aligned} \quad (6.9)$$

where  $n(i, j, k)$  is the number of particles at the site  $(x, y) = (i\delta x, j\delta y)$  at the time  $t = k\delta t$  and the  $\delta n$  are binomial random variables describing the number of particles waiting at the initial lattice site or jumping to the first-neighbor sites. To the drift and diffusion coefficients of the transport problem,  $V_x(x, y, t)$ ,  $V_y(x, y, t)$ ,  $D_x(x, y, t)$  and  $D_y(x, y, t)$ , one associates dimensionless parameters

$$v_x = V_x \frac{\delta t}{\delta x}, \quad v_y = V_y \frac{\delta t}{\delta y}, \quad r_x = D_x \frac{2\delta t}{\delta x^2}, \quad r_y = D_y \frac{2\delta t}{\delta y^2}. \quad (6.10)$$

Instead of (6.6), the average over BGRW runs of the terms in (6.9) are now related by

$$\begin{aligned} \overline{\delta n(i, j | i, j, k)} &= (1 - r_x - r_y) \overline{n(i, j, k)}, \\ \overline{\delta n(i \pm 1, j | i, j, k)} &= \frac{1}{2}(r_x \pm v_x) \overline{n(i, j, k)}, \\ \overline{\delta n(i, j \pm 1 | i, j, k)} &= \frac{1}{2}(r_y \pm v_y) \overline{n(i, j, k)}. \end{aligned} \quad (6.11)$$

The reduced fluctuations BGRW is implemented similarly to (6.8). As shown in Appendix B.3, the BGRW algorithm fulfils the requirements (2.4)-(2.8) and, unlike the unbiased GRW, it is free of round-off errors in the representation of the drift coefficients.



Defining the particle density  $\rho(x, y, t) = \bar{n}(i, j, k)$ , summing up the contributions coming from the first neighbors to a lattice site, and using (6.9-6.11) one obtains

$$\begin{aligned} & \frac{\rho(x, y, t + \delta t) - \rho(x, y, t)}{\delta t} + \\ & \frac{(V_x \rho)(x + \delta x, y, t) - (V_x \rho)(x - \delta x, y, t)}{2\delta x} + \\ & \frac{(V_y \rho)(x, y + \delta y, t) - (V_y \rho)(x, y - \delta y, t)}{2\delta y} = \\ & \frac{(D_x \rho)(x + \delta x, y, t) - 2(D_x \rho)(x, y, t) + (D_x \rho)(x - \delta x, y, t)}{\delta x^2} + \\ & \frac{(D_y \rho)(x, y + \delta y, t) - 2(D_y \rho)(x, y, t) + (D_y \rho)(x, y - \delta y, t)}{\delta y^2}. \end{aligned} \quad (6.12)$$

The relation (6.12) is the forward-time centered-space finite difference scheme for the Fokker-Planck equation

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(V_x \rho) + \frac{\partial}{\partial y}(V_y \rho) = \frac{\partial^2}{\partial x^2}(D_x \rho) + \frac{\partial^2}{\partial y^2}(D_y \rho). \quad (6.13)$$

As follows from (6.11), the BGRW algorithm is subject to the following restrictions

$$r_x + r_y \leq 1, \quad |v_x| \leq r_x, \quad |v_y| \leq r_y. \quad (6.14)$$

By the last two inequalities in (6.14), the Courant numbers  $V_x \delta t / \delta x$  and  $V_y \delta t / \delta y$  are sub-unity, which ensures that the BGRW algorithm is free of overshooting errors. If, in addition, one imposes the conditions  $r_x \leq 0.5$  and  $r_y \leq 0.5$ , the von Neumann's criterion for stability is also satisfied. Thus, the convergence of the scheme (6.12) is implied by the Lax-Richtmyer Equivalence Theorem [91].

*Under the conditions stated above, the numerical solutions of the BGRW algorithm (6.9-6.11) converge with the order  $O(\delta x^2)$  to the solutions of the Fokker-Planck equation (6.13) for initial value problems.*

As shown by (6.12), the BGRW algorithm is equivalent to a finite difference scheme even if the velocity field is a space-time function, unlike in case of unbiased GRW, for which the equivalence holds only for constant velocity. Instead, since advection is accounted for by biased jump probabilities, BGRW is no longer equivalent to an Euler scheme for the Itô equation.

The advection-diffusion equation which corresponds to Fick's law,

$$\frac{\partial \rho}{\partial t} + \frac{\partial}{\partial x}(V_x^* \rho) + \frac{\partial}{\partial y}(V_y^* \rho) = \frac{\partial}{\partial x}(D_x \frac{\partial \rho}{\partial x}) + \frac{\partial}{\partial y}(D_y \frac{\partial \rho}{\partial y}),$$

is equivalent to the Fokker-Planck equation (6.13) if the drift coefficients are defined by  $V_x = V_x^* + \partial D_x / \partial x$  and  $V_y = V_y^* + \partial D_y / \partial y$  (see (2.3)).

The BGRW algorithm is highly accurate but more expensive than the unbiased GRW, because of the restriction of sub-unity Courant numbers in (6.14). Therefore, BGRW was mainly used to validate the faster but less accurate unbiased GRW algorithm (see [97, 96, 94]).

#### 6.4. Coupled MFEM-GRW simulations

Flow and transport problems associated to (3.1) and (3.2) can be efficiently solved by coupling flow solutions obtained by a mixed finite element method (MFEM) [81, 13] and GRW solutions

of the advection-diffusion problem. The coupled MFEM-GRW approach benefits of accurate velocity fields while avoiding the drawback of numerical diffusion in MFEM methods.

The new approach was illustrated for two-dimensional transport of a passive scalar in a random velocity field with short-range correlation [107]. A log-normal hydraulic conductivity field  $K$  with exponential correlation was generated by the Kraichnan method as a superposition of random periodic modes [81], which ensures reliable simulations of transport if the number of modes is of the order of the total simulation time [95, 35]. MFEM solutions to the incompressible flow problem associated to (3.2), for given samples of the  $K$  field, were computed in a rectangular domain and GRW simulations of the passive transport described by (3.1) were performed in a smaller region inside the domain, to avoid boundary effects. Velocity values defined on MFEM elements were then interpolated to the nodes of the GRW lattice. A good resolution of the velocity field and small overshooting errors were ensured with a mean Courant number of 2/3.

For validation purposes, full MFEM solution to both flow and transport for a small grid-Peclet number of 0.1 were compared with coupled MFEM-GRW solutions. The Lagrangian velocity and the effective dispersion coefficients estimated by the two methods were in a very good agreement, with a small overestimation of the longitudinal dispersion coefficient by the full MFEM solution, identified as the inherent numerical diffusion of the MFEM scheme [81]. The coupled MFEM-GRW achieved a speed-up of computation of a factor of ten as compared to the full MFEM solution [107].

## 7. GRW solutions to PDF evolution equations

### 7.1. Modeled PDF evolution equations

Analytical and semi-analytical solutions for the evolution of the PDF of the solute concentrations governed by dispersion and reaction in random velocity fields have been developed for particular cases and under simplifying hypotheses [83, 85, 29]. By neglecting the local dispersion and assuming small fluctuations of the velocity field, the explicit expressions derived by Dorini and Cunha [32] for both one-point and two-points PDF of nonreactive concentrations could be used in the frame of the consistent first-order approximation (Sect. 5.2). PDF equations and closure approximations for advective-reactive transport, amenable to analytical solutions, derived by Venturi et al. [115] account for the randomness of both velocity field and reaction rates. Functional PDF evolution equations were also introduced, by forcing the application to partial differential concentration balance equations of the van Kampen's Lemma [53, 54, 86], valid however only for systems of ordinary differential equations [116, Sect. 18]. Formal functional Fokker-Planck equations associated to stochastic partial differential reaction-diffusion equations presented in the textbook of Gardiner make sense as discrete schemes, but effective computational tools still have to be developed [43, Chap. 13]. Moreover, such numerical approaches for functional probabilities are being developed for additive noise, whereas the usual situation in hydrogeological problems is that of multiplicative noise, induced by random coefficients.

