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STATE OF THE ART ON UPSCALING TECHNIQUES MILESTONE (N°:M2.2.D.2**)**

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Foreword

The work presented in this report was developed within the Integrated Project PAMINA: **P**erformance **A**ssessment **M**ethodologies **I**N **A**pplication to Guide the Development of the Safety Case. This project is part of the Sixth Framework Programme of the European Commission. It brings together 25 organisations from ten European countries and one EC Joint Research Centre in order to improve and harmonise methodologies and tools for demonstrating the safety of deep geological disposal of long-lived radioactive waste for different waste types, repository designs and geological environments. The results will be of interest to national waste management organisations, regulators and lay stakeholders.

The work is organised in four Research and Technology Development Components (RTDCs) and one additional component dealing with knowledge management and dissemination of knowledge:

- In RTDC 1 the aim is to evaluate the state of the art of methodologies and approaches needed for assessing the safety of deep geological disposal, on the basis of comprehensive review of international practice. This work includes the identification of any deficiencies in methods and tools.
- In RTDC 2 the aim is to establish a framework and methodology for the treatment of uncertainty during PA and safety case development. Guidance on, and examples of, good practice will be provided on the communication and treatment of different types of uncertainty, spatial variability, the development of probabilistic safety assessment tools, and techniques for sensitivity and uncertainty analysis.
- In RTDC 3 the aim is to develop methodologies and tools for integrated PA for various geological disposal concepts. This work includes the development of PA scenarios, of the PA approach to gas migration processes, of the PA approach to radionuclide source term modelling, and of safety and performance indicators.
- In RTDC 4 the aim is to conduct several benchmark exercises on specific processes, in which quantitative comparisons are made between approaches that rely on simplifying assumptions and models, and those that rely on complex models that take into account a more complete process conceptualization in space and time.

The work presented in this report was performed in the scope of RTDC 2.

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INDEX

PART 1 – Upscaling of Flow Parameters

- 1. Introduction**
- 2. Block conductivity**
 - 2.1. Definition
- 3. Evolution of block conductivity upscaling**
 - 3.1. Local techniques
 - 3.2. Non-local techniques
 - 3.3. Block Geometry
 - 3.4. Direct block-conductivity generation
- 4. Summary**

REFERENCES

PART 2 – Upscaling of Transport Parameters

A - Upscaling transport under the Fickian Approach

- 1. Basic definitions and transport processes**
- 2. The stochastic approach**
 - 2.1 Definitions and fundamental assumptions
 - 2.2 Covariance function and spectral representation
 - 2.3 Eulerian derivation of macrodispersion
 - 2.4 A few analytical solutions
- 3. Fractal models of heterogeneity**
 - 3.1 Application to solute transport
 - 3.2 Fractal geometry and spectral analysis
- 4. Inclusion models**
 - 4.1 Conceptual model
 - 4.2 Advective transport by the Lagrangian approach
- 5. Conclusions**



B - Upscaling transport parameters under the non-Fickian Approach

1. Introduction

2. Continuous Time Random Walk Framework

- 2.1. Conceptual Picture. Tracer transitions
- 2.2. Basic Formulation of Transport
- 2.3. CTRW Transport Equations
- 2.4. Numerical Inversion of Laplace Transforms
- 2.5. Critique of the CTRW Approach

3. Advection-Dispersion Equation and Upscaling

- 3.1. Volume Averaging
- 3.2. Stochastic Approach

4. Alternative Effective Transport Formulations

- 4.1. Multirate Mass Transfer
- 4.2. Fractional Derivative Equations

5. Conclusions

REFERENCES



PART 1

UPSCALING OF FLOW PARAMETERS

PART 1 – UPSCALING OF FLOW PARAMETERS

Hydraulic conductivity upscaling is a process that transforms a grid of hydraulic conductivity defined at the scale of the measurements, into a coarser grid of block conductivity tensors amenable for input to a numerical flow simulator. The need for upscaling stems from the disparity between the scales at which measurements are taken and the scale at which aquifers are discretized for the numerical solution of flow and transport.

The techniques for upscaling range from the simple averaging of the heterogeneous values within the block to sophisticated inversions, after the flow equation at the measurement scale within an area embedding the block being upscaled.

