

# Numerical Investigations on Ergodicity of Solute Transport in Heterogeneous Aquifers

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**Abstract.** [1] Darcy velocities for log-normal hydraulic conductivity with small variance and finite correlation length were approximated by periodic random fields. Accurate simulations of two-dimensional advection-dispersion processes were achieved with the Global Random Walk algorithm, using  $10^{10}$  particles in every transport realization. Reliable statistical estimations were obtained by averaging over 256 realizations. The main result is a numerical evidence for the convergence, in mean square limit, of the actual concentrations to the macrodispersion process predicted by a known limit theorem. For small initial plumes the ergodic behavior can be expected after thousands of advection time scales, when the mean square deviation from the theoretical prediction of the cross-section space averaged concentrations falls under 20%. The increase of the transverse dimension of the plumes slows down the approach to the quasi-ergodic state and has an unexpected nonlinear effect on the variability of the actual concentrations and dispersivities. *INDEX TERMS:* 1831 Hydrology: Groundwater quality; 1832 Hydrology: Groundwater transport; 1869 Hydrology: Stochastic hydrology; Mathematical Geophysics: 3275 Uncertainty quantification; 3294 Mathematical Geophysics: Instruments and techniques; *KEYWORDS:* ergodicity, macrodispersion, global random walk

## 1. Introduction

[2] It is generally admitted that groundwater quality is mainly affected by the transport of dissolved chemicals through soils and aquifers. The classical model is based on a dispersion and advection mechanism which describes the transport at some “local scale”. Further, one assumes that the variability of the solute movement in subsurface water is caused by the heterogeneity of the hydraulic conductivity which, for a given natural formation, is efficiently described as a realization of a random space function [Sposito *et al.*, 1986; Hassan *et al.*, 1998]. The corresponding advection velocity field becomes a random function also and the transport in natural porous media is described by a stochastic model [Dagan, 1984] which follows the approach for turbulent diffusion in atmosphere [Taylor, 1921], or, in terms of the mathematical theory of stochastic processes, as a diffusion in a random velocity field [Matheron and de Marsily, 1980; Avellaneda and Majda, 1992].

[3] As shown in [Sposito *et al.*, 1986], once the advection-dispersion model for local scale has been inferred, the stochastic modeling of transport in groundwater consists of two successive steps. First, the behavior of the ensemble averaged concentration has to be investigated to look for the existence of an up-scaled diffusive behavior called “macrodispersion”. The second issue is to assess the applicability of the ensemble statistics to predictions made for a single groundwater system. The latter, which is the central problem in stochastic modeling, is generally referred to

as “ergodicity” in hydrogeological literature [Dagan, 1984, 1987; Kabala and Sposito, 1994; Sposito, 1997; Fiori, 1998; Trefry *et al.*, 2003; Janković *et al.*, 2003]. It is in this sense that the term ergodicity will be used in the following.

[4] Even though abundant literature has been produced in the last two decades, the investigations on ergodicity were in most cases limited to the study of the second moments of the solute plume and the conclusions often disagree. For instance, it is accepted that the length scale to reach the asymptotic limit predicted by the stochastic model is impractical for real contamination problems [Berkowitz, 2001; Schwarze *et al.*, 2001; Dentz *et al.*, 2002, 2003; Eberhard, 2004]. However, recent numerical investigations conclude that, for extended initial plumes, the dispersivities behave ergodically, at relatively small distances from the injection domain [Janković *et al.*, 2003]. These conclusions do not agree with the results of Trefry *et al.* [2003], which show that the dispersivities significantly differ from realization to realization even after hundreds of heterogeneity scales and the concentrations do not reach the Gaussian limit predicted by the stochastic macrodispersion model. The result of Trefry *et al.* [2003] is consistent with other numerical simulations which show that the attainment of a quasi-ergodic state is more complicated than indicated by some analytical approaches [Naff *et al.*, 1998b].

[5] To examine whether, when and how accurately the stochastic model predicts the behavior in actual aquifers, we propose numerical quantitative estimations of the quasi-ergodic behavior in the spirit of the “operational ergodicity” of Kabala and Sposito [1994]. We use a rigorous mathematical proof of the existence of the up-scaled macrodispersion process to check whether the numerical method is accurate enough for our purpose. Further, we use the same theoretical result to investigate the ergodicity. That is to say, we are looking for those indicators of the contamination in actual plumes that can be predicted by the theoretical result, in the limits of acceptable errors. The numerical task is carried out with the “Global Random Walk” algorithm (GRW) [Vamoș *et al.*, 2003]. Superseding the limitations encountered by the classical particle tracking method, the GRW algorithm performs the simulation of advection-dispersion displacements over thousands of advection time scales of tens of billions of particles, initially distributed over hundreds of heterogeneity scales.

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[6] For the sake of clarity and for computational reasons, we consider only the classical stochastic model, two-dimensional transport problems and small variance of the velocity field in our numerical investigations. This permits detailed analyses of transport in velocity fields with finite correlation lengths, which are not possible in less restrictive conditions. In the following we discuss these limitations and present some reasons to choose this methodological frame.

[7] More recently, stochastic models free of the Fickian hypothesis were proposed as alternatives to the classical stochastic model. These models generally describe ensemble averaged concentrations and their parameters can, in principle, be derived from measurable properties of the medium (breakthrough curves or hydraulic conductivities). The theory proposed by *Cushman and Moroni* [2001] generalizes the statistical mechanical approach for Hamiltonian systems to an arbitrary statistical ensemble with invariant probability measure and it enables the description of anomalous dispersion induced by velocity fluctuations evolving over a hierarchy of scales on the scale of observation. *Berkowitz and Scher* [2001] presented a general approach, based on the ensemble average of a master equation, equivalent to a continuous time random walk over a range of length scales on which the statistical homogeneity can be assumed. This approach was extended to a Fokker-Planck equation with memory term, which integrates the transport behavior over homogeneous units of the medium, each of them described by the ensemble averaged master equation [*Cortis et al.*, 2004]. Another promising stochastic model for transport in saturated porous media describes the trajectories of the solute particles, in the position-velocity phase space, by means of a Langevin stochastic differential equation which accounts for non-Fickian features of the transport as well [*Kurbanmuradov et al.*, 2003]. The ensemble average of the classical advection-dispersion equations can be obtained under appropriate limiting conditions as particular cases of the three stochastic models mentioned above.

[8] The classical model is also able to capture the complexity of transport in groundwater. Anomalous diffusion in the pre-asymptotic transport regime presumably occurs under quite broad conditions [*Trefry et al.*, 2003]. For more restrictive conditions (perfectly stratified aquifers), the ensemble averaged solution of the classical model can be superdiffusive at all times [*Matheron and de Marsily*, 1980]. However, what really makes the classical model attractive for applications is the existence of mathematical proofs for the diffusive behavior of the ensemble averaged concentration, for typical groundwater transport problems, characterized by velocity fields with finite correlations lengths. Since the classical model describes the transport in given velocity fields, the quantitative approach to ergodicity is straightforward and consists in analyzing the sample-to-sample fluctuations and the deviation of the ensemble averaged solutions from the macrodispersion process. Therefore, in the following we consider only the model based on the advection-dispersion mechanism. The conclusions of such an investigation could be useful in assessing the predictive power of the stochastic modeling which does not assume the Fickian behavior at a local scale.

[9] Two-dimensional models can be very useful tools to predict contamination in natural aquifers [*Hassan et al.*, 1998]. They may be applied to the case of hydraulic conductivity which is isotropic in the horizontal plane but has a much smaller correlation length in the vertical direction as well as to transport at regional scale [*Dagan*, 1987]. Two-dimensional numerical simulations in vertical planes oriented along the mean flow direction were successful in reproducing the experimental results obtained in tracer tests [*Moltyaner et al.*, 1993]. The two-dimensional simulations also provide insight into the convergence of the transport process to the Gaussian limit [*Trefry et al.*, 2003]. This

is mainly relevant when ergodicity is investigated, as suggested by *Dagan* [1984; 1987], through averages over space domains with large transverse dimensions. Then, the behavior of the space mean concentration is mainly governed by the longitudinal dispersivities which, for typical two- and three-dimensional transport problems are quite close for any time, as shown by both theory [*Dagan*, 1987, 1984; *Fiori et al.*, 2003] and numerical simulations [*Schwarze et al.*, 2001; *Dentz et al.*, 2002, 2003].

[10] The presumption that the hydraulic conductivity has a log-normal distribution and small variance is an accepted simplification leading to Gaussian velocity fields which can capture the essential features of the stochastic model [*Cortis et al.*, 2004; *Eberhard*, 2004]. In the present context, this choice is not a limitation since the existence of the up-scaled Gaussian distribution for the ensemble averaged concentration, used as reference in our investigations, is ensured for Gaussian velocity fields when the velocity variance goes to zero.

[11] The paper is structured as follows. Section 2 contains some definitions and results concerning the notions of macrodispersion and ergodicity. Section 3 contains some general considerations on numerical modeling as well as the statement of our numerical method. Section 4 presents the main numerical results. Conclusions are drawn in Section 5. Appendix A presents the GRW algorithm and details on the numerical computations. Appendix B is dedicated to technical details concerning the transport problem which approximately fulfils the theoretical requirements for the existence of up-scaled Gaussian diffusion and the statistics of numerically generated velocity fields.

## 2. Macrodispersion and Ergodicity

### 2.1. The Macrodispersion Stochastic Model

[12] For slowly variable porosity which can be taken as a constant, and for non-reactive solutes, the mathematical model of transport in saturated porous media is given by an advection-dispersion equation for the concentration field  $c(\mathbf{x}, t)$ ,

$$\partial_t c + \mathbf{V} \nabla c = \mathbf{D} \nabla^2 c. \quad (1)$$

The constant “local dispersion coefficient”  $\mathbf{D}$  accounts for both the molecular diffusion and the hydrodynamic mixing due to the small scale variability of the velocity field [*Sposito et al.*, 1986; *Kapoor and Gelhar*, 1994; *Labolle and Fogg*, 2001; *Janković et al.*, 2003]. The stochastic approach considers stationary velocities  $\mathbf{V}(\mathbf{x})$  which are realizations of a random field (random space function) that is statistically homogeneous.

[13] A stochastic process has “diffusive behavior” when the mean squared displacement, or variance, is linear as function of time. The typical example is the Brownian motion, i.e. the 1-dimensional Gaussian process  $X(t)$  with zero mean and variance  $\sigma^2(t) = \langle X^2 \rangle(t) = 2Dt$ . In this case, the diffusion coefficient  $D$  describes both the shape of the Gaussian distribution and the width of the diffusion front  $\langle X^2 \rangle$ . In the case of the process described by the equation (1), and, generally, in systems with space-time variable properties, the width of the diffusion fronts is no longer given by the diffusion coefficients alone. Instead, the rate of increase of the second centered moment  $\sigma^2(t)$  defines “effective diffusion coefficients”

$$\mathbf{D}^{eff}(t) = \frac{\sigma^2(t)}{2t}, \quad (2)$$

which can be used to check whether the process has a diffusive behavior [*Avellaneda and Majda*, 1992]. The existence

of a constant limit for  $t \rightarrow \infty$  of the effective coefficients (2) is ensured, for every realization of the velocity field, by some weak conditions on the partial derivatives of  $\mathbf{V}$  (bounded vector potential) [Avellaneda and Majda, 1989; Tatarinova et al., 1991].