A consensus seems to be emerging that the appropriate approach is to adapt to transport in groundwater [83, 68, 115] well established methods for reactive flows in turbulence and combustion theory [78, 49, 47]. An advantage of this approach is that the PDF evolution equation can be put in the form of a Fokker-Planck equation and numerical solutions for the equivalent Itô equations can be used to approximate the solution. A numerical solution similar to PDF methods in turbulence has been proposed by Meyer et al. [68]. In their approach, the PDF of a passive scalar is represented by an ensemble of notional particles tracked in space by the random

Lagrangian velocity, modeled by an Itô equation, and in the concentration space by a “mixing model”, accounting for the effect of the local scale dispersion. Since turbulence models, based on Navier-Stokes equations cannot be used for groundwater flows, the parameters of the velocity Itô equation have been calibrated by Monte Carlo simulations of the Darcy flow governed by the equations (3.2).

Lagrangian “composition” PDF codes used in turbulence [41, Sect. 7.3] solve a system of ordinary stochastic differential equations describing the evolution of an ensemble of notional particles in physical and concentration spaces. The corresponding Fokker-Planck equation describes the evolution of the *joint concentration-position* PDF  $p(\mathbf{c}, \mathbf{x}, t)$ , where  $\mathbf{c}$  is a vector composed of the random concentrations associated to the system of chemical reactions. The Eulerian PDF of  $\mathbf{c}$ , for given  $\mathbf{x}$  and  $t$ , is the conditional probability density  $p(\mathbf{c} | \mathbf{x}, t) = p(\mathbf{c}, \mathbf{x}, t)/p(\mathbf{x}, t)$ . If the position PDF  $p(\mathbf{x}, t)$  is chosen to be uniform for all  $t$ , the Fokker-Planck equation coincides with the Eulerian PDF evolution equation derived from the concentration balance equation [41, p. 291]. With this choice, the coefficients of the PDF equations can be inferred from turbulence models [78, 16, 41]. Uniform  $p(\mathbf{x}, t)$  is ensured by uniform initial locations of the notional particles [41]. Giving up this restriction,  $p(\mathbf{x}, t)$  is the probability to find a notional particle at the position  $\mathbf{x}$ , at the time  $t$ , in the ensemble of all the realizations of the diffusion process and of the random velocity field; that is,  $p(\mathbf{x}, t)$  has the meaning of an ensemble mean concentration.

Hence, a general representation of the PDF by notional particles can be designed by considering an upscaled process driving the mean concentration, with trajectories  $\{X_i, i = 1, 2, 3\}$  described by the Itô equations

$$dX_i(t) = \mathcal{V}_i(\mathbf{X}, t)dt + d\tilde{W}_i(\mathbf{X}, t), \quad (7.1)$$

where  $\mathcal{V}_i$  is an upscaled velocity,  $W_i$  is a Wiener process with  $E\{\tilde{W}_i^2(\mathbf{X}, t)\} = 0$  and  $E\{\tilde{W}_i^2(\mathbf{X}, t)\} = 2 \int_0^t \mathcal{D}_{ii}(\mathbf{X}, t')dt'$ , and  $\mathcal{D}_{ij}$  are upscaled dispersion coefficients [108]. In case of stochastic upscaling,  $\mathcal{V}_i$  is the mean Lagrangian velocity, equal with the constant mean Eulerian velocity [104, Fig. 2], and  $\mathcal{D}_{ij}$  is the ensemble dispersion coefficient derived from the second moment  $\Sigma_{ij}$  of the ensemble mean concentration. In case of upscaling by spatial averages, the probabilistic description is given by a “filtered” density function (FDF),  $\mathcal{V}_i$  describes the filtered velocity field, and  $\mathcal{D}_{ij}$  is the upscaled coefficient accounting for local dispersion and unresolved velocity fluctuations [16].

The evolution of the time-random concentrations sampled at the positions of the notional particles  $C_\alpha(t) = C_\alpha(\mathbf{X}(t))$ , where  $\alpha = 1, \dots, N_\alpha$ , with  $N_\alpha$  denoting the number of chemical species, is described by the equations

$$dC_\alpha(t) = M_\alpha(C_\alpha(t))dt + S_\alpha(\mathbf{C}(t))dt, \quad (7.2)$$

where  $S_\alpha(\mathbf{C}(t))$  are reaction terms and the coefficients  $M_\alpha(C_\alpha(t))$  describe the mixing in the concentration space due to local dispersion [78, 16]. Eventually, if the system of reactions involves immobile species  $\bar{\mathbf{C}}$  defined by functions with spatial support on the surface of the solid matrix, then  $S_\alpha = S_\alpha(\mathbf{C}(t), \bar{\mathbf{C}}(t))$  and (7.2) have to be supplemented by new equations  $d\bar{C}_\beta(t) = \bar{S}_\beta(\mathbf{C}(t), \bar{\mathbf{C}}(t))dt, \beta = 1, \dots, N_\beta$  [108].

Pope [78] proposed a mixing model in the form of an Itô equation describing a diffusion process in the concentration space,

$$M_\alpha(C_\alpha(t))dt = A_\alpha(C_\alpha(t))dt + B_\alpha(C_\alpha(t))dW(t),$$

where  $W(t)$  is the standard Wiener process. The drift term is the so called “interaction by exchange with the mean” (IEM) mixing model,  $A_\alpha \propto (C_\alpha - \langle C_\alpha \rangle)$ . The diffusion coefficient in concentration space proposed by Pope has the generic form  $B_\alpha \propto \langle (C_\alpha - \langle C_\alpha \rangle)^2 \rangle^{1/2}$  [78]. In FDF approaches, a supplementary drift term which describes the attenuation of the mean concentration by diffusion may be considered to improve the IEM model [69]. Since this diffusion process would generate negative concentrations, Fox [41] derived a diffusion model with suitable boundary constraints to keep the concentrations in the allowable range  $[0, 1]$ . Discussions on advantages and limitations of the above, and some other, mixing models can be found in [41, 47, 48].

By the equivalence of the Itô and Fokker-Planck representations of the diffusion processes [31, 43], one associates to the position ( $X_i$ ) and concentration ( $C_\alpha$ ) Itô equations a Fokker-Planck equation describing the evolution of the joint concentration-position PDF  $p(\mathbf{c}, \mathbf{x}, t)$ ,

$$\frac{\partial p}{\partial t} + \frac{\partial}{\partial x_i}(\mathcal{V}_i p) + \frac{\partial}{\partial c_\alpha}(M_\alpha p) = \frac{\partial^2}{\partial x_i \partial x_j}(\mathcal{D}_{ij} p) - \frac{\partial}{\partial c_\alpha}(S_\alpha p). \quad (7.3)$$

Equation (7.3) has the form of PDF/FDF equations for the conditional Eulerian PDF  $p(\mathbf{c} | \mathbf{x}, t)$  derived, by different methods, in studies on turbulent reacting flows [78, 41, 16, 47]. The reaction terms  $S_\alpha$  are in a closed form, the same as in the concentration balance equation, which is a considerable advantage of the PDF methods with respect to averaging procedures for upscaling reactive transport [78, 16]. The drift and diffusion coefficients in physical space,  $\mathcal{V}_i$  and  $\mathcal{D}_{ij}$ , and the mixing terms  $M_\alpha$  are not closed and require modeling.