All techniques have their own advantages and limitations. The definition of the geometry of the grid has been intimately linked to the upscaling problem; promising results have been obtained using elastic gridding. The need to perform Monte-Carlo analyses, involving many realizations of hydraulic conductivity, has steered the development of methods that generate directly the block conductivities in accordance with the rules of upscaling, yet conditional to the measurement data.

1. Introduction

An important issue in the numerical simulation of groundwater flow and mass transport is the problem of scales. Data are collected at a scale different from (usually smaller than) the one used to discretize the aquifer in the numerical model. For instance, field sampled hydraulic conductivities (e.g. from core measurements, slug tests or packer tests) have measurement supports in the order of centimetres to meters, whereas numerical models for groundwater flow require conductivities representative of tens to hundreds of meters.

Since the 1960s different approaches have been used to transform a detailed description of the spatial variability of hydraulic conductivity to a coarser description, as sketched in Fig.1.

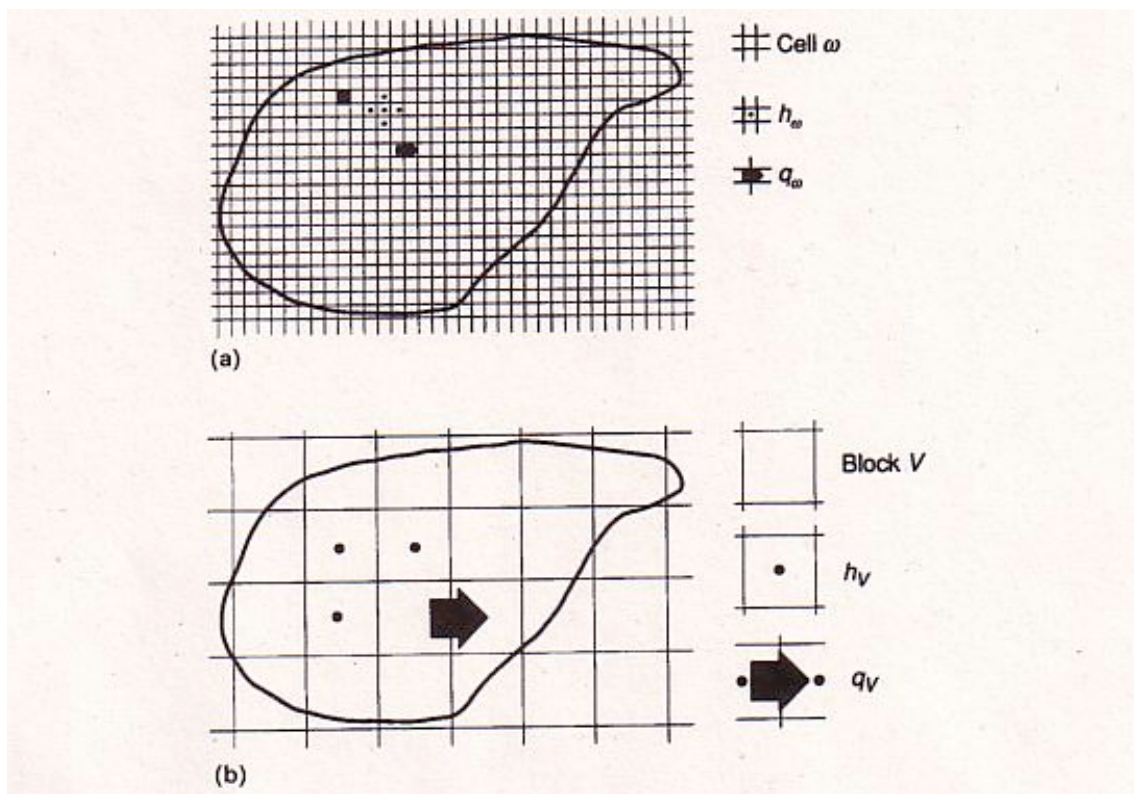


Fig. 1.- The upscaling process. (a) Grid at the measurement scale, with possibly millions of cells. (b) Grid at the numerical scale on which the flow problem will be solved. Computing the conductivity block values in (b) from the corresponding values in (a) is the objective of upscaling.