[14] The definition (2) was mainly used in hydrological applications for comparisons between theory and field tests [Dagan, 1987] and to compute the first order approximations of dispersivities by travel time statistics [Vanderborght and Vereecken, 2002; Ferrndez-Garcia et al., 2005a,b]. Sometimes, in analytical approaches [Attinger et al., 1999; Dentz et al., 2000a] or numerical studies [Tompson and Gelhar, 1990; Trefry et al, 2003] the dispersion is described by the local slope,  $d\sigma^2/dt$  or by the mean slope of the variance

$$\tilde{\mathbf{D}}(t) = \frac{\sigma^2(t) - \sigma^2(0)}{2t} = \mathbf{D}^{eff}(t) - \frac{\sigma^2(0)}{2t}. \quad (3)$$

At large times  $\tilde{\mathbf{D}}$  tends to  $\mathbf{D}^{eff}$  and the slope of the variance can be used as well to define the asymptotic effective coefficients. However, the time behavior of the solute plume is properly described by the rate of increase of the second moment (2), which, unlike the mean slope (3), is positively defined at all times.

[15] Since disconnected, bimodal or asymmetric plumes could have the same second moment as a Gaussian plume, the existence of the coefficients (2) do not yet prove the existence of the Gaussian limit process. A limit theorem was demonstrated by Kesten and Papanicolaou [1979]. Neglecting the local dispersion in (1), considering velocity fields with non-vanishing mean  $\mathbf{U}$  and small fluctuations  $\varepsilon\mathbf{u}$ ,  $\varepsilon \ll 1$ ,  $\mathbf{V} = \mathbf{U} + \varepsilon\mathbf{u}$ , and making the assumption that the field has some "strong mixing" property, as characterized by a suitable fast decay of the correlation function  $\mathbf{r}(\mathbf{x})/\varepsilon^2 = \langle \mathbf{u}(\mathbf{0})\mathbf{u}(\mathbf{x}) \rangle$ , the authors proved that the average of the transport process over the realizations of the velocity field can be up-scaled to a Gaussian diffusion. In the "weak random limit" ( $\varepsilon \rightarrow 0$ ,  $t \rightarrow \infty$ ,  $\varepsilon^2 t = \text{constant}$ ), the ensemble averaged concentration verifies an advection-diffusion equation with the up-scaled diffusion coefficients given by

$$\mathbf{D}^* = \int_0^\infty \mathbf{r}(\mathbf{U}t) dt.$$

Under these conditions, the statement of Taylor [1921] gets a rigorous proof.

[16] Using a scaling argument, Winter et al. [1984] show that when the local coefficients  $\mathbf{D}$  are of the order  $\varepsilon^2$ , an extension of the exact result of [Kesten and Papanicolaou, 1979] to advection-diffusion processes is possible and the up-scaled diffusion coefficients are of the form

$$\mathbf{D}^* = \mathbf{D} + \int_0^\infty \mathbf{r}(\mathbf{U}t) dt. \quad (4)$$

For incompressible velocity fields, the up-scaled velocity equals the mean velocity  $\mathbf{U}$ . We remark here that the up-scaled coefficient (4) has the same form as the first order approximation of the "macrodispersion coefficient" derived in [Dagan, 1984]. A test for the accuracy of the numerical simulations which mimics the previous conditions is to check whether the deviations of the computed up-scaled coefficients from the values  $\mathbf{D}^*$  given by (4) are one order of magnitude smaller than the local dispersion coefficient  $D$ .

## 2.2. Ergodicity

[17] Strictly speaking, the macrodispersion model is directly applicable to a single aquifer if the same asymptotic Gaussian approximation holds for each realization [Sposito et al., 1986]. Hereafter we call this strong property "asymptotic ergodicity". Sufficient conditions for asymptotic ergodicity are provided if the ensemble average of the actual concentrations tend to the solution of the macrodispersion

model and the sample-to-sample fluctuations tend to zero. In this case, the effective coefficients in every realization necessarily also tend to the macrodispersion coefficients.

[18] The assumption underlying the concept of ergodicity is that suitable space averages of the actual concentration can be described by the solution of the macrodispersion model, when the spatial variability of the concentration encompasses the variability from realization to realization. In [Dagan, 1984; 1987] it is assumed that the space and the ensemble mean are interchangeable if the variance of the space averaged concentration tends to zero. It was shown that the spatially averaged concentration in single realizations is close to the macrodispersion solution after tens of correlation lengths of the hydraulic conductivity, if the initial solute body or the domain of the space average extends over a few correlation lengths across the mean flow [Dagan, 1984, p. 165]. This result was derived in a Lagrangian frame for a normal distribution of the displacements of the solute particles, inferred by a first order approximation of the transport equations. A similar approach, using another approximation technique [Dagan, 1987, eq. (3.14)], led however to a different result indicating a non-ergodic behavior, manifested by a finite limit of the concentration fluctuations at the plume center of mass, which is practically reached after a few correlation lengths [Dagan and Fiori, 1997, figure 3]. The same approximation led to a finite asymptotic variance of the second longitudinal moment of the plume [Fiori, 1998, figures 4 and 5], which also indicates non-ergodic behavior. These results contradict other Lagrangian approaches [Pannone and Kitanidis, 1999] and Eulerian theories (which are limited in turn by closure approximations) [Kapoor and Gelhar, 1994; Kapoor and Kitanidis, 1998]. A renewed Lagrangian result of Fiori and Dagan [2000] corrects the previous one, showing that the concentration coefficient of variation tends to zero (after much larger travel times, corresponding to thousands of correlation scales) but predicts a large time behavior which is still different from that obtained in Eulerian approaches.

[19] The ergodic behavior of individual plumes was recently investigated numerically. Janković et al. [2003] found a good agreement between the behavior of the individual plumes and the predictions of the macrodispersion model, for both two- and three-dimensional transport simulations, which suggests an ergodic behavior of the extended plumes as predicted by Dagan [1984]. On the contrary, Trefry et al. [2003], who simulated the concentration field in single realizations of transport for two-dimensional plumes with initial extension of tens of correlation lengths across the mean flow, found that the ergodic behavior is not reached even when the plumes have traveled hundreds of correlations lengths. The last result is apparently in agreement with that found by Fiori and Dagan [2000]. Yet, the two numerical approaches are not completely comparable. Trefry et al. [2003] performed a direct investigation, by comparing the dispersivities in given realizations, defined by the effective coefficients (3) divided by the mean velocity, to the macrodispersivities corresponding to the up-scaled coefficients (4) of the stochastic model. They also checked whether the concentration becomes Gaussian. Janković et al. [2003] did not investigate the concentration field and in their paper the macrodispersivities were computed through a Taylor formula, similar to (4) (see eq. (14) in [Janković et al., 2003]) which gives smoother results and can explain the different conclusions in the two papers.

[20] In spite of the common belief that extended initial plumes have an ergodic behavior, there are no general mathematical proofs for that. The relevance of the macrodispersion model for each realization of the medium is not an immediate consequence of the existence of the Gaussian up-scaling and is not ensured either by the ergodic properties

of the random velocity field [*Sposito et al.*, 1986; *Kabala and Sposito*, 1994]. Moreover, in the limiting case of vanishing local dispersion, it was proved that groundwater flows governed by the Darcy law are geometrically constrained against becoming chaotic and, consequently, the purely advective transport is in general not ergodic [*Sposito*, 1997, 2001]. The stratified aquifer model of *Matheron and de Marsily* [1980] provides another counter example, for the complete advection-dispersion model. The exact expressions derived by *Clincy and Kinzelbach* [2001] show that the fluctuations of the longitudinal effective coefficient tend to a finite limit, even if the flow is not aligned with the strata and the transport has asymptotic diffusive behavior. Since the asymptotic effective coefficients in given realizations do not tend to their expectation (a necessary condition for ergodicity), the transport is not ergodic. Quantitative numerical estimations for the deviation from the macrodispersion model of the transport in realizations of a Gaussian velocity field with finite correlation lengths (in both transverse and longitudinal directions) were recently obtained, for the case of point-like initial plumes [*Eberhard*, 2004]. The numerical computations of *Eberhard* [2004], based on approximate solutions of the transport equation, show that the fluctuations of the longitudinal effective coefficient tend to zero, indicating that a necessary condition for ergodicity is fulfilled. To prove the ergodicity of transport in velocity fields with finite correlation lengths it is necessary to check whether the sufficient conditions, formulated for actual concentrations, are verified. It is also useful to investigate the behavior of the effective coefficients for extended plumes and their relation with ergodicity.

[21] To achieve our goals, we introduce a definition which is general enough to include various conceptual features of the term ergodicity cited above. Let  $A(t)$  be the value of an observable at time  $t$ ,  $A^*(t)$  the theoretical prediction and  $\Delta A = \langle (A - A^*)^2 \rangle^{1/2}$  the mean square deviation from theory (the angular brackets denote averaging over the ensemble of realizations of the velocity field). *The observable  $A$  is ergodic within the range  $\eta$ ,  $\eta > 0$ , if  $\Delta A \leq \eta$ .* Since the theory usually predicts  $A^*$  as an asymptotic limit and the observable  $A$  is known at finite times, in practice a more flexible definition is necessary. From the relation  $(\Delta A)^2 = \sigma_A^2 + (\Delta \langle A \rangle)^2$ , where  $\sigma_A = \langle (A - \langle A \rangle)^2 \rangle^{1/2}$  is the standard deviation of  $A$  and  $\Delta \langle A \rangle = \langle A \rangle - A^*$  the deviation of the mean  $\langle A \rangle$  with respect to  $A^*$ , one obtains the equivalent definition

$$(e1) \quad |\Delta \langle A \rangle| \leq \eta_1, \quad (e2) \quad \sigma_A \leq \eta_2. \quad (5)$$

If the conditions (5) are fulfilled, then the observable  $A$  is ergodic within the range  $\eta = (\eta_1^2 + \eta_2^2)^{1/2}$ . The asymptotic ergodicity in a strict sense, i.e. as discussed in [*Sposito et al.*, 1986], is ensured when the observable  $A$  is the concentration and (5) holds in the large time limit for arbitrary small and positive  $\eta_1$  and  $\eta_2$ . When the observable  $A$  is a space averaged concentration and the conditions (5) are fulfilled at finite times for dimensions of the averaging domain tending to infinity, then the space averaged concentration converges in the mean square limit to the ensemble averaged concentration and the space and ensemble averages are interchangeable. The condition (e2) was used in [*Dagan*, 1984, 1987] to investigate the ergodicity under the assumption that the ensemble averaged concentration is already Gaussian at finite times. The condition (e2) also formulates the “self-averaging” property investigated in [*Clincy and Kinzelbach*, 2001; *Eberhard*, 2004] for the longitudinal effective coefficient. The condition (e1) alone, applied to effective coefficients or to second moments of the plume, is often referred to as “ergodicity condition” [*Fiori*, 1998; *Naff et al.*, 1998b; *Zhang and Seo*, 2004; *Dagan*, 2004]. For finite times and ranges  $\eta$ , the definition (5) corresponds to the operational interpretation for ergodicity, proposed by *Kabala and Sposito* [1994], which seeks conditions that lead to

acceptably small deviations of the experimentally observable concentrations from the predictions of the stochastic model. The observables  $A$  used to quantify the ergodicity in this study are the cross-section space averaged concentration and the effective diffusion coefficients. The corresponding theoretical predictions  $A^*$  are the solutions of the up-scaled macrodispersion model.