The coefficients  $\mathcal{V}_i$  and  $\mathcal{D}_{ij}$  needed to solve the PDF transport equation (7.3) correspond to stochastic upscaling and can be estimated by Monte Carlo simulations (Section 4) or first-order approximations (Section 5). For the FDF approach, these coefficients can in principle be obtained from homogenization MFEM approximations for non-periodic media and random coefficients (e.g., [74, 82]). The IEM mixing model performs well in FDF approaches, where only unresolved concentration fluctuations about the local resolved-scale need to be modeled [48, p. 125]. In case of transported PDF, the IEM model, which preserves the shape of the initial PDF, has to be replaced by more complex descriptions of the mixing [41]. Once all the coefficients have been established, (7.3) may be efficiently solved by a GRW algorithm in physical and concentration spaces. In case of filtering upscaling, MFEM solutions of filtered flow may be imported into the GRW lattice to compute the transported FDF by the coupled MFEM-GRW approach (see Section 6.4).

## 7.2. GRW solutions to modeled PDF equations

The feasibility of the GRW-PDF approach has been illustrated in [108] for the two-dimensional passive transport problem considered in Section 4. The Monte Carlo results for transverse slab sources of length  $100\lambda$  presented in [95] were processed statistically to infer various correlations and PDFs [106]. The strong correlation of the cross-section space-average concentration at the plume center of mass,  $C(t)$ , with the longitudinal dispersion coefficient and the smallness of the other input-output correlations [106, Fig. 6] provide numerical support for a one dimensional model (7.1), with constant  $\mathcal{V}$  and time-variable  $\mathcal{D}$ . For passive transport, the evolution of the random concentration  $C(t)$  is described by the equation (7.2) without reaction terms.

Self-averaging estimates of the ensemble dispersion coefficient  $\mathcal{D} = \mathcal{D}_{11} = \frac{1}{2}d\Sigma_{11}/dt$  have been obtained by using a single trajectory of the diffusion in a realization of the Kraichnan

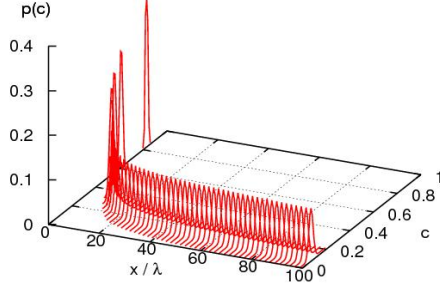


Figure 12: Transported PDF at the plume center of mass,  $p(c | x = \mathcal{V}t)$ .

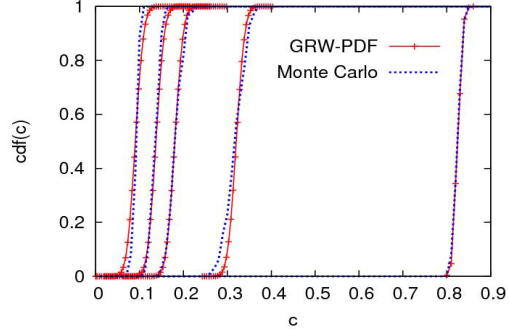


Figure 13: GRW and Monte Carlo cumulative distribution functions  $cdf(c)$  at  $t = 0, 10, 30, 50$ , and 100 days (from right to left).

velocity field, sampled at  $S$  constant time intervals  $\tau$ , with the discrete version of (5.11) [102],

$$\mathcal{D}(S\tau) = (X^2(S\tau) - X^2(S\tau - \tau))/(2\tau),$$

where

$$X^2(S\tau) = \sum_{s=1}^S \delta X_s^2 + 2 \sum_{r=1}^{S-1} \sum_{s=1}^{S-r} \delta X_s \delta X_{s+r}, \quad \delta X_s = X_{s\tau} - X_{(s-1)\tau}.$$

The drift term  $\mathcal{V}$  in (7.1) was set to the constant mean Eulerian velocity. The initial condition for the GRW solution to the Fokker-Planck equation (7.3) was given by the PDF of the cross-section spatially averaged concentration at the first time step in the Monte Carlo simulations [106], multiplied by  $N = 10^{24}$  computational particles.

Some tests with combinations between the IEM model and diffusion in the concentration space as models for the mixing term  $M$  showed that IEM alone preserves the initial PDF and a small amount of diffusion is needed to transport the PDF in the concentration space. The marginal probability density  $p(x, t)$  of the one-dimensional position process (7.1), obtained by integrating over  $c$  the GRW solution  $p(c, x, t)$ , was found to be very close to the Monte Carlo estimate of the ensemble averaged cross-section concentration, which is a consistency requirement for the GRW-PDF approach based on equations (7.1) and (7.2). However the simulated PDF remained significantly different from the reference Monte Carlo PDF [108].

If the rate of decrease of the mean concentration at the center of mass is considered instead of the IEM model, the results of the GRW-PDF simulations improve considerably. In this approach, the mixing model  $M$  consists of a sum of a smooth drift, given by the rate of decrease on the ensemble mean concentration  $\langle C(t) \rangle$  inferred by Monte Carlo simulations [106], and a noise term with decreasing amplitude, similar to those separated from single-realization concentration series  $C(t)$  by an automatic algorithm [113]. The evolution of the joint concentration-position PDF  $p(c, x, t)$  is simulated with a GRW algorithm which spreads the initial distribution of computational particles on a two-dimensional  $(c, x)$  lattice. The Eulerian concentration PDF is further computed as conditional PDF by  $p(c | x, t) = p(c, x, t)/p(x, t)$  [41, 68]. Figure 12 shows the behavior of the PDF on the trajectory  $x = \mathcal{V}t$  of the center of mass. The comparison given in Figure 13 of the cumulative probability distributions at the center of mass shows a good agreement with the Monte Carlo results.

Fairly good results are also obtained if one replaces the rate of decrease of the mean concentration  $\langle C(t) \rangle$  by that of a single-realization of the process  $C(t)$ . One expects therefore that mixing models, adapted to specific transport problems, can be inferred from concentration data, provided by simulations or by in situ measurements, using methods well established in time series analysis [111, 112, 114]. For the transported PDF problem considered here, one can reasonably assume the ergodicity of the concentration process  $C(t)$ . Then, the drift and the noisy components of the mixing model  $M$  could be inferred by separating the deterministic trend and the stationary noise from a single-realization of  $C(t)$  with the automatic trend estimation algorithm of Vamoş and Crăciun [113].

## 8. Conclusions

The mathematical model of diffusion in random velocity fields can be parameterized by experimentally inferred local dispersion and drift coefficients. For applications to contaminant transport in groundwater, the space variable drift coefficients are given by solutions of boundary value problems for the flow equations, with hydraulic conductivity provided as a sample of a random space function inferred by geostatistical interpretations of field-scale measurements.

For either diffusion in velocity fields with short-range correlations or anomalous diffusion in Gaussian fields with power law correlations, the first two moments are finite at finite times and the variance of the process can be decomposed exactly into dispersion and memory terms. The former describe the enhanced spreading of the solute, which explains the scale effect, and the latter account for the dependence on initial conditions. The memory effects are quantified by correlations of the increments of the process induced by the spatial variability of the drift coefficients. The memory may be transitory, for short-range velocity correlations, or indefinitely persistent, in case of power-law correlations.

Diffusion processes with variable drift coefficients can be approximated numerically by particle methods. Their efficiency is considerably increased by the global spreading of the computational particles on regular lattices. GRW algorithms are not only free of numerical diffusion but also insensitive to the increase of the number of particles, which allows accurate representations of the concentration fields. GRW based Monte Carlo investigations on dispersion in velocity fields with short-range correlations highlighted the transitory memory effects as well as the asymptotic ergodic and self-averaging behavior of the solute dispersion, consistent with theoretical predictions based on first-order approximations.