We will refer to the scale corresponding to the detailed description in Fig. 1(a) as the measurement scale, and to the scale corresponding to the coarser description in Fig. 1(b) as the numerical scale. We will use the terms cell conductivity and block (or equivalent) conductivity to refer to conductivity values at the measurement and numerical scales respectively. We do not discuss the ways in which a grid at the measurement scale can be produced from a few sparse measurements, we will just mention that, in general, such a grid is filled by some (geo) statistical technique (see for instance Deutsch and Journel, 1992). Our starting point is a grid (or several) of conductivity values at the measurement scale that is (are) to be “upscaled” to the numerical scale for input to a numerical groundwater flow simulator.

Some authors use the term “effective conductivity” to refer to block conductivities. We choose not to use it in this sense to avoid confusion with the specific meaning that effective conductivity has in stochastic hydrogeology. The effective conductivity defined in stochastic hydrogeology is a property of the random function model adopted to describe the spatial variability of conductivity: it is not a block property but a point property representing an average process through the ensemble of possible realizations at a point. Only under certain random function models, the effective conductivity is constant in space and coincident with the block conductivity of an infinite block (Matheron, 1967; Dagan, 1979, 1982a,b, 1989). In this respect, effective conductivities can be used as a partial check of upscaling techniques. Although effective conductivities have been the subject of many studies (e.g. Matheron, 1967; Dagan, 1979, 1982a, 1989; Gutjahr et al., 1978, Gelhar and Axness, 1983; Poley, 1988; Ababou and Wood, 1990; Naff 1991; Neuman and Orr, 1993) they are not addressed in this work. The interested reader should refer to the work of Neuman and Orr (1993) which presents the most general results. This document is organized as follows. First, block conductivity is defined, then a review of upscaling methods in a sequence of increasing complexity is given. We include only upscaling methods that deal with single-phase saturated conductivity. Readers interested in conductivity upscaling for unsaturated flow are referred to Yeh et al. (1985), Mantoglou and Gelhar (1987) and Russo (1992). Readers interested in multiphase flow are referred to Haldorsen (1986), Muggeridge (1991) and Fayers and Hewett (1992).

2. Block conductivity

The usage of the terms equivalent, block, effective or upscaled, applied to conductivity, instead of the simpler usage of the term average, reflects the fact that the conductivity is not an additive property. It is well known for electrical conductance analogy that the equivalent conductivity for a group of cells serially arranged is equal to their harmonic average, whereas if the cells are arranged in parallel the equivalent conductivity is equal to the arithmetic average. Cardwell and Parsons (1945) proved that the equivalent conductivity of a heterogeneous block is bounded above and below by the arithmetic and harmonic averages, respectively.

2.1. Definition

Following Rubin and Gómez-Hernández (1990), block conductivity, $\mathbf{K}_V$ is defined from an extension of Darcy's law as:

$$\frac{1}{V} \int_V \mathbf{q}_w(\mathbf{u}) d\mathbf{u} = -\mathbf{K}_V \left(\frac{1}{V} \int_V \nabla h_w(\mathbf{u}) d\mathbf{u} \right) \quad (1)$$

where:

V : represents the block support

$\mathbf{q}_w$ is the specific discharge vector at cell w within the block

$\mathbf{u}$ is the position vector that sweeps the inside of the block

∇h_w is the gradient of the piezometric head at w .

Vector integration is performed by integration of its components. In words, block conductivity is the tensor that relates the block spatial average of the specific discharge vector to the spatial average of the piezometric head gradient vector.

The cell conductivities $\mathbf{K}_w$ are implicit in Eq. (1) since $\mathbf{q}_w$ and ∇h_w are related at the measurement scale through $\mathbf{K}_w$:

$$\mathbf{q}_w = -\mathbf{K}_w \nabla h_w$$

Notice that, by definition, $\mathbf{K}_v$ is, like $\mathbf{K}_w$, a tensor.

In the different approaches to upscaling described next, the definition in Eq. (1) is not always explicitly adopted; in some cases it is implicit to the formulation, in others, alternative definitions are employed. When the latter occurs, the alternative definition is indicated. However, in all cases, the purpose of the upscaling procedure is to obtain a description of conductivity spatial variability at the numerical scale that reproduces some average behaviour of the conductivity field at the measurement scale.