### 3. Numerical Approach

#### 3.1. Prerequisites for Numerical Investigations

[22] Numerical investigations on the existence of the diffusion limit and ergodicity require the simulation of large ensembles of realizations of the transport over large traveled distances. Because this task generally surpasses the available computing resources, some compromise was accepted and the efforts focussed by now on one or two of the three objectives:

- (a) accurate concentration field in a given realization,
- (b) simulations of the transport over large time scales,
- (c) reliable statistics for the ensemble of realizations.

[23] For instance, the objective (a) was pursued in [*Smith and Schwartz*, 1980; *Tompson and Gelhar*, 1990; *Moltyaner et al.*, 1993; *Naff et al.*, 1998b; *Kapoor and Kitanidis*, 1998; *Trefry et al.*, 2003; *Janković et al.*, 2003] where given realizations of the transport were simulated over distances still too small to describe the asymptotic behavior (with the exception of the confined aquifer case considered in [*Kapoor and Kitanidis*, 1998]). Reliable statistical ensembles, the objective (c), aiming to compute the up-scaled coefficients (4), were obtained by tracking one particle in 1500 realizations of the velocity field [*Bellin et al.*, 1992], 20 particles in 500 realizations [*Salandin and Fiorotto*, 1998], 20 particles in 1600 realizations [*Zhang and Seo*, 2004], or 10000 particles in 20 realization [*Fernandez-Garcia et al.*, 2005a], and averaging over realizations. The computational constraints did not allow the simulation over more than a few of velocity correlation lengths and the asymptotic regime, i. e. constant coefficients  $\mathbf{D}^*$ , was not reached.

[24] The objectives (b) and (c) were aimed at in [*Schwarze et al.*, 2001; *Dentz et al.*, 2002, 2003], in the study of the large time behavior of the effective coefficients in the case of point-like injection. The velocity fluctuations  $\epsilon \mathbf{u}$  were numerically approximated using the generator of *Kraichnan* [1970]. The coefficients were computed in two ways: as average over the trajectories of a single particle in thousands of realizations, which corresponds to  $\mathbf{D}^*$  in (4), and as average over realizations of the coefficients corresponding to  $\mathbf{D}^{eff}$  (2), obtained by tracking a number of particles (between tens and hundreds) released at the same point in each realization. The time behavior of the two coefficients is different but both tend to the same constant limit, after travel distances of more than 1000 correlations lengths. The numerically simulated limit coefficients were close to the approximations of the order  $\epsilon^2$  provided by perturbation analyses.

[25] The objective (a) has not yet been attained at the same time with (b) and (c) due to the limitations of the computational resources. For instance, with regard to the particle tracking method which is the most frequently used in large scale simulations, it is recognized that the number of particles should be enormous if we want to obtain accurate concentrations in the limit of a few significant figures [*Sun*, 1996, p. 95]. Recent investigations show that, for the transport problems discussed here, the necessary number of particles is of the order of tens of billions, which is prohibitive for the particle tracking algorithms [*Vamoş et al.*, 2003; *Suciu et al.*, 2004].

[26] Our numerical approach uses the GRW algorithm, a generalized random walk method for which there are no limitations as to the maximum number of particles. In [Suciú *et al.*, 2002; 2004] it was shown that GRW is appropriate to simulate large scale transport in groundwater. In this paper we show that GRW fulfils the requirements (a), (b), and (c) from above and makes possible a direct investigation on the ergodicity issue, based on the definition (5).

### 3.2. Implementation of the GRW Method

[27] We considered two-dimensional divergence-free velocity fields with constant mean  $\langle \mathbf{V} \rangle = \mathbf{U} = (U, 0)$ ,  $U = 1$  m/day, given by the Darcy law for normal log-hydraulic conductivity  $y$ , with isotropic correlation length  $\lambda_y = 1$  m, and variance  $\sigma_y^2 = 0.1$ . They were generated numerically with the Kraichnan procedure which is frequently used in large scale simulations of transport [Jaekel and Vereecken, 1997; Schwarze *et al.*, 2001; Dentz *et al.* 2002, 2003; Eberhard, 2004]. The Kraichnan method ensures the incompressibility and approximates the realizations of the Gaussian velocity field, given by the first order approximation in  $\sigma_y$  of Darcy and continuity equations, by means of a superposition of sine (or cosine) periodic modes.

[28] In every realization of the velocity field the simulation of an isotropic diffusion ( $D_{ll} = D = 0.01$  m<sup>2</sup>/day,  $D_{lm} = 0$  for  $l \neq m$ ) was conducted for dimensionless times  $Ut/\lambda_y$  corresponding to thousands of correlation lengths, using the reduced fluctuations GRW algorithm presented in Appendix A1. In each realization of the velocity field,  $N = 10^{10}$  particles were initially uniformly distributed in a vertical band or located at the origin of the grid. Because the theoretical result presented in subsection 2.1 was obtained for unbounded domains, the grid was chosen to be larger than the maximum extension of the plume. Implementation details are discussed in Appendix A2. Some preliminary tests have shown that the longitudinal local dispersion has little influence on the resulting concentration fields, in agreement with the results concerning the longitudinal effective coefficients presented by Fiori [1996, figure 1] and by Dentz *et al.* [2000a, Appendix B]. Thus  $D$  mainly describes the strength of the transverse local dispersion.

[29] We chose the transport parameters  $\sigma_y^2 = 0.1$  and  $D = 0.01$  m<sup>2</sup>/day after preliminary investigations, presented in Appendix B1. These parameters minimize numerical artifacts inherent in two-dimensional simulations. The comparison presented in Appendix B2 show that the fluctuations have similar large time behavior for exponential and Gaussian shape for the correlation of the log-hydraulic conductivity field, provided that the number of periods in Kraichnan routine and the number of realizations are large enough. For the detailed investigations on ergodicity presented in the following we chose the exponential correlation shape,  $Np = 6400$  and  $R = 256$  realizations. In Appendix B3 it was shown that the numerically generated velocities approximate a Gaussian random field and the squared fluctuations  $\varepsilon^2$  have roughly the same order of magnitude as the local dispersion coefficient  $D$  (see second line of table B1), in agreement with the theoretical assumptions leading to an up-scaled Gaussian process. The corresponding theoretical values of the longitudinal and transverse effective diffusion coefficients, computed from the 1-st order estimation of the correlations under the integral in (4) [Dagan, 1984], have the values

$$D_{11}^* = 0.11 \text{ m}^2/\text{day}, D_{22}^* = 0.01 \text{ m}^2/\text{day}. \quad (6)$$

[30] The simulations started with a uniform initial distribution of the  $10^{10}$  particles inside rectangles  $\lambda_y \times L\lambda_y$ , with  $L = 10, 50$  and  $100$ , oriented across the mean flow. In

the case of instantaneous point source, all the particles were released from the origin of the grid at the initial time. The total simulation time was of 2000 days for  $L = 100$ , 2700 days for  $L = 50$ , and 4000 days for  $L = 10$  and for the point source. The cross-section space averaged concentrations in given realizations  $C(x_1, t; L)$  were computed according to (A1) by the number of particles in a domain  $\lambda_y \times (160 + L)\lambda_y$  divided by the total number of particles  $N$ . The normalized concentrations were obtained through division by the initial concentrations:  $C(x_1, t) = C(x_1, t; L)/C(0, 0; L)$ . The averaging domain, oriented across the mean flow and centered at  $x_1$ , corresponds to the ideal sampling across reference planes aimed at in field tracer tests [Vanderborght and Vereecken, 2002] as well as in laboratory and numerical experiments [Fernández-García *et al.*, 2005a,b]. We stored the space averaged concentration at the plume center of mass,  $C(\langle x_1 \rangle, t)$ , as well as the concentration field  $C(x_1, t)$  at several fixed times. The effective coefficients (2) were computed according to (A2). Further, we computed the mean concentrations  $\langle C \rangle$  and the mean effective coefficients  $\langle D_u^{eff} \rangle$ , as averages over the ensemble of  $R$  realizations of the transport. Since in all the simulations the mean flow velocity was  $U = 1$  m/day, the numerical values of the effective coefficients coincide with the dispersivities  $\mathbf{D}^{eff}/U$ , measured in meters.

## 4. Numerical Results on Ergodicity

### 4.1. Cross-section Averaged Concentrations

[31] Since the width of the averaging domain is larger than the transverse dimension of the plume, the transport can be described by a one-dimensional problem for the spatially averaged concentration  $C(x_1, t)$ . The corresponding theoretical concentration  $C^*$  is the one-dimensional Gaussian distribution of coefficient  $D_{11}^* = 0.11$  m<sup>2</sup>/day which describes the cross section average of the concentration predicted by the stochastic macrodispersion model. The ergodicity condition (e1) in (5) was investigated by means of the relative deviation of the ensemble average of the cross-section averaged concentration from the theoretical value,  $\Delta\langle C \rangle/C^* = (\langle C \rangle - C^*)/C^*$ . The deviations  $\Delta\langle C \rangle/C^*$ , computed at the plume center of mass  $\langle x_1 \rangle$  presented in figure 1 show that in the case of point source at  $t = 4000\lambda_y/U$  the condition (e1) is fulfilled within a range  $\eta_1 \simeq 0.17C^*$ . The increase of  $L$  reduces the deviations at early times. For instance, for  $L \geq 50$ ,  $\eta_1 \simeq 0.13C^*$  at 100 advection time scales  $\lambda_y/U$  (or, equivalently at one dispersion time scale  $\lambda_y^2/D$ ).

[32] To check the second ergodicity condition (e2) we used the standard deviation of the cross-section averaged concentration divided by the theoretical solution  $\sigma_C/C^*$ , where  $\sigma_C = ((C^2) - \langle C \rangle^2)^{1/2}$ . The results presented in figure 2 show that for point source at  $t = 4000\lambda_y/U$  the condition (e2) is fulfilled within a range  $\eta_2 \simeq 0.11C^*$ . Thus, according to (5) the ergodicity range is  $\eta = (\eta_1^2 + \eta_2^2)^{1/2} \simeq 0.2C^*$ . The monotonous decay of the norm  $(\Delta C)^2 = \sigma_C^2 + (\Delta\langle C \rangle)^2$  indicate the convergence in mean square limit of the cross-section averaged concentration to the solution of the macrodispersion process.