First-order approximations of dispersion coefficients may be used to derive useful approximate expressions for the mean and the variance of the concentration fields [40]. Assessments of contamination risk require, beyond characterizations by mean values and variances, the knowledge of the full concentration PDF. The model of diffusion in random fields for transport in groundwater allows a straightforward derivation of the PDF evolution equation, based on Itô equations for the upscaled transport process and mixing models describing the dynamics of the species concentrations. Efficient solutions to PDF evolution equations can be obtained by GRW simulations of transport in physical and concentration spaces of large ensembles of particles which represent the PDF. The GRW-PDF approach avoids the increase with the number of particles of the computational costs as well as the numerical diffusion associated with incomplete localness of the mixing step in grid-free particle methods [58].

A major challenge in modeling the evolution of the concentration PDF is to identify suitable mixing models for the dynamics of the concentration at fixed spatial locations of the computational particles. Mixing models used in turbulence and combustion theory may be a starting point

[68]. However, given the structural difference between Navier-Stokes and Darcy flows, they cannot be simply transferred and applied in subsurface hydrology. Preliminary results with the use of concentration time series in modeling the mixing process are promising and suggest the need to get closer to experiments. The deterministic trend and the noisy component of a time series, which may be separated automatically in some cases [113], could provide the coefficients of the Itô process describing the mixing in the concentration space. Given the hierarchical structure of scales and the low flow velocity in groundwater systems, it is also possible that measured concentration time series show features of a polydisperse processes, consisting of a superposition of Gaussian processes associated to local thermodynamic equilibrium states at different scales [46]. A mechanism which generates such polydisperse time series may then serve as a mixing model.

### Acknowledgements

This work was supported in part by the Deutsche Forschungsgemeinschaft under Grant SU 415/2-1 and by the Jülich Supercomputing Centre in the frame of the Project JICG41. The author thanks P. Knabner, A. Greven, J. Barth for supervising the progress of the work, I. Neuweiler, R. Helmig, C. Lécot for carefully reading an earlier version of the manuscript, S. Attinger, F. A. Radu, and C. Vamoş for fruitful discussions.

### Appendix A. Relations between spatial moments of probability densities and statistics of the process trajectories

#### Appendix A.1. Finite-dimensional probability distributions

Let be  $B = B_1 \times \dots \times B_n$ ,  $B_i \in \mathcal{B}$  (the Borel  $\sigma$ -algebra on  $\mathbb{R}$ ),  $1_{B_i}(y)$  the characteristic functions of the sets  $B_i$ ,  $i = 1, 2, 3$  ( $1_{B_i}(y) = 1$  if  $y \in B_i$  and  $1_{B_i}(y) = 0$  if  $y \notin B_i$ ),  $\{X_t(\omega) = X(t, \omega), t \geq 0, \omega \in \Omega\}$  a stochastic process defined on the canonical probability space  $(\Omega, \mathcal{A}, P)$ ,  $\langle \cdot \rangle$  the stochastic average with respect to  $P$ , and  $\delta(\cdot)$  the singular Dirac function. Further, consider the set function

$$P_{t_1, \dots, t_n}(B) = \int_{B_1} dx_1 \dots \int_{B_n} dx_n \langle \delta(x_1 - X_{t_1}(\omega)) \dots \delta(x_n - X_{t_n}(\omega)) \rangle. \quad (\text{A.1})$$

By Fubini's theorem, integration permutes with stochastic averaging [59, p. 59]. Then, if  $B_n = \mathbb{R}$ , the integral with respect to  $dx_n$  in (A.1) equals 1 (as value of the Dirac functional) and one obtains the marginal set function  $P_{t_1, \dots, t_{n-1}}$ . Obviously, (A.1) is invariant to permutations in the order of integrals. Thus, (A.1) fulfils the formal consistency conditions for finite-dimensional probability distributions [31, 59].

Considering the characteristic functions

$$1_{B_i}(X_{t_i}(\omega)) = \int_{\mathbb{R}} \delta(x_i - X_{t_i}(\omega)) 1_{B_i}(x) dx_i = \int_{B_i} \delta(x_i - X_{t_i}(\omega)) dx_i,$$

(A.1) can be rewritten as

$$\begin{aligned} P_{t_1, \dots, t_n}(B) &= \int_{\Omega} 1_{B_1}(X_{t_1}(\omega)) \dots 1_{B_n}(X_{t_n}(\omega)) P(d\omega) \\ &= P(\{X_{t_1} \in B_1, \dots, X_{t_n} \in B_n\}), \end{aligned}$$



which shows that (A.1) is a measure of cylindrical sets on  $\mathcal{B}^n$ , that is, the distribution of the  $n$ -dimensional random vector  $\{X_{t_1} \cdots X_{t_n}\}$ . Thus, (A.1) defines consistent  $n$ -dimensional distributions [31] of the process  $\{X_t(\omega)\}$ .

The integrand from (A.1) was used by van Kampen [117] to define consistent finite-dimensional probability densities. Similar stochastic averages of  $\delta$  functions are often used in the literature and are referred to as “probability densities” (e.g., [78]). Even though these densities are singular space functions, their integration with respect to the spatial variables yields well defined stochastic averages, as applications of Dirac functionals.

#### Appendix A.2. Diagonal components of the covariance (2.11)

Consider  $\Omega = \mathbb{R}^3 \times \Omega_D$ , where  $\Omega_D$  is the space of events of the diffusion process starting from a fixed initial position. Let  $\langle \cdot \rangle = \langle \langle \cdot \rangle_D \rangle_{x_0} = \langle \cdot \rangle_{Dx_0}$  be the expectation defined as average over  $\Omega_D$  and over the initial positions  $\mathbf{X}(0) \in \mathbb{R}^3$ . Further, consider a constant diffusion coefficient  $D$  and the time-stationary drift coefficients  $V_i(\mathbf{x})$ . Within this setup, and using (A.1), one proves that the diagonal components of the covariance (2.11) have the equivalent representation (2.14):

For  $D$  constant, the second term of (2.11) gives the term  $2D(t - t_0)$  in (2.14). For  $i = j$ , the average with respect to the joint probability density  $g(\mathbf{x}, t' | \mathbf{x}', t'')g(\mathbf{x}', t'' | \mathbf{x}_0, t_0)c(\mathbf{x}_0, t_0) = p(\mathbf{x}, t'; \mathbf{x}', t''; \mathbf{x}_0, t_0)$  in (2.12), can be computed, according to (A.1), as average with respect to the singular density  $\langle \delta(x - X_{t'}(\omega))\delta(x' - X_{t''}(\omega))\delta(x_0 - X_{t_0}(\omega)) \rangle_{Dx_0}$ , which gives the term in the second line of (2.14). The third line of (2.14) is obtained similarly by expressing the average with respect to  $g(\mathbf{x}, t' | \mathbf{x}_0, t_0)c(\mathbf{x}_0, t_0) = p(\mathbf{x}, t'; \mathbf{x}_0, t_0)$  in (2.13) as average with respect to the singular probability density  $\langle \delta(x - X_{t'}(\omega))\delta(x_0 - X_{t_0}(\omega)) \rangle_{Dx_0}$ .

### Appendix B. GRW solutions to Fokker-Planck equations

#### Appendix B.1. GRW approximations for continuous diffusion processes

The definition of a diffusion process can be reformulated in terms of transition probabilities and conditional expectations, without requiring that the transition probability has a density (e.g., [59, p. 68 and p. 142]).