[33] For  $L = 100$  at one dispersion time scale one obtains in a similar way  $\eta_2 \simeq 0.1C^*$  and  $\eta \simeq 0.16C^*$ . The results for ensemble averaged concentration as function of the distance from the center of the initial plume for a fixed time of  $100\lambda_y/U$ , presented in figures 3 and 4, indicate that  $\eta$  has a minimum at  $x_1 = 100\lambda_y$  (which corresponds to the mean center of mass coordinate). A rough prediction of the maximum concentration estimated by the cross-section averaged concentration at the plume center of mass,  $C^* \pm 3\eta$ , is reliable for almost all the realizations of the ensemble defined by a given statistical structure of the log-hydraulic conductivity. In the somewhat ideal case analyzed here, for initial plumes extending over 100 correlation lengths across the mean flow,

the prediction based on the macrodispersion model and the ergodic hypothesis of the space averaged concentration  $C$  in actual aquifers is affected by uncertainties of the order  $6\eta \simeq 0.9C^*$ .

[34] The behavior of standard deviations presented in figure 2 indicate a non-linear dependence on the plume dimension at early times. For large sources ( $L \geq 50$ ) the concentration fluctuations  $\sigma_C/C^*$  are smaller than in the case of point source, decrease with  $L$  but remain almost constant, at values about 0.1, over thousands of advection time scales. The monotonous decrease of the fluctuations, i.e. the asymptotic ergodicity, is expected to occur at times much larger than in the case of the point or small sources.

#### 4.2. Effective Coefficients

[35] The relative deviation of the ensemble averaged effective coefficients from the theoretical values given in (6) can be expressed using (3) by

$$\begin{aligned} \Delta \langle D_{ii}^{eff} \rangle / D_{ii}^* &= (\langle D_{ii}^{eff} \rangle - D_{ii}^*) / D_{ii}^* \\ &= \Delta \langle \tilde{D}_{ii} \rangle / D_{ii}^* + \sigma_{0,ii}^2 / (2tD_{ii}^*). \end{aligned} \quad (7)$$

Since the contribution of the initial plume  $\sigma_{0,ii}^2 / (2tD_{ii}^*)$  is a deterministic quantity which tends to zero for large times, to compare the asymptotic behavior of the effective coefficients for different  $L$  we used the deviation of the mean slope of the second centered moment of the plume  $\Delta \langle \tilde{D}_{ii} \rangle / D_{ii}^*$ . The results for longitudinal coefficients are presented in figure 5. The ergodicity condition (e1) for the mean slope is fulfilled within a range  $\eta_1 \simeq 0.11D_{11}^*$  in the case of point source at 4000 advection times and within a range  $\eta_1 \simeq 0.05D_{11}^*$  in the case  $L = 100$  at 100 advection times. Because  $\sigma_{0,11}^2 = 0.1m^2$  in all cases, at  $t = 100\lambda_y/U$  its contribution in (7) is already only 0.0045 and therefore the same range  $\eta_1$  characterizes the longitudinal effective dispersion coefficients.

[36] The fluctuations  $\sigma_{D_{11}^{eff}} / D_{11}^*$  of the longitudinal effective dispersion coefficient are given in figure 6. For a small increase of the plume dimension, the fluctuations increase (similarly to the results reported by *Naff et al.* [1998b, figure 15]) and they decrease when the plume dimension is further increased, like the fluctuations of the cross-section averaged concentration in figure 2. The ergodicity condition (e2) is fulfilled within a range  $\eta_2 \simeq 0.16D_{11}^*$  for point source at  $t = 4000\lambda_y/U$  and within a range  $\eta_2 \simeq 0.14D_{11}^*$  in the case  $L = 100$  at  $t = 100\lambda_y/U$ . It follows that, according to (5), the corresponding ergodicity ranges are  $\eta \simeq 0.2D_{11}^*$  (point source) and  $\eta \simeq 0.15D_{11}^*$  ( $L = 100$ ). The behavior for small sources ( $L \leq 10$ ) indicate the asymptotic ergodicity of the longitudinal coefficient. The deviations from the macrodispersion model of the mean slope of the transverse second moment and the fluctuations of the transverse effective coefficients, presented in figures 7 and 8 respectively, indicate that the transverse coefficient is also asymptotically ergodic.

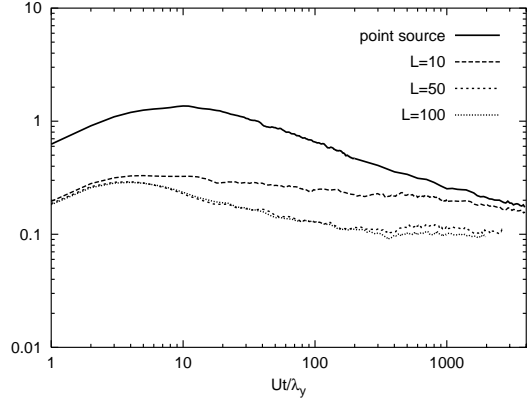
[37] The asymptotic effective coefficients and their deviation from the theoretical values  $D_{ii}^*$  were computed in the case  $L = 100$  as follows. First, the temporal averages of the mean slopes  $\tilde{D}_{ii}$  between  $t = 200\lambda_y/U$  and  $t = 2000\lambda_y/U$ ,  $[\tilde{D}_{ii}]$ , were computed in every realization. Then, averages over realizations were used to estimate the mean asymptotic coefficients  $D_{ii}^\infty = \langle [\tilde{D}_{ii}] \rangle$  and the deviations

$$\Delta[\tilde{D}_{ii}] = \langle ([\tilde{D}_{ii}] - D_{ii}^*)^2 \rangle^{1/2}$$

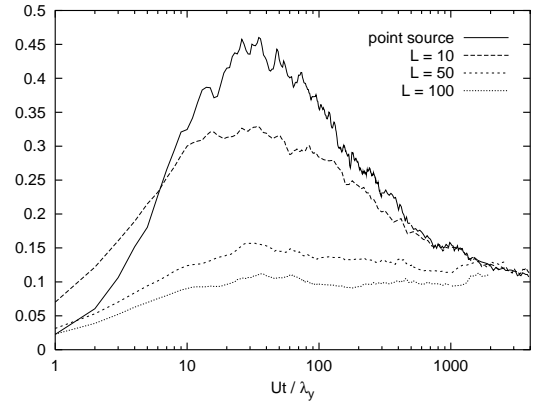
with respect to  $D_{ii}^*$ . The results are presented in figure 9 as functions of the number of realizations  $R$ . The fact that the deviations of the mean coefficients  $D_{ii}^\infty$  from  $D_{ii}^*$  are one order of magnitude smaller than the local dispersion coefficient  $D$ , in very good agreement with (4), constitutes a test for

the accuracy of the numerical simulations. The behavior of the deviations  $\Delta[\tilde{D}_{ii}]$  (thin lines in figure 9) indicate that the time averaged coefficients  $[\tilde{D}_{ii}]$  are ergodic within a range of the order of the local dispersion coefficient  $\eta \simeq D = 0.01 m^2/day$ .

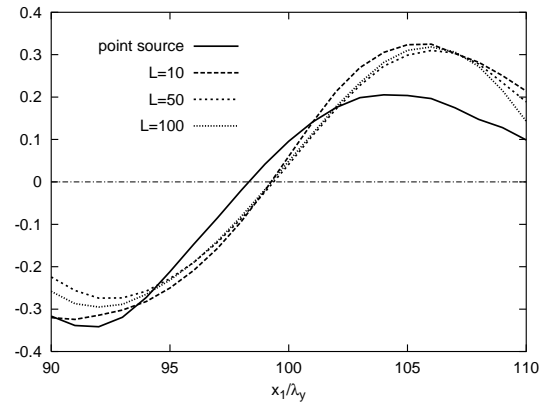
[38] Even if the the mean slope is ergodic within an acceptable small range, the macrodispersion coefficients  $D_{ii}^*$



**Figure 1.** Deviations from the macrodispersion model of the mean concentration at the plume center of mass  $\Delta \langle C \rangle / C^*(\langle x_1 \rangle, t)$ .



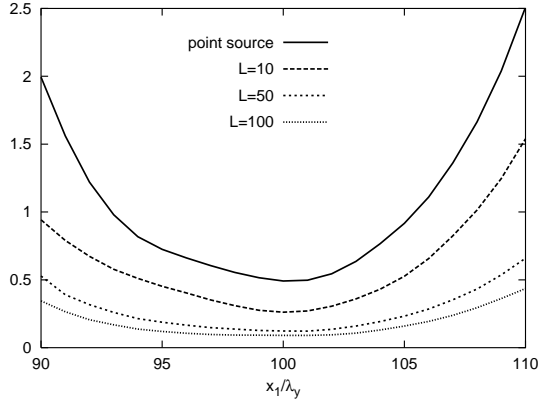
**Figure 2.** Standard deviations of the concentration at plume center of mass  $\sigma_C / C^*(\langle x_1 \rangle, t)$ .



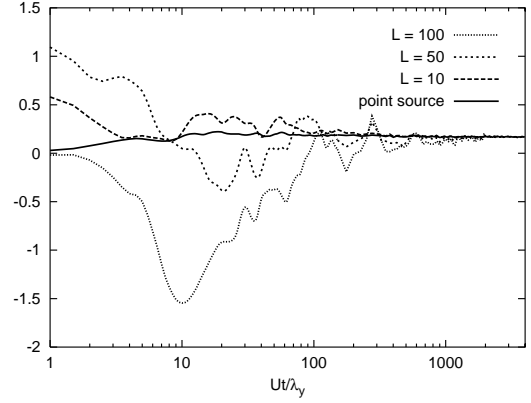
**Figure 3.** Deviations from the macrodispersion model of the mean concentration as space function  $\Delta \langle C \rangle / C^*(x_1, 100\lambda_y/U)$ .

describe the time behavior of the second moments of the plume with errors smaller than 100% only when, according to (7),  $\sigma_{0,u}^2/(2tD_{ii}^*) \leq 1$ . This implies that the ergodicity time scale is at least as large as  $\sigma_{0,u}^2/D_{ii}^*$ . In the cases presented in this paper, for the transverse coefficient the time  $\sigma_{0,22}^2/(2D)$  can be very large (tens of thousands of advection scales for  $L \geq 50$ ) and increases proportionally with  $L^2$ . The increase of the ergodicity scale with the plume dimension  $L$

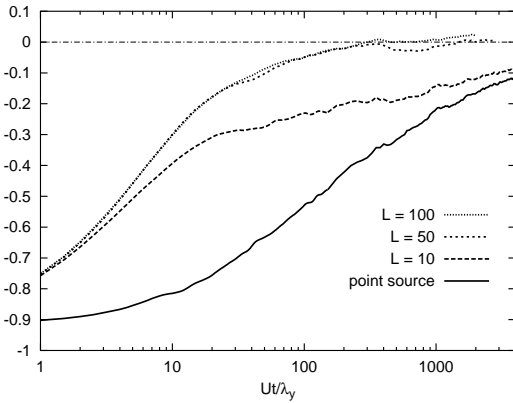
is also indicated by the behavior of the fluctuations in figures 2, 6 and 8. The total time in our simulations is still too small to allow the estimation of the ergodicity scale, but some hint can be obtained by a comparison with the analytical result of *Clincy and Kinzelbach* [2001]. The figure 4 in their paper shows that the fluctuations of the longitudinal coefficient tend to an asymptotic value (which is finite in



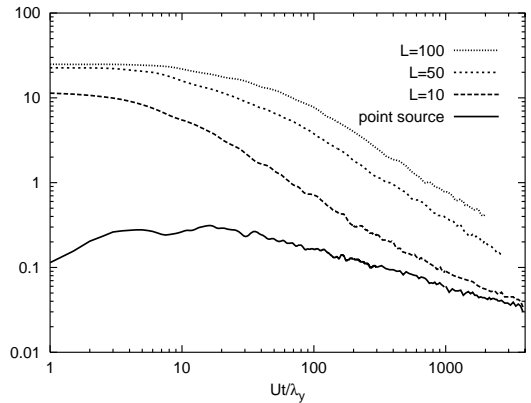
**Figure 4.** Standard deviations of the concentration as space function  $\sigma_C/C^*(x_1, 100\lambda_y/U)$ .