Condition (2.4), reformulated as  $\lim_{\delta t \rightarrow 0} \frac{1}{\delta t} \text{Prob}\{|\hat{X}_{k+1} - \hat{X}_k| > \epsilon\} = 0$ , is fulfilled if for every  $\epsilon > 0$  there exists a small  $\delta t$  such that  $\text{Prob}\{|\hat{X}_{k+1} - \hat{X}_k| > \epsilon\} = 0$ . According to (6.4),  $|\hat{X}_{k+1} - \hat{X}_k| = |v\delta x + \xi|$  takes on a maximum value of  $(|v| + d)\delta x$ . Using (6.5), one finds that if  $\delta t \leq \delta t^* = \frac{rd^2\epsilon^2}{2D(|v|+d)^2}$ , then  $(|v| + d)\delta x \leq \epsilon$  with probability 1. Thus, the condition (2.4) is fulfilled because  $\text{Prob}\{|\hat{X}_{k+1} - \hat{X}_k| > \epsilon\} = 1 - \text{Prob}\{|\hat{X}_{k+1} - \hat{X}_k| \leq \epsilon\} = 0$ . Since transitions outside the interval  $(-\epsilon, \epsilon)$  have probability zero if  $\delta t \leq \delta t^*$ , the conditions (2.7-2.8) for the first two moments of  $\hat{X}_{k+1} - \hat{X}_k$  are fulfilled as well.

Condition (2.5), reformulated as an expectation for fixed  $\hat{X}_k$  and  $\delta t \leq \delta t^*$ , yields

$$\lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{\hat{X}_{k+1} - \hat{X}_k\} = \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{V\delta t + \Delta v\delta x + \xi\} = V + \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} \Delta v\delta x, \quad (\text{B.1})$$

where  $E\{\xi\} = 0$  according to (6.5) and  $\Delta v = v - V \frac{\delta t}{\delta x}$  defines the truncation error of the advective displacement.

Condition (2.6) is verified exactly:

$$\frac{1}{2} \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{(\hat{X}_{k+1} - \hat{X}_k)^2\} = \frac{1}{2} \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{V^2\delta^2 t + 2V\xi\delta t + \xi^2\} = D, \quad (\text{B.2})$$



where one uses (6.5), which implies  $E\{\xi\} = 0$  and  $E\{\xi^2\} = 2D\delta t$ .

Thus, the discrete process  $\hat{X}$  approximates, up to truncation errors, a continuous diffusion process  $X(t)$  with finite first two moments satisfying (2.4-2.8). Accordingly, the distribution of the computational particles on the GRW lattice approximates the solution of the Fokker-Planck equation (2.1).

#### Appendix B.2. Strict equivalence between GRW and the weak Euler scheme for constant $V$

In case of a constant velocity, there are no truncation errors at all if one chooses  $V\delta t = v\delta x$ , which cancels  $\Delta v$  in (B.1). The first three moments of the random walk  $\xi$  with jump probabilities given by (6.5) satisfy

$$|E(\xi)| + |E(\xi^3)| + |E(\xi^2) - \delta t| = 0 \leq C\delta t^2,$$

for any positive constant  $C$ , condition required for a consistent first-order truncation of the Itô-Taylor expansion [59, Section 5.12].

Thus, if  $V$  is a real constant, then the discrete process (6.4) is a weak Euler scheme with convergence order  $O(\delta t)$  for the Itô equation  $dX(t) = Vdt + dW(t)$ ,  $E(dW) = 0$  and  $E((dW)^2) = 2D\delta t$ .

#### Appendix B.3. BGRW approximations for continuous diffusion processes

Consider without loss of generality the one-dimensional BGRW with jump probabilities  $P\{\delta x\} = r + v$ ,  $P\{-\delta x\} = r - v$ ,  $P\{0\} = 1 - r$ , where  $r = 2D\delta t/\delta x^2$  and  $v = V\delta t/\delta x$ .

Since in BRGW algorithms only jumps to neighbor lattice sites are allowed, the conditions (2.4), (2.7), and (2.8) are verified for all  $\epsilon > 0$  if  $\epsilon = \delta x$ .

Similarly to (B.1) and (B.2), one obtains

$$\begin{aligned} \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{\hat{X}_{k+1} - \hat{X}_k\} &= \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} \left[ \frac{1}{2}(r + v)\delta x + \frac{1}{2}(r - v)(-\delta x) \right] \\ &= \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} v\delta x = V, \\ \frac{1}{2} \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} E\{(\hat{X}_{k+1} - \hat{X}_k)^2\} &= \frac{1}{2} \lim_{\delta t \rightarrow 0} \frac{1}{\delta t} \left[ \frac{1}{2}(r + v)\delta x^2 + \frac{1}{2}(r - v)\delta x^2 \right] \\ &= \lim_{\delta t \rightarrow 0} r \frac{\delta x^2}{2\delta t} = D. \end{aligned}$$

Thus, BGRW fulfils exactly the conditions (2.5) and (2.6).

## References

- [1] Aït-Sahalia, Y. (2002), Telling from discrete data whether the underlying continuous-time model is a diffusion, *Journal of Finance*, 57, 2075–2112.
- [2] Attinger, S., Dentz, M., H. Kinzelbach, and W. Kinzelbach (1999), Temporal behavior of a solute cloud in a chemically heterogeneous porous medium, *J. Fluid Mech.*, 386, 77–104.
- [3] Avellaneda, M., and M. Majda (1989), Stieltjes integral representation and effective diffusivity bounds for turbulent diffusion, *Phys. Rev. Lett.* 62(7), 753–755.

- [4] Avellaneda, M., and M. Majda (1992), Superdiffusion in nearly stratified flows, *J. Stat. Phys.*, 69(3/4), 689–729.
- [5] Balescu, R. (1988), Transport Processes in Plasmas, North-Holland, Amsterdam.
- [6] Balescu, R. (2000), Memory effects in plasma transport theory, *Plasma Phys. Control. Fusion* 42, B1–B13.
- [7] Balescu, R., H.-D. Wang, and J. H. Misguich (1994), Langevin equation versus kinetic equation: Subdiffusive behavior of charged particles in a stochastic magnetic field, *Phys. Plasmas*, 1(12), 3826–3842.
- [8] Bear, J. (1961), On the tensor form of dispersion in porous media, *J. Geophys. Res.*, 66(4), 1185–1197.
- [9] Berkowitz, B., and H. Scher (1997), Anomalous transport in random fracture networks, *Phys. Rev. Lett.*, 79(20), 4038–4041.
- [10] Berkowitz, B., and H. Scher (2010), Anomalous transport in correlated velocity fields, *Phys. Rev. E*, 81, 011128, <http://dx.doi.org/10.1103/PhysRevE.81.011128>.
- [11] Bouchaud, J.-P., and A. Georges (1990), Anomalous diffusion in disordered media: Statistical mechanisms, models and physical applications, *Phys. Rep.*, 195, 127–293.
- [12] Bouchaud, J.-P., A. Georges, J. Koplik, A. Provata, and S. Redner (1990), Superdiffusion in random velocity fields, *Phys. Rev. Lett.*, 64, 2503–2506.
- [13] Brunner, F., F. A. Radu, M. Bause, P. Knabner (2012), Optimal order convergence of a modified BDM1 mixed finite element scheme for reactive transport in porous media, *Adv. Water Resour.*, 35 163–171.
- [14] Chilès, J. P., and P. Delfiner (1999), *Geostatistics: Modeling Spatial Uncertainty*, John Wiley & Sons, New York.
- [15] Clincy, M., and H. Kinzelbach (2001), Stratified disordered media: exact solutions for transport parameters and their self-averaging properties, *J. Phys. A: Math. Gen.* 34, 7142–7152.
- [16] Colucci, P. J., F. A. Jaber, and P. Givi (1998), Filtered density function for large eddy simulation of turbulent reacting flows, *Phys. Fluids*, 10(2), 499–515.
- [17] Cushman, J. H. (1986), On measurement, scale, and scaling, *Water Resour. Res.*, 22, 129–134.
- [18] Cushman, J. H. (1990), *Dynamics of Fluids in Hierarchical Porous Media*, J. H. Cushman (Ed.), Academic Press. London.
- [19] Cushman, J.H. (1997), *The Physics of Fluids in Hierarchical Porous Media: Angstroms to Miles*, Springer Science+ Business Media, Dordrecht.
- [20] Cushman, J.H., and T.R. Ginn (1993), Nonlocal dispersion in porous media with continuously evolving scales of heterogeneity, *J. Transport in Porous Media*, 13(1), 123–138.