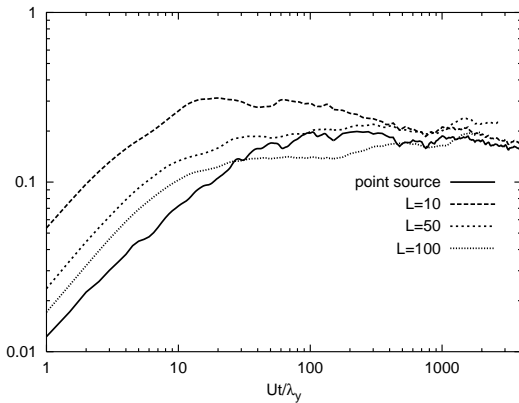
**Figure 7.** Deviations from the macrodispersion model of the mean slope of the transverse second moment  $\Delta\langle\tilde{D}_{22}\rangle/D_{22}^*$ .



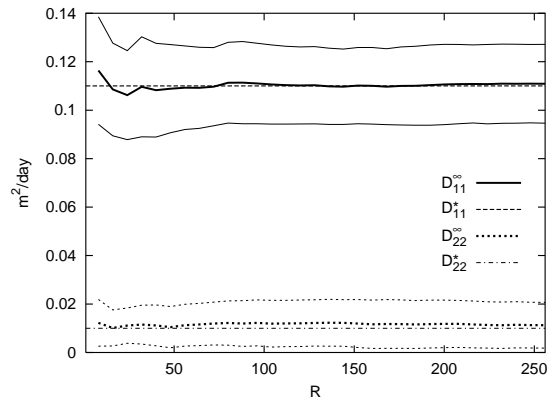
**Figure 5.** Deviations from the macrodispersion model of the mean slope of the longitudinal second moment  $\Delta\langle\tilde{D}_{11}\rangle/D_{11}^*$ .



**Figure 8.** Fluctuations of the transverse effective dispersion coefficient  $\sigma_{D_{22}^{eff}}/D_{22}^*$ .



**Figure 6.** Fluctuations of the longitudinal effective dispersion coefficient  $\sigma_{D_{11}^{eff}}/D_{11}^*$



**Figure 9.** Asymptotic effective coefficients and deviations from the theoretical values (6) for  $L = 100$ , as functions of the number of realizations  $R$ .

the case of the model of Matheron and de Marsily studied there) after times of the order of  $L^2/D$ , i.e. the time for a dispersive spreading of the solute over the width  $L$  of the initial plume.

### 4.3. The Time Behavior of the Effective Coefficients and Ergodicity

[39] As shown by equation (A3) in Appendix A1, the GRW procedure computes the variance of displacements  $\mathbf{X}$  in a single realization as an average over the realizations of the local dispersion process and over the distribution of the particles inside the initial plume. The ensemble average of the variance can be written as

$$\begin{aligned} \langle \sigma_{il}^2 \rangle_V &= \langle \langle X_l^2 \rangle_{D, X_0} - \langle X_l \rangle_{D, X_0}^2 \rangle_V \\ &= \langle \langle X_l^2 \rangle_{D, X_0, V} - \langle X_l \rangle_{D, X_0, V}^2 \rangle_V \\ &\quad - \langle \langle X_l \rangle_{D, X_0}^2 \rangle_V + \langle X_l \rangle_{D, X_0, V}^2, \end{aligned} \quad (8)$$

where the subscripts  $D$ ,  $X_0$  and  $V$  denote the average over the realizations of the local dispersion, the initial distribution of the particles, and the realizations of the random velocity field respectively. This obvious relation shows that  $\langle \sigma_{il}^2 \rangle_V$  is the difference between the variance with respect to the ensemble average of the center of mass  $R_l = \langle X_l \rangle_{D, X_0}$  and the variance of the center of mass  $R_{ll} = \langle R_l^2 \rangle_V - \langle R_l \rangle_V^2$ . Assuming that the averages over initial positions and velocity realizations have the following permutation property  $\langle \cdots \rangle_{D, X_0, V} = \langle \cdots \rangle_{D, V, X_0}$ , the first term in (8) becomes

$$\langle \langle X_l^2 \rangle_{D, V} - \langle X_l \rangle_{D, V}^2 \rangle_{X_0} + \langle \langle X_l \rangle_{D, V}^2 \rangle_{X_0} - \langle X_l \rangle_{D, X_0, V}^2.$$

For statistical homogeneous velocity fields it seems reasonable to assume the independence of the averages  $\langle \tilde{X}_l \rangle_{D, V}$  and  $\langle \tilde{X}_l^2 \rangle_{D, V}$ , where  $\tilde{X}_l = X_l - X_{0l}$ , from the initial state  $\mathbf{X}_0$ . Then, the last two terms above give the initial variance  $\sigma_{0, ll}^2 = \langle X_{0l}^2 \rangle_{X_0} - \langle X_{0l} \rangle_{X_0}^2$  and the first term becomes independent of  $\mathbf{X}_0$  and represents the variance around the ensemble averaged center of mass for the process starting with a point-like injection at  $\tilde{X}_l = 0$ ,  $\tilde{X}_{ll} = \langle \tilde{X}_l^2 \rangle_{D, V} - \langle \tilde{X}_l \rangle_{D, V}^2$ . Finally, the ensemble average (8) of the second centered moment of the plume becomes

$$\langle \sigma_{il}^2 \rangle = \sigma_{0, ll}^2 + \tilde{X}_{ll} - R_{ll}. \quad (9)$$

The variance  $\tilde{X}_{ll}$  is just the  $ll$  component of the “one-particle displacement covariance or the second spatial covariance of an ergodic plume” [Zhang and Seo, 2004] frequently used in investigations on ergodicity. When the local dispersion is neglected, (9) is identical to the relation (11) in [Dagan, 1990], derived in the hypothesis of “Lagrangian stationarity” and using the permutation of averages over initial states and velocity realizations. The explicit dependence of  $\tilde{X}_{ll}$  on local dispersion and velocity correlations can be derived from descriptions of the transport process in terms of trajectories [Rajaram and Gelhar, 1993a; Fiori, 1998] or by using the advection-dispersion equation [Kitanidis, 1988; Rajaram and Gelhar, 1993b].

[40] Dividing both sides of (9) by  $2t$  and using (2), the effective coefficients can be written as

$$\langle D_{il}^{eff} \rangle(t) - \frac{\sigma_{X_{0, ll}}^2}{2t} = D_{il}^{erg}(t) - D_{il}^{cm}(t). \quad (10)$$

The “center of mass coefficient”  $D_{il}^{cm}$  corresponds to the “pseudodispersivity” investigated numerically by Naff *et al.* [1998b]. The first term in the right side of (10) is the so called “ergodic coefficient” which is expected to become constant and equal to the up-scaled macrodispersion coefficient in the large time limit [Dagan, 1990]. The condition

$D_{il}^{cm} = 0$  is referred to as “ergodicity condition” [Fiori, 1998, Naff *et al.*, 1998b; Zhang and Seo, 2004; Dagan, 2004]. The ergodic coefficients correspond to the “ensemble coefficients” introduced by Attinger *et al.* [1999] (where the ensemble and effective coefficients are defined by the time derivative of the corresponding variances related by (8)). Under the assumption of statistical homogeneity of the log hydraulic conductivity the ensemble coefficients were also shown to be independent of the shape and dimension of the initial plume and equal to the coefficients for the case of a point source [Dentz *et al.*, 2000b; Clincy and Kinzelbach, 2001]. Zhang and Seo [2004] have shown that, even in anisotropic media, the longitudinal and transverse ergodic second moments given by theory can be retrieved in numerical simulations by using the relation (9). However, analyzing the fluctuations of the longitudinal effective coefficient from realization to realization, Naff *et al.* [1998b] found a “non-ergodic behavior”, indicated by the increase of the fluctuations with the transverse dimension of the plume, and suggested that the approach to a quasi-ergodic state is more complicated than described by the equation (10). In the following we investigate this issue in the light of our GRW simulations.

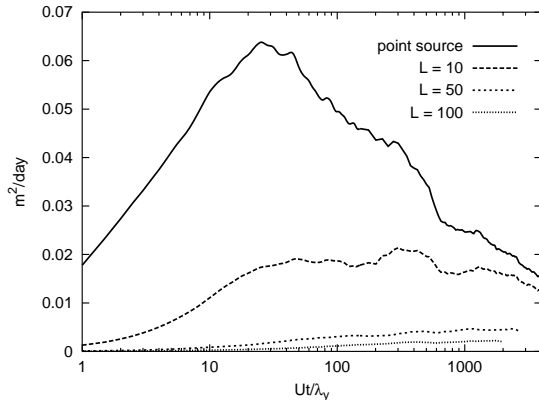
[41] The longitudinal center of mass coefficient decreases with the plume dimension (figure 10) and the ergodic coefficient derived from (10) is practically independent of the plume dimensions (figure 11). This agrees with the result for the ergodic second moments of the plume obtained by Zhang and Seo [2004, figure 5] and the results for the longitudinal center of mass coefficient in [Naff *et al.*, 1998b, figure 14].  $D_{il}^{cm}$  is the deviation of the mean slope, given by the left side of (10), from the ergodic coefficient. When  $D_{il}^{erg}$  is the theoretical coefficient (given for instance by first-order approximations),  $D_{il}^{cm} = 0$  is the ergodicity condition (e1) written for a range  $\eta_l = 0$ . The increase of fluctuations with the plume dimension reported by Naff *et al.* [1998b, figure 15] simply means that the vanishing center of mass coefficients in (10) is not sufficient to ensure the ergodicity of the mean slope of the second moment of the plume. Even though the center of mass coefficients become negligible quantities and the ensemble averaged slope approach the ergodic coefficient, the sample-to-sample fluctuations can be still large. This situation is dramatically illustrated in the case of the transverse coefficients. After 1000 advection times the first ergodicity condition (e1) is fulfilled within a range two orders of magnitude smaller than the local dispersion coefficient, as shown by the behavior of  $D_{22}^{cm}$  in figure 12. The fluctuations of the mean slope (10), which are equal to the fluctuations of the effective coefficients in figure 8, indicate that the second condition (e2) is not fulfilled in the same range. Moreover, the larger the transverse dimension of the plume is, the less ergodic the transverse coefficients are.