- [21] Cushman, J.H., and T.R. Ginn (1993), On dispersion in fractal porous media, *Water Resour. Res.*, 29(10), 3513–3515.
- [22] Cushman, J.H., X. Hu, and T.R. Ginn (1994), Nonequilibrium statistical mechanics of preasymptotic dispersion, *J. Stat. Phys.* 75, 859–878.
- [23] Dagan, G. (1984), Solute transport in heterogeneous porous formations, *J. Fluid Mech.*, 145, 151–177.
- [24] Dagan, G. (1987), Theory of solute transport by groundwater, *Annu. Rev. Fluid Mech.*, 19, 183–215.
- [25] Dagan, G. (1989), *Flow and Transport in Porous Formations*, Springer, Berlin.
- [26] Dagan, G. (1990), Transport in heterogeneous porous formations: Spatial moments, ergodicity, and effective dispersion, *Water Resour. Res.*, 26(6), 1281–1290.
- [27] Deng, W., and E. Barkai (2009), Ergodic properties of fractional Brownian-Langevin motion, *Phys. Rev. E*, 79, 011112, <http://dx.doi.org/10.1103/PhysRevE.81.021103>.
- [28] 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, 3591–3604.
- [29] Dentz, M., and D. M. Tartakovsky (2010), Probability density functions for passive scalars dispersed in random velocity fields, *Geophys. Res. Lett.*, 37, L24406, <http://dx.doi.org/10.1029/2010GL045748>.
- [30] Dentz, M., and F. P. J. de Barros (2013), Dispersion variance for transport in heterogeneous porous media, *Water Resour. Res.*, 49, 3443–3461, <http://dx.doi.org/10.1002/wrcr.20288>.
- [31] Doob, J. L. (1990), *Stochastic Processes*, John Wiley & Sons, London.
- [32] Dorini, F.A., and M. C. C. Cunha (2011), On the linear advection equation subject to random velocity fields, *Math. Comput. Simulat.* 82, 679–690, <http://dx.doi.org/10.1016/j.matcom.2011.10.008>
- [33] Dybiec, B., and E. Gudowska-Nowak (2009), Discriminating between normal and anomalous random walks, *Phys. Rev. E*, 80, 061122, <http://dx.doi.org/10.1103/PhysRevE.80.061122>.
- [34] Eberhard, J. (2004), Approximations for transport parameters and self-averaging properties for point-like injections in heterogeneous media, *J. Phys. A: Math. Gen.*, 37, 2549–2571.
- [35] Eberhard, J., N. Suciu, and C. Vamos (2007), On the self-averaging of dispersion for transport in quasi-periodic random media, *J. Phys. A: Math. Theor.*, 40, 597–610, <http://dx.doi.org/10.1088/1751-8113/40/4/002>.
- [36] El Haddad, R., C. Lécot, and G. Venkiteswaran (2010), Diffusion in a nonhomogeneous medium: quasi-random walk on a lattice, *Monte Carlo Methods Appl.*, 16, 2011–230, 10.1515/MCMA.2010.009.

- [37] El Haddad, R., C. Lécot, and G. Venkiteswaran (2009), Quasi-Monte Carlo simulation of diffusion in a spatially nonhomogeneous medium, pp. 339–354 in *Monte Carlo and Quasi-Monte Carlo Methods 2008*, Ed. Pierre L’Ecuyer and Art B. Owen, Springer, Berlin.
- [38] Fannjiang, A., and T. Komorowski (2002), Diffusive and nondiffusive limits of transport in nonmixing flows, *SIAM J. Appl. Math.*, 62, 909–923.
- [39] Fiori, A. (2001), On the influence of local dispersion in solute transport through formations with evolving scales of heterogeneity, *Water Resour. Res.*, 37(2), 235–242
- [40] Fiori, A., and G. Dagan (2000), Concentration fluctuations in aquifer transport: a rigorous first-order solution and applications, *J. Contam. Hydrol.*, 45, 139–163.
- [41] Fox, R. O. (2003), *Computational Models for Turbulent Reacting Flows*, Cambridge University Press, New York.
- [42] Fried, J. J., *Groundwater Pollution*, Elsevier, New York, 1975.
- [43] Gardiner, C. (2009), *Stochastic Methods*, Springer, Berlin.
- [44] Gelhar, L. W. (1986), Stochastic subsurface hydrology from theory to applications, *Water Resour. Res.*, 22(9S), 135S–145S.
- [45] Gelhar, L. W. and C. Axness (1983), Three-dimensional stochastic analysis of macrodispersion in aquifers, *Water Resour. Res.*, 19(1), 161–180.
- [46] Gheorghiu, S., and M. O. Coppens (2004), Heterogeneity explains features of anomalous thermodynamics and statistics, *PNAS*, 101(45), 15852–15856, <http://dx.doi.org/10.1073/pnas.0407191101>.
- [47] Haworth, D. C. (2010), Progress in probability density function methods for turbulent reacting flows, *Prog. Energy Combust. Sci.*, 36, 168–259, <http://dx.doi.org/10.1016/j.pecs.2009.09.003>.
- [48] Haworth, D. C., and S.B. Pope (2011), Transported probability density function methods for Reynolds-averaged and large-eddy simulations, in: *Turbulent combustion modeling, Fluid Mechanics and Its Applications*, 95, Ed. T. Echekki and E. Mastorakos, pp. 119–142, Springer, Dordrecht.
- [49] Heinz, S. (2007), Unified turbulence models for LES and RANS, FDF and PDF simulations, *Theor. Comput. Fluid Dyn.*, 21, 99–118, <http://dx.doi.org/10.1007/s00162-006-0036-8>.
- [50] Jeon, J.-H., and R. Metzler (2010), Fractional Brownian motion and motion governed by the fractional Langevin equation in confined geometries, *Phys. Rev. E*, 81, 021103, <http://dx.doi.org/10.1103/PhysRevE.81.021103>.
- [51] Kabala, Z. J., and G. Sposito (1991), A stochastic model of reactive solute transport with time-varying velocity in a heterogeneous aquifer, *Water Resour. Res.*, 27(3), 341–350.
- [52] Kavvas, M. L., and A. Karakas (1996) On the stochastic theory of solute transport by unsteady and steady groundwater flow in heterogeneous aquifers, *J Hydrol*, 179, 321–351.

- [53] Kavvas, M. L. (2001) General conservation equation for solute transport in heterogeneous porous media, *J. Hydrolog. Eng.*, 6(2), 341–350.
- [54] Kavvas, M.L. (2003) Nonlinear hydrologic processes: Conservation equations for determining their means and probability distributions, *J. Hydrolog. Eng.*, 8(2), 44–52.
- [55] Karapiperis, T., and B. Blankleider (1994), Cellular automaton model of reaction-transport processes, *Physica D*, 78, 30–64.
- [56] Kesten, H., and G. C. Papanicolaou (1979), A limit theorem for turbulent diffusion, *Commun. math. Phys.*, 65, 97–128.
- [57] Kitanidis, P. K. (1988), Prediction by the method of moments of transport in a heterogeneous formation, *J. Hydrol.*, 102, 453–473.
- [58] Klimenko, A. Y. (2007), On simulating scalar transport by mixing between Lagrangian particles, *Phys. Fluids* 19, 031702, <http://dx.doi.org/10.1063/1.2711233>.
- [59] Kloeden, P. E., and E. Platen (1999), *Numerical Solutions of Stochastic Differential Equations*, Springer, Berlin.
- [60] Komorowski, T., and G. Papanicolaou (1997), Motion in a Gaussian incompressible flow, *Ann. Appl. Probab.*, 7(1), 229–264.
- [61] Kraichnan, R. H. (1970), Diffusion by a random velocity field, *Phys. Fluids*, 13(1), 22–31.
- [62] Le Doussal, P., and J. Machta (1989), Annealed versus quenched diffusion coefficient in random media, *Phys. Rev. B*, 40(12), 9427–9430.
- [63] Lécot, C., and I. Coulibaly (1998), A particle method for some parabolic equations, *J. Comput. Appl. Math.*, 90, 25–44.
- [64] Lumley, J. L. (1962b), The mathematical nature of the problem of relating Lagrangian and Eulerian statistical functions in turbulence, pp , 17–26 in *Mécanique de la Turbulence (Coll. Intern. du CNRS à Marseille)*, Ed. CNRS, Paris.
- [65] Majda, A. J., and P. R. Kramer (1999), Simplified models for turbulent diffusion: Theory, numerical modelling, and physical phenomena, *Phys. Rep.*, 14, 237–574.
- [66] Majumdar, S. N. (2003), Persistence of a particle in the Matheron - de Marsily velocity field, *Phys. Rev. E*, 68, 050101(R), <http://dx.doi.org/10.1103/PhysRevE.68.050101>.
- [67] Matheron, G., and G. de Marsily (1980), Is transport in porous media always diffusive?, *Water Resour. Res.*, 16, 901–917.
- [68] Meyer, D. W., P. Jenny, and H. A. Tchelepi (2010), A joint velocity-concentration PDF method for tracer flow in heterogeneous porous media, *Water Resour. Res.*, 46, W12522, <http://dx.doi.org/10.1029/2010WR009450>.
- [69] McDermott, R., and S. B. Pope (2007), A particle formulation for treating differential diffusion in filtered density models, *J. Comput. Phys.*, 226, 947–993, <http://dx.doi.org/10.1016/j.jcp.2007.05.006>.

- [70] Monin, A. S., and A. M. Yaglom (1975) *Statistical Fluid Mechanics: Mechanics of Turbulence*, MIT Press, Cambridge, M A.
- [71] Morales-Casique, E., S.P. Neuman, and A. Gaudagnini (2006), Nonlocal and localized analyses of nonreactive solute transport in bounded randomly heterogeneous porous media: Theoretical framework, *Adv. Water Resour.*, 29, 1238–1255, <http://dx.doi.org/10.1016/j.advwatres.2005.10.002>.
- [72] Morales-Casique, E., S.P. Neuman, and A. Gaudagnini (2006), Nonlocal and localized analyses of nonreactive solute transport in bounded randomly heterogeneous porous media: Computational analysis, *Adv. Water Resour.*, 29, 1399–1418, <http://dx.doi.org/10.1016/j.advwatres.2005.10.014>.
- [73] Neuman, S. P., and D. M. Tartakovsky (2009), Perspective on theories of non-Fickian transport in heterogeneous media, *Adv. Water Resour.*, 32, 670–680, <http://dx.doi.org/10.1016/j.advwatres.2008.08.005>.
- [74] Nolen, J., G. Papanicolaou, and O. Pironeau (2008), A framework for adaptive multiscale methods for elliptic problems, *Multiscale Model. Simul.*, 7, 171–196, <http://dx.doi.org/10.1137/070693230>.
- [75] O’Malley, D., and J. H. Cushman (2012) A renormalization group classification of nonstationary and/or infinite second moment diffusive processes, *J. Stat. Phys.*, 146(5), 989–1000, <http://dx.doi.org/10.1007/s10955-012-0448-3>.
- [76] O’Malley, D., and J. H. Cushman (2012), Two scale renormalization group classification of diffusive processes, *Phys. Rev. E*, 86(1), 011126, <http://dx.doi.org/10.1103/PhysRevE.86.011126>.
- [77] Papoulis, A., and S. U. Pillai (2002), *Probability, Random Variables and Stochastic Processes*, McGraw-Hill, Singapore.
- [78] Pope, S. B. (1985), PDF methods for turbulent reactive flows, *Prog. Energy Combust. Sci.*, 11(2), 119–192.
- [79] Pope, S. B. (2011), Simple models of turbulent flows, *Phys. Fluids*, 23, 011301, <http://dx.doi.org/10.1063/1.3531744>.
- [80] Port, S. C., and C. J. Stone (1976), Random measures and their application to motion in an incompressible fluid. *J. Appl. Prob.*, 13, 498–506.
- [81] Radu, F. A., N. Suciu, J. Hoffmann, A. Vogel, O. Kolditz, C-H. Park, S. Attinger (2011), Accuracy of numerical simulations of contaminant transport in heterogeneous aquifers: a comparative study, *Adv. Water Resour.*, 34, 47–61, <http://dx.doi.org/10.1016/j.advwatres.2010.09.012>.
- [82] Ray, N, T. van Noorden, F. Frank, and P. Knabner (2012), Multiscale modeling of colloid and fluid dynamics in porous media including an evolving microstructure, *Transp. Porous Med.*, 95, 669–696, <http://dx.doi.org/10.1007/s11242-012-0068-z>.

- [83] Sanchez-Vila, X., A. Guadagnini, and D. Fernandez-Garcia (2009), Conditional probability density functions of concentrations for mixing-controlled reactive transport in heterogeneous aquifers, *Math. Geosci.* 41, 323–351, <http://dx.doi.org/10.1007/s11004-008-9204-2>
- [84] Scheidegger, A. E. (1961), General theory of dispersion in porous media, *J. Geophys. Res.*, 66(10), 3273–3278.
- [85] Schwede, R. L., O. A. Cirpka, W. Nowak, and I. Neuweiler (2008), Impact of sampling volume on the probability density function of steady state concentration, *Water Resour. Res.*, 44(12):W12433, 2008. <http://dx.doi.org/10.1029/2007WR006668>.
- [86] Sirin, H. (2013), On the using cumulant expansion method and van Kampen's lemma for stochastic differential equations with forcing, *Stoch. Environ. Res. Risk Assess.*, 27, 91–110 <http://dx.doi.org/10.1007/s00477-012-0591-z>.
- [87] Sirin, H., and M. A. Marinõ (2008), On the cumulant expansion up scaling of ground water contaminant transport equation with nonequilibrium sorption, *Stoch. Environ. Res. Risk Assess.*, 22, 551–565, <http://dx.doi.org/10.1007/s00477-007-0174-6>.
- [88] Sposito, G. and G. Dagan (1994), Predicting solute plume evolution in heterogeneous porous formations, *Water Resour. Res.*, 30(2), 585–589.
- [89] Sposito, G., W. A. Jury, and V. K. Gupta (1986), Fundamental problems in the stochastic convection-dispersion model of solute transport in aquifers and field soils, *Water Resour. Res.*, 22,(1), 77–88.
- [90] Sposito, G., and D. A. Barry (1987), On the Dagan model of solute transport in groundwater: foundational aspects, *Water Resour. Res.*, 23(10), 1867–1875, <http://dx.doi.org/10.1029/WR023i010p01867>.
- [91] Strikwerda, J. C. (1989), *Finite difference schemes and partial differential equations*, Wadsworth & Brooks, Pacific Grove, California.
- [92] Suciu N. (2010), Spatially inhomogeneous transition probabilities as memory effects for diffusion in statistically homogeneous random velocity fields, *Phys. Rev. E*, 81, 056301, <http://dx.doi.org/10.1103/PhysRevE.81.056301>.
- [93] Suciu N., C. Vamoş, J. Vanderborght, H. Hardelauf, and H. Vereecken (2004), Numerical modeling of large scale transport of contaminant solutes using the global random walk algorithm, *Monte Carlo Methods Appl.*, 10(2), 153–177.
- [94] Suciu, N., C. Vamoş, P. Knabner, and U. Ruede (2005) Biased global random walk, a cellular automaton for diffusion, in: *Simulationstechnique, 18-th Symposium in Erlangen, September 2005*, Ed. F. Hülsemann, M. Kowarschik, and, U. Rude, pp. 562–567, SCS Publishing House e. V., Erlangen.
- [95] Suciu, N., C. Vamoş, J. Vanderborght, H. Hardelauf, and H. Vereecken (2006), Numerical investigations on ergodicity of solute transport in heterogeneous aquifers, *Water Resour. Res.*, 42, W04409, <http://dx.doi.org/10.1029/2005WR004546>.