[42] We comment here that the coefficient corresponding to  $L = 100$  in figure 13 has negative values at early times. This non-physical behavior occurs because in the left side of (10) the contribution of the initial plume was extracted from the total variance. This “bad result” shows that the definition of the effective coefficients by the mean slope of the variance fails to describe the plume at finite times. We also note that the negative effective transverse dispersivities obtained by Zhang *et al.* [1996] are due to their definition by the local slope of the second moment, and are not “an artifact of the first-order approximation”, as the authors suggest. It is indeed easy to see that there are no negative values if the dispersivities are computed by using the positively defined coefficient (2) and the variances shown in figure 2b of the quoted paper.

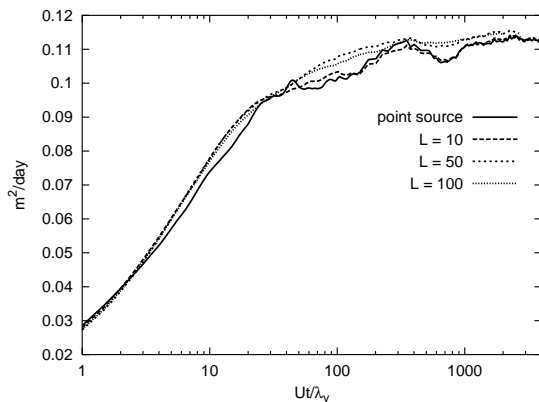
[43] The large differences between the coefficient for point source and the coefficients for  $L \geq 10$  shown in figure 13 prove that for plumes with large transverse dimensions the



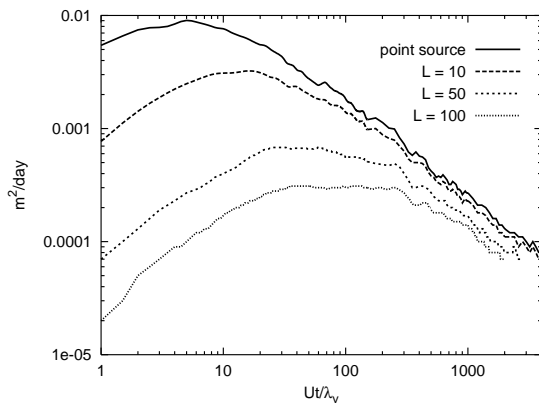
ergodic coefficient for pre-asymptotic regime cannot be defined by (10). Unlike the center of mass coefficients (figure 12) which go to zero, the differences between the ergodic coefficients increase with the plume dimension. These deviations can be neglected only for small plumes (as was the case for  $L \leq 4$  in [Zhang and Seo, 2004], figures 5b,c). This dependence on the plume dimension could be a consequence of the inherent non-homogeneity of the numerically generated velocity field. But, in practice, the statistical homogeneity is always an approximation. This is shown, for instance,



**Figure 10.** Time behavior of the longitudinal center of mass coefficient  $D_{11}^{cm}$



**Figure 11.** Time behavior of the longitudinal ergodic coefficient  $D_{11}^{erg}$



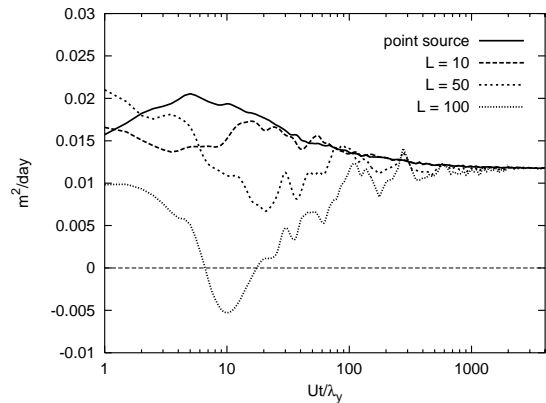
**Figure 12.** Time behavior of the transverse center of mass coefficient  $D_{22}^{cm}$

by the behavior of the confidence intervals rendered by the uncertainty of the statistical parameter estimates in carefully designed laboratory experiments [Fernandez-Garcia et al., 2005b], which are very similar to those for the numerical velocity field presented in figure B7. However, even if the lack of strict statistical homogeneity can produce the small differences for the longitudinal coefficients in figure 11, it does not explain the large differences shown in figure 13. Therefore, the very validity of the relation (10) can be questioned.

[44] The assumption that the average over initial positions permutes with the average over the realizations of the velocity field, on which (10) is based, is not always true. For instance, when local dispersion was neglected and the transport process was described in a Lagrangian framework, the above permutation of averages was possible only under the “simplifying assumption of ergodicity in the plume spatial moments” [Sposito and Dagan, 1994, p. 588] (carrying the implicit hypothesis of “dynamically identical” solute particles described by a single statistical ensemble [Sposito, 1997]). It was already shown by Sposito and Dagan [1994] that in the purely advective case the relation (10) is not complete if the interdependence between the initial positions and the velocities of the solute particles is taken into account. Because for Darcy flows such interdependencies cannot be ignored (unless some restrictions on the flow domain are imposed) [Sposito, 1997; 2001], it follows that in general the relation (10) is not true. Since the dynamical system approach used in the papers quoted above is restricted to the advective case, the description of the dispersion and its dependence on initial state, in the case of non-vanishing local dispersion, calls for further investigations based on appropriate methods.

## 5. Conclusions

[45] The results obtained in the present study, indicate that the numerical approach was appropriate for a numerical investigation on the ergodicity of transport in heterogeneous aquifers. The requirements of accurate concentration in every realization of the random field, long time simulations of transport and large statistical ensembles of realizations were carried out with the GRW algorithm. The large scale simulations were also possible owing to the fast generator of the first order approximated Darcy velocity fields, based on the Kraichnan routine. The approximation of the Gaussian random velocity fields with periodic fields was shown to be reliable for 6400 modes in the Kraichnan algorithm. The quantitative assessment of ergodicity for space averaged



**Figure 13.** Time behavior of the transverse ergodic coefficient  $D_{22}^{erg}$

concentrations and effective diffusion coefficients was done via comparisons with a rigorous mathematical result on the existence of the up-scaled macrodispersion process which describes the ensemble averaged concentration asymptotically.

[46] A numerical evidence for the asymptotic ergodic behavior of the two-dimensional transport was supplied by the simulations in the case of point-like and small initial plumes. The time to reach acceptably small deviations from the predictions of the macrodispersion model is of thousands of advection time scales. In rapidly fluctuating velocity fields with advection times of the order of seconds, for instance in the case of turbulent transport in atmosphere, the ergodic behavior manifests after a few hours. Since the advection times in groundwater are of the order of days, the ergodic behavior in a strict sense can be expected when the plume has traveled tens of years. This could be useful in applications for persistent contaminants, like the long life radionuclides.

[47] For sufficiently large initial plumes, the macrodispersion model can be used to predict the contamination with errors that could be acceptable in forecasting at smaller time scales. For instance, when the initial plume extends over one hundred heterogeneity scales across the direction of the mean flow, and the solute plume has traveled hundreds of heterogeneity scales, the “three sigma” rule indicates that the cross-section averaged concentration and the longitudinal effective coefficient in given realizations can be predicted within a range of uncertainty of about 90%. This uncertainty remains almost constant over thousands of heterogeneity scales. In the same conditions, the uncertainty of the transverse coefficient is tens of times larger.

[48] Nevertheless, the common belief that large plumes have ergodic behavior should be amended. The fluctuations from realization to realization have an intricate non-linear dependence on the transverse dimension of the initial plume, for both cross-section space averaged concentrations and effective diffusion coefficients. For concentration and longitudinal effective coefficient, the fluctuations decrease when the transverse plume dimension is larger than ten correlation lengths, but the travel time to reach the monotonous decay towards a quasi-ergodic state is much larger than for small sources. For the transverse effective coefficient the fluctuations increase with the dimension of the initial plume at all times. It is expected that the time scale which characterizes the ergodicity increases like the square of the transverse dimension of the initial plume.

[49] The evolution of the ensemble averaged effective coefficients also show features not accounted for by the existing theory. The slope of the displacements variance, often used to estimate the effective coefficients, yields non-physical (negative) estimations of the transverse coefficients at tens of advection time scales. Therefore, the rate of increase of the variance, which describes the spatial extension of the plume and is positively defined, is the appropriate definition for the effective coefficients. The condition of vanishing center of mass coefficient in the large time limit was also found to be not sufficient for the assessment of the ergodic behavior. The failure of the usual approach to define a transverse “ergodic coefficient” for extended initial plumes indicates a dependence on initial conditions, similar to the purely advective case, which deserves further investigations.

## Appendix A: Global Random Walk

### A1. The Algorithm

[50] The GRW algorithm is a generalization of particle tracking method which increases the speed of the computations and considerably improves the accuracy of the numerical simulations [Vamoş *et al.*, 2003]. The solution of a parabolic equation of form (1) is described using  $N$  particles which move in a grid, undergoing advective displacements

and diffusive jumps according to the random walk law. The concentration field at a given time  $t = k\delta t$  and at a grid point  $(x_1, x_2) = (i_1\delta x_1, i_2\delta x_2)$  is given by

$$c(x_1, x_2, t) = \frac{1}{N\Delta_1\Delta_2} \sum_{i'_1=-s_1}^{s_1} \sum_{i'_2=-s_2}^{s_2} n(i_1 + i'_1, i_2 + i'_2, k), \quad (A1)$$

where  $\Delta_l = 2s_l\delta x_l$ ,  $l = 1, 2$ , are the lengths of the symmetrical intervals centered at  $x_l$  and  $n(i_1, i_2, k)$  is the number of particles which at time step  $k$  lie at the grid point  $(i_1, i_2)$ .

[51] The one-dimensional GRW algorithm describes the scattering of the  $n(i, k)$  particles from  $(x_i, t_k)$  by

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

where  $v_j$  are discrete displacements in a given velocity field and  $d$  describes the diffusive jumps. The quantities  $\delta n$  are Bernoulli random variables and describe respectively, the number of particles which remain at the same grid site after an advective displacement, the number of particles jumping to the left and those jumping to the right (with respect to the advected position). The distribution of the particles at the next time  $(k+1)\delta t$  is given by

$$n(i, k+1) = \sum_j \delta n(i, j, k).$$

The average number of particles undergoing diffusive jumps and the average number of particles remaining at the same node after the displacement  $v_j$  are given by the relations

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

$$\overline{\delta n(j, j+v_j, k)} = (1-r) \overline{n(j, k)},$$

where  $0 \leq r \leq 1$ . The diffusion coefficient  $D$  is related to the grid steps by the relation

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

For two and three-dimensional cases, the same procedure is repeated for all space directions.

[52] Because the total number of particles  $N$  contained in the grid is conserved, the GRW algorithm is stable. The condition  $r \leq 1$ , ensures that there is no numerical diffusion. In [Vamoş *et al.*, 2003] it was shown that for Gaussian diffusion the numerical solution converges as  $\mathcal{O}(\delta x^2) + \mathcal{O}(N^{-1/2})$ , i.e. for large numbers of particles the convergence order is  $\mathcal{O}(\delta x^2)$ , the same as for the finite differences scheme. A comparison with a particle tracking code (diffusion over ten time steps of  $N$  particle starting at the center of a cubic grid) shows that while in GRW algorithm there is practical no limitation,  $N > 10^9$  particles becomes prohibitive for the particle tracking method.