- [96] Suciu N., C. Vamoş, and J. Eberhard (2006), Evaluation of the first-order approximations for transport in heterogeneous media, *Water Resour. Res.* 42, W11504, <http://dx.doi.org/10.1029/2005WR004714>.
- [97] Suciu N., and C. Vamoş (2006), Evaluation of overshooting errors in particle methods for diffusion by biased global random walk, *Rev. Anal. Num. Th. Approx. (Rom. Acad.)*, 35, 119–126.
- [98] Suciu N., and C. Vamoş (2007), Comment on “Nonstationary flow and nonergodic transport in random porous media” by G. Darvini and P. Salandin, *Water Resour. Res.*, 43, W12601, <http://dx.doi.org/10.1029/2007WR005946>.
- [99] Suciu, N., C. Vamoş, H. Vereecken, K. Sabelfeld, and P. Knabner (2008), Ito equation model for dispersion of solutes in heterogeneous media, *Rev. Anal. Num. Th. Approx. (Romanian Academy)*, 37, 221–238.
- [100] Suciu N., C. Vamoş, H. Vereecken, K. Sabelfeld, and P. Knabner (2008), Memory effects induced by dependence on initial conditions and ergodicity of transport in heterogeneous media, *Water Resour. Res.* 44, W08501, <http://dx.doi.org/10.1029/2007WR006740>.
- [101] Suciu N., and P. Knabner (2009), Comment on ‘Spatial moments analysis of kinetically sorbing solutes in aquifer with bimodal permeability distribution’ by M. Massabo, A. Bellin, and A. J. Valocchi, *Water Resour. Res.*, 45, W05601, <http://dx.doi.org/10.1029/2008WR007498>.
- [102] Suciu N., and C. Vamoş (2009), Ergodic estimations of upscaled coefficients for diffusion in random velocity fields, pp. 617–626 in *Monte Carlo and Quasi-Monte Carlo Methods 2008*, Ed. Pierre L’Ecuyer and Art B. Owen, Springer, Berlin.
- [103] Suciu, N., C. Vamoş, I. Turcu, C.V.L. Pop, and L. I. Ciortea (2009), Global random walk modeling of transport in complex systems, *Computing and Visualization in Science*, 12, 77–85, <http://dx.doi.org/10.1007/s00791-007-0077-6>.
- [104] Suciu N., C. Vamoş, F. A. Radu, H. Vereecken, and P. Knabner (2009), Persistent memory of diffusing particles, *Phys. Rev. E*, 80, 061134, <http://dx.doi.org/10.1103/PhysRevE.80.061134>.
- [105] Suciu, N., S. Attinger, F.A. Radu, C. Vamoş, J. Vanderborght, H. Vereecken, P. Knabner (2011), Solute transport in aquifers with evolving scale heterogeneity, *Preprint No. 346*, Mathematics Department - Friedrich-Alexander University Erlangen-Nuremberg (<http://fauams5.am.uni-erlangen.de/papers/pr346.pdf>).
- [106] Suciu, N., C. Vamoş, H. Vereecken, and P. Knabner (2011), Global random walk simulations for sensitivity and uncertainty analysis of passive transport models, *Annals of the Academy of Romanian Scientists, Series on Mathematics and its Applications*, 3(1), 218–234.
- [107] Suciu N., F. A. Radu, A. Prechtel, and P. Knabner (2013), A coupled finite element–global random walk approach to advection–dominated transport in porous media with random hydraulic conductivity, *J. Comput. Appl. Math.*, 246, 27–37 <http://dx.doi.org/10.1016/j.cam.2012.06.027>.



- [108] Suciu, N. , C. Vamos, S. Attinger, and P. Knabner (2012), Global random walk solutions to PDF evolutions equations, paper presented at International Conference on Water Resources CMWR, University of Illinois at Urbana-Champaign, June 17-22, 2012.
- [109] Taylor, G. I. (1921), Diffusion by continuous movements, *Proc. London Math. Soc.*, 2(20), 196–212.
- [110] Vamoş, C., N. Suciu, and H. Vereecken (2003), Generalized random walk algorithm for the numerical modeling of complex diffusion processes, *J. Comp. Phys.*, 186(2), 527-544, [http://dx.doi.org/10.1016/S0021-9991\(03\)00073-1](http://dx.doi.org/10.1016/S0021-9991(03)00073-1).
- [111] Vamoş, C., M. Craciun (2008), Serial correlation of detrended time series, *Phys. Rev. E*, 78, 036707, <http://dx.doi.org/10.1103/PhysRevE.78.036707>.
- [112] Vamoş, C., M. Craciun (2010), Separation of components from a scale mixture of Gaussian white noises, *Phys. Rev. E*, 81, 051125, <http://dx.doi.org/10.1103/PhysRevE.81.051125>.
- [113] Vamoş, C., M. Craciun (2012), *Automatic Trend Estimation*, Springer, Dordrecht.
- [114] Vamoş, C., M. Craciun (2013), Numerical demodulation of a Gaussian white noise modulated in amplitude by a deterministic volatility, *The European Physical Journal B*, 86, 166, <http://dx.doi.org/10.1140/epjb/e2013-31072-x>.
- [115] Venturi, D., D. M. Tartakovsky, A. M. Tartakovsky, G. E. Karniadakis (2013), Exact PDF equations and closure approximations for advective-reactive transport, *J. Comput. Phys.* 243, 323–343, <http://dx.doi.org/10.1016/j.jcp.2013.03.001>.
- [116] van Kampen, N. G. (1976), Stochastic differential equations, *Phys. rep.*, 24(3), 171–228.
- [117] van Kampen, N. G. (1981), *Stochastic Processes in Physics and Chemistry*, North-Holland, Amsterdam.
- [118] Yaglom, A. M. (1987), *Correlation Theory of Stationary and Related Random Functions, Volume I: Basic Results*, Springer, New York.
- [119] Zirbel, C. L. (2001), Lagrangian observations of homogeneous random environments, *Adv. Appl. Prob.*, 33, 810–835.
- [120] Zwanzig, R. (1961), Memory effects in irreversible thermodynamics, *Phys. Rev.* 124(4), 983-992.