[53] The “reduced fluctuations” GRW algorithm is defined by

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

where  $n = n(j, k) - \delta n(j, j+v_j, k)$ ,  $[n/2]$  is the integer part of  $n/2$  and  $\theta$  is a variable taking the values 0 and 1 with probability 1/2. This algorithm is appropriate for large scale problems, for two reasons. Firstly, the diffusion front does not extend beyond the limit concentration defined by one particle at a grid point, keeping a physical significant shape (unlike in finite differences where a pure diffusion front has

a cubic shape of side  $\sim (2Dt)^{1/2}$ ). Secondly, the “reduced fluctuations” algorithm requires only a minimum number of calls of the random number generator. The figure 1A illustrates the reduced fluctuations GRW algorithm for  $r = 1$  and the figure 2A presents the resulting concentration field computed by (A1).

[54] In the following we describe the computation of the diagonal effective coefficients, according to the GRW algorithm. The variance of particles displacements,  $\sigma_{il}^2$ ,  $l = 1, 2$ , in dimensionless form, is given by

$$\frac{1}{(\delta x)^2} \sigma_{il}^2(k\delta t) = \frac{1}{N} \sum_{i_1, i_2} i_l^2 n(i_1, i_2, k) - \left[ \frac{1}{N} \sum_{i_1, i_2} i_l n(i_1, i_2, k) \right]^2. \quad (\text{A2})$$

Using (A2), the effective coefficients are computed as

$$D_{il}^{eff}(k\delta t) = \sigma_{il}^2 / (2k\delta t).$$

[55] Let us consider  $N_{x_0}$  points uniformly distributed inside the initial plume,  $N/N_{x_0}$  particles at each initial point and let  $n(i_1, i_2, k; i_{01}, i_{02})$  be the distribution of particles at the time step  $k$  given by the GRW procedure for a diffusion process starting at  $(i_{01}\delta x_1, i_{02}\delta x_2)$ . Writing the distribution for the extended plume as

$$n(i_1, i_2, k) = \sum_{i_{01}, i_{02}} n(i_1, i_2, k; i_{01}, i_{02}),$$

the averages from (A2) can be rewritten in the form

$$\frac{1}{N} \sum_{i_1, i_2} \alpha n(i_1, i_2, k) = \frac{1}{N_{x_0}} \sum_{i_{01}, i_{02}} \left( \frac{N_{x_0}}{N} \sum_{i_1, i_2} \alpha n(i_1, i_2, k; i_{01}, i_{02}) \right), \quad (\text{A3})$$

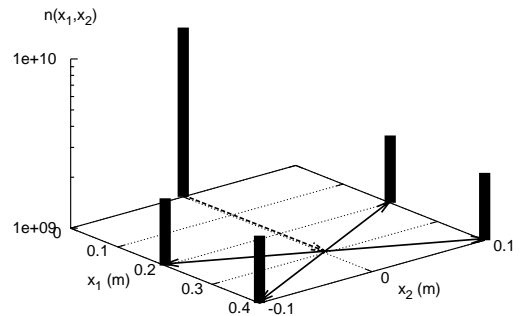
where  $\alpha$  stands for  $i_l$  and  $i_l^2$  respectively. It follows from (A3) that the variance (A2) is an average over the trajectories of the diffusion process starting at given initial positions and over the distribution of the initial positions.

## A2. GRW Parameters

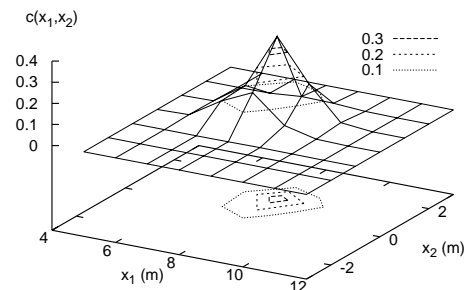
[56] The large scale computations reported in [Schwarze *et al.*, 2001; Dentz *et al.*, 2002, 2003] were performed with the particle tracking procedure. Although it was possible to obtain estimations of the ensemble averaged effective coefficients, the number of particles used in these simulations, limited due to computational reasons at  $N \sim 100$ , does not suffice to simulate accurate concentrations. Even in small scale one-dimensional problems, more than one million particles should be used in particles methods to reach the same precision as the finite difference scheme [Vamos̄ *et al.*, 2003]. Moreover, in [Suci *et al.*, 2004] it was shown that for the large scale transport problem considered here, a too small number of particles induces large numerical errors in the simulation of the time behavior of the effective coefficients. The statistical convergence of the simulations for a given realization of the velocity is ensured only when billions of particles are used. In the present numerical investigations the number of particles was fixed at  $N = 10^{10}$  so that all the simulations of transport realizations were statistically convergent.

[57] The other GRW parameters used for the computation of the ensembles of realizations presented in this paper are the space steps  $\delta x_1 = \delta x_2 = \delta x = 0.1$  m, the time step  $\delta t = 0.5$  day and the amplitude of the diffusive jumps (see

Appendix A1)  $d = 2$ . The accuracy of the numerical velocity field is governed by the ratio of the log-hydraulic conductivity correlation length to the space step. In our case,  $\lambda_y/\delta x = 10$  and fulfils the condition  $\lambda_y/\delta x \geq 4$ , generally recommended in literature [Ababou *et al.*, 1989; Hassan *et al.*, 1998]. To reduce the “overshooting” errors in particles methods one imposes that the mean displacement in a time step does not surpass a given threshold [Roth and Hammel, 1995; Janković *et al.*, 2003]. In [Suci *et al.*, 2004] it was shown that, for the same overshooting, the error in GRW simulations is mainly influenced by the discretization of the velocity, as described by the parameter  $U\delta t/\delta x$ . Our choice  $U\delta t/\delta x = 5$  means that, in average, the particles overpass 5 space steps, but it also means that the smallest advective displacement accounted for in the GRW procedure is  $\delta x/\delta t = U/5 = 0.2$  m/day. The tests for a crude estimation of the discretization errors, for fixed  $\delta t = 0.5$  day and increasing  $U\delta t/\delta x$  from 5 to 10 ( $\delta x/\delta t$  from 0.2 m/day to 0.1 m/day), show that the simulated effective coefficients differ with less than 2% (N. Suci *et al.*, *Internal Report ICG-IV 00204, Forschungszentrum Jülich*, 2004). A comparison for the first 100 days with a GRW algorithm without overshooting led to error estimations for the effective coefficients in given realizations, calculated with the GRW procedure and the parameters used in this paper, which were one order of magnitude smaller than the up-scaled coefficients (6) (N. Suci *et al.*, *Manuscript in preparation*, 2005).



**Figure A1.** Advective displacement and diffusive jumps of  $10^{10}$  particles starting at  $(0, 0)$ , for  $d = 1$  and  $r = 1$ .



**Figure A2.** Concentration field, according to (A1), at  $t = 10\delta t$ , for  $\delta x_1 = \delta x_2 = 0.1$  m and  $\Delta_{x_1} = \Delta_{x_2} = 1$  m.

## Appendix B: Large Scale Simulations

### B1. The Transport Problem

[58] The transport depends on both the heterogeneity of the advection velocity field, described by the variance of the log hydraulic conductivity  $\sigma_y^2$ , and the local dispersion coefficient  $D$ . To select the parameters to be used in the present numerical investigations, several combinations of  $\sigma_y^2$  and  $D$  were investigated in the case of point source (N. Suciú et al., *Internal Report ICG-IV 00204, Forschungszentrum Jülich*, 2004). The diffusion fronts, defined by grid points containing at least one particle, are compared in figure B1. We note that large variances of the log-hydraulic conductivity ( $\sigma_y^2 = 1$ ) yield non-Gaussian asymmetric plumes.

[59] It should be noted that the asymmetry of the diffusion fronts can be due to a numerical artifact occurring in all the two-dimensional simulations based on particles methods. In the absence of the third component of the velocity, the probability of occurrence of very small or null advection displacements is high enough to delay some particles with respect to the plume center of mass. This effect is compensated by diffusive displacements, when the local dispersion is large enough [Suciú et al., 2002]. At the limit of zero local dispersion, trapping zones occur causing the fragmentation of the plume and the linear increase of the effective coefficients [Dentz et al., 2003]. Therefore, the usefulness of the two-dimensional simulations based on particles methods is limited to small variability of the velocity and non-vanishing local dispersion.

[60] The averages of the effective coefficients, over 256 realizations of the velocity, for fixed  $\sigma_y^2 = 0.1$  and three different values of the local dispersion coefficients ( $D = 0.01$  m<sup>2</sup>/day,  $D = 0.001$  m<sup>2</sup>/day, and  $D = 0.0001$  m<sup>2</sup>/day respectively) are presented in the figures B2 and B3 as functions of time and the corresponding Péclet numbers  $Pe = U\lambda_y/D$ . The comparisons from figures B2 and B3 show that, besides the small asymmetry shown in figure B1, the increase of  $Pe$  considerably increases the time necessary to reach the asymptotic coefficients  $D_{11}^*$ .

### B2. The Number of Periods $Np$ , the Number of Realizations $R$ and the Correlation Shape

[61] The periodic fields generated with the Kraichnan algorithm approximate Gaussian fields for  $Np \rightarrow \infty$ . While ensemble averages are well approximated for tens of periods  $Np$  in the Kraichnan routine [Jaekel and Vereecken, 1997; Schwarze et al., 2001], to approximate fluctuations much larger  $Np$  are necessary [Eberhard, 2004]. To assess the value of  $Np$  we compared the fluctuations of the cross-section concentration and of the longitudinal effective coefficient, for fixed number of realizations  $R = 1024$ , considering exponential and Gaussian shape of the correlation of the log hydraulic conductivity, with the same  $\lambda_y = 1$  m and  $\sigma_y^2 = 0.1$ . The results presented in figure B4 and figure B5 suggest that  $Np$  must be at least as large as the total number of time steps in simulations. (The fluctuations of the transverse coefficient, not presented here, are already reliable for  $Np = 64$ .) Therefore, for times up to  $t = 4000\lambda_y/U$ , we used  $Np = 6400$  to approximate the behavior of the transport in Gaussian velocity fields.

[62] Figure B6 presents the fluctuations of the longitudinal effective coefficient for fixed  $Np = 6400$  and increasing number of realizations  $R$ , in the case of exponential correlation of the log hydraulic conductivity. The increase of  $R$  from 256 to 1024 has little influence on the time behavior of the fluctuations. We also found that  $R = 256$  ensures

the statistical reliability for all the quantities investigated in this study.

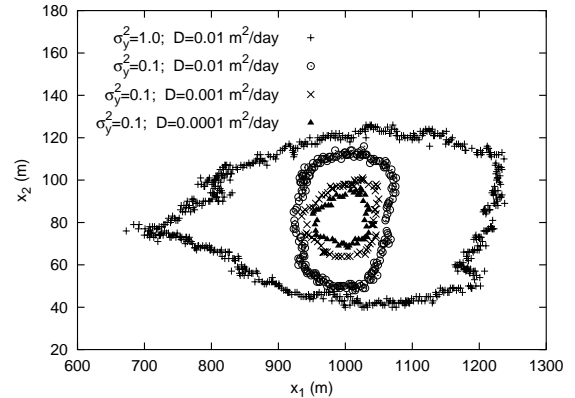


Figure B1. Diffusion fronts at  $t = 1000$  days.

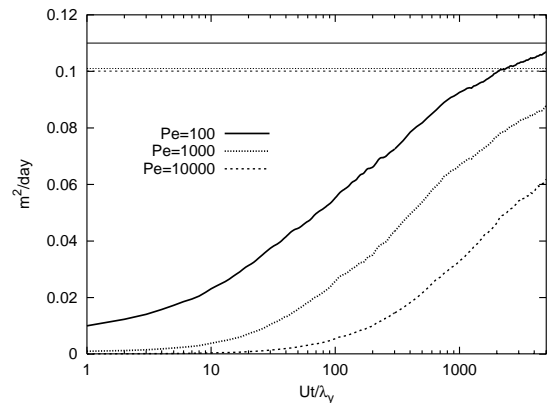


Figure B2. Longitudinal ensemble averaged effective coefficient  $\langle D_{11}^{eff} \rangle$  for different Péclet numbers.

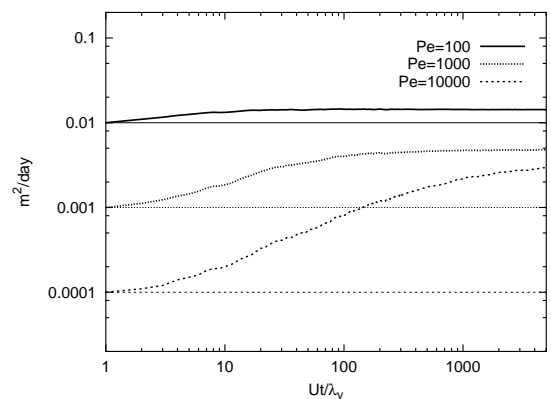
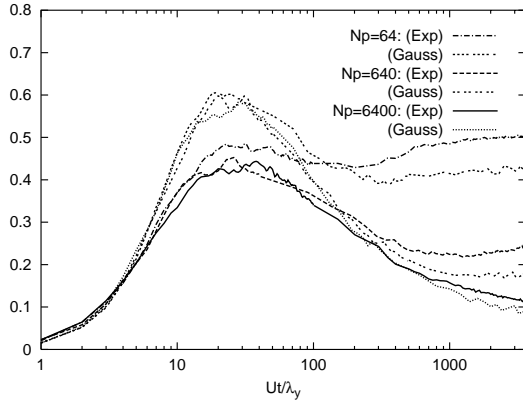
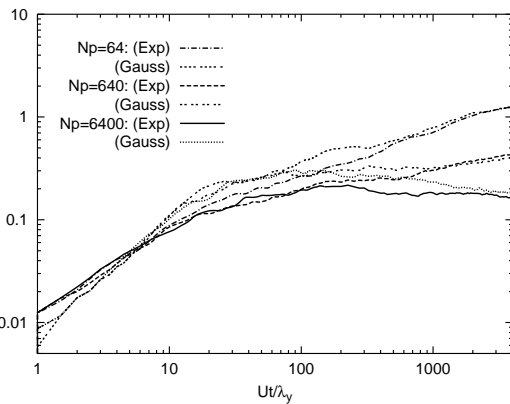


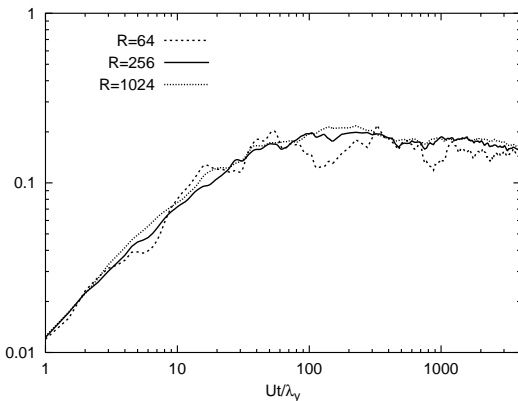
Figure B3. Transverse ensemble averaged effective coefficient  $\langle D_{22}^{eff} \rangle$  for different Péclet numbers.



**Figure B4.** Concentration fluctuations at the plume center of mass for  $R = 1024$  and different  $Np$ .



**Figure B5.** Fluctuations of the longitudinal effective coefficient for  $R = 1024$  and different  $Np$ .



**Figure B6.** Fluctuations of the longitudinal effective coefficient for  $Np = 6400$  and different  $R$ .

### B3. The Statistics of the Darcy Velocity Fields

[63] In most of numerical studies on the stochastic model [Chin and Wang, 1992; Bellin et al., 1992; Salandin and Fiorotto, 1998; Naff et al., 1998a; Hassan et al., 1998] the Eulerian statistics of the numerically generated veloc-

ity fields was estimated, under the implicit assumption of statistical homogeneity, by space averages in given realizations followed by averages over realizations. This procedure usually underestimates the true statistical parameters. To show that, let us consider the components of the velocity fluctuation  $u_l(\mathbf{x}) = V_l(\mathbf{x}) - U_l$ ,  $l = 1, 2$ , supposed to be statistically homogeneous variables, and the arithmetic mean over  $P$  space points  $\langle u_l(\mathbf{x}_p) \rangle_P = \frac{1}{P} \sum_{p=1}^P u_l(\mathbf{x}_p)$ . Because the realizations of the velocity computed at different space points belong to the same statistical ensemble, the order of the space and ensemble averages can be interchanged and due to the statistical homogeneity, we have the relations  $\langle \langle u_l \rangle_P \rangle = \langle \langle u_l \rangle_P \rangle = \langle u_l \rangle = 0$  and  $\langle \langle u_l^2 \rangle_P \rangle = \langle \langle u_l^2 \rangle_P \rangle = \langle u_l^2 \rangle$ . The average over realizations of the variance defined through space averages,

$$\langle \langle u_l^2 \rangle_P \rangle - \langle u_l \rangle_P^2 = \langle u_l^2 \rangle - \langle \langle u_l \rangle_P^2 \rangle,$$

underestimates the true variance  $\sigma_{u_l}^2 = \langle u_l^2 \rangle$  of the homogeneous variable  $u_l$  with the term  $\langle \langle u_l \rangle_P^2 \rangle$ , which is the variance of the space mean  $\langle u_l \rangle_P$ . The last quantity vanishes only when the space mean equals the ensemble mean  $\langle u_l \rangle_P = \langle u_l \rangle = 0$ . The numerical fields have poor ergodic properties and, as already noted by Bellin et al. [1992], they are not strictly statistically homogeneous. Therefore, the statistical properties of the numerical velocity fields should be investigated through ensemble averages followed by space averages. This procedure allows the estimation of the non-homogeneity. For instance, the mean velocity  $\langle u_l \rangle$  is estimated through space averages  $\langle \langle u_l \rangle_P \rangle$ , with the standard error of the mean given by

$$\sqrt{\frac{\langle \langle u_l \rangle_P^2 \rangle - \langle \langle u_l \rangle_P \rangle^2}{P-1}}.$$

In our present numerical investigations we used such standard errors to estimate the precision for the velocity moments.

[64] Using 512 velocity values generated by Kraichnan routine, at 512 different space points inside a square the side of which was  $10 \lambda_y$ , the velocity probability densities were found to be very close to Gaussian homogeneous distributions. The first three moments of the longitudinal and transverse velocity are presented in table B1. The first and third moment are close to zero. The longitudinal and transverse variances (the second line in table B1) are respectively  $\simeq \frac{3}{8} \sigma_y^2$  and  $\simeq \frac{1}{8} \sigma_y^2$ , in agreement with the first order asymptotic expansions of the Darcy and the continuity equations [Dagan, 1984].

**Table B1.** The first three moments of the longitudinal and transverse velocity components.

	$l = 1$	$l = 2$
$\langle \langle u_l \rangle_P \rangle$	$0.00214 \pm 0.00033$	$-0.00051 \pm 0.00021$
$\langle \langle (u_l - \langle u_l \rangle)^2 \rangle_P \rangle$	$0.03801 \pm 0.00010$	$0.01268 \pm 0.00004$
$\langle \langle (u_l - \langle u_l \rangle)^3 \rangle_P \rangle$	$-0.00014 \pm 0.00003$	$0.00000 \pm 0.00001$

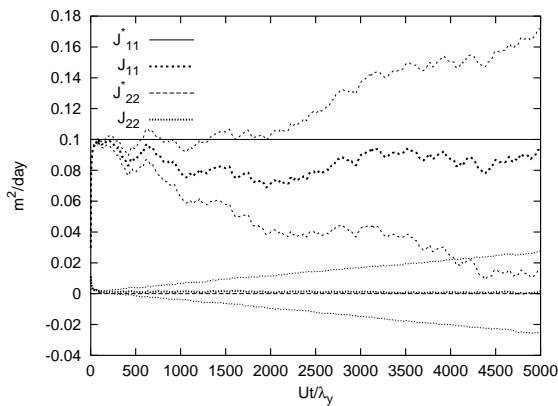
[65] The velocity correlations

$$r_u(x) = \langle \langle u_l(x_{01}, x_{02}) u_l(x_{01} + x, x_{02}) \rangle \rangle_P, \quad l = 1, 2,$$

were computed as averages over 512 realizations of the velocity and over  $P = 11011$  points  $(x_{01}, x_{02})$  (all the grid points in a band of  $\lambda_y \times 100 \lambda_y$ , which corresponds to the largest initial plume in the present simulations). The integrals of the correlation functions  $r_u$  give the numerical estimation of the second terms in (4), which describe the contribution of the velocity fluctuations to the up-scaled diffusion coefficients,

$$J_u(t) = \int_0^t r_u(Ut') dt' = \frac{1}{U} \int_0^{Ut} r_u(x) dx.$$

The numerical integrations between 0 and  $t = 5000\lambda_y/U$  of the correlation functions are presented in the figure B4. The values of  $J_{ii}$  are close to the theoretical values (6),  $J_{11}^* = D_{11}^* - D = 0.1 \text{ m}^2/\text{day}$  and  $J_{11}^* = D_{22}^* - D = 0 \text{ m}^2/\text{day}$ . Because the correlations computed by ensemble averages  $\langle u_i(x_{01}, x_{02})u_i(x_{01} + x, x_{02}) \rangle$  differ from point to point, i.e. the random field is not strictly homogeneous, at large distances the upper estimate of  $r_{ii}$  (i.e. space mean plus standard error) is mainly positive and the lower estimate mainly negative. As a direct consequence, the confidence intervals of  $J_{ii}$  grow linearly with  $x$  (see thin lines in figure B4). Since the standard errors decrease as  $(P-1)^{-1/2}$ , reliable estimations of the up-scaled effective dispersion coefficients require averaging over large space domains. This remark is valid not only in the case of numerical fields generated by the Kraichnan algorithm but also for all large scale numerical simulations, where the accumulation of the numerical errors can result in large uncertainty of the numerical estimations.



**Figure B7.** The progress of the time integral of the velocity correlation functions; mean values and confidence intervals.

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