3. Evolution of block conductivity upscaling

We start with the local techniques, that is, those techniques that assume that the block conductivity tensor is intrinsic to the cell conductivities within the block. Then we continue with the non-local techniques, in which block conductivities depend not only on the cell conductivities within the block, but also on the flow boundary conditions necessary to determine $\mathbf{q}_w$ and ∇h_w in Eq. (1). Then, another set of techniques in which the definition of block geometry becomes part of the upscaling problem is presented. Finally, a set of techniques for the direct generation of numerical scale grids from measurement scale data is presented.

3.1. Local techniques

Local techniques consider that block conductivity is intrinsic to the cell conductivities within the block as would be the case if block conductivity is a material property. Local techniques are the natural extension of the one-dimensional results, for which it is known that block conductivity is equal to the harmonic average of the heterogeneous conductivities. In the local techniques the block conductivity is an explicit function of the cell conductivities. The methods described in this subsection rely on the assumption that the cell conductivity tensor $\mathbf{K}_w$ degenerates into a scalar K_w . The simple average approach and the renormalization technique also assume that the resulting block conductivity tensor $\mathbf{K}_V$ is also a scalar K_V . While the first assumption can be justifiable, the second one is more difficult to justify, since the tensorial nature of block conductivities is partly a consequence of the anisotropic spatial correlation of cell conductivities (Lake, 1988), even for the case of scalar cell conductivities.

3.1.1. Simple average

For 1-D flow, block conductivity is equal to the harmonic mean of the cell conductivities within the block. For 2-D flow, there is a very strong result from the theory of effective parameters (Matheron, 1967) that applies for infinite blocks with heterogeneous conductivities having an isotropic spatial correlation and a frequency

distribution which is identical to the frequency distribution of their reciprocals (as is the case if conductivity follows a lognormal distribution). Matheron (1967) proved that, under these conditions, block conductivity is equal to the geometric mean. This result, which, in principle, applies only to infinite blocks has been used extensively in the petroleum and hydrology literature for finite blocks without much justification (e.g. Dagan, 1982b, 1985; Clifton and Neumann, 1982; Hoksema and Kitanidis, 1984, 1985).

Through numerical experiments in 3-D, Warren and Price (1961) concluded that the geometric average is the most appropriate estimator of block conductivities for spatially uncorrelated cell values. Bouwer (1969) used analog simulations to arrive to the same conclusion.

Grindheim (1990) and Durlafsky (1992) investigated the use of simple average methods to compute block conductivities in 2-D for different spatial distribution of the cell conductivities (uncorrelated and correlated, statistically isotropic and anisotropic, and sand-shale binary distributions). Some of the averages investigated include: arithmetic, geometric, harmonic, arithmetic-harmonic and harmonic-arithmetic. By comparing the flow results in the grid at the measurement scale and the flow results in the upscaled grid they concluded that there is no simple average that is valid for all heterogeneous formations.

Gómez-hernández and Wen (1994) showed that, in 2-D, the geometric mean gives good estimates of the block conductivity as long as the spatial variability of cell conductivities does not display a strong anisotropy.

3.1.2. Power average

Cardwell and Parsons (1945) proved that block conductivities must lie in between the arithmetic and harmonic averages of the cells within the block. Based on this statement, Journel et al. (1986) proposed the use of a power average to compute equivalent block conductivities:

$$\mathbf{K}_V = \left(\frac{1}{V} \int_V \mathbf{K}_w^p(\mathbf{u}) d\mathbf{u} \right)^{1/p}$$

by varying the exponent p between -1 and 1, the power average varies between the harmonic and the arithmetic averages, with the geometric mean corresponding to $p=0$. They argue that the exponent p depends on the specific type of cell conductivity spatial heterogeneity and can be obtained by calibration with the results obtained from detailed numerical simulations in a fraction of the blocks being upscaled. The technique was later successfully applied by Deutsch (1989), Gómez-Hernández and Gorelick (1989), Bachu and Cuthiell (1990), Desbarats and dimitrakopoulos (1990) and Desbarats (1992b).

Some of their findings are:

- (i) the power p is case-specific and is function of the type of heterogeneity within the block, the block shape and size, and the flow conditions within the block
- (ii) for the case of statistically anisotropic cell conductivities, p is direction dependent and can be used to identify the components of a block tensor given that their principal directions are known
- (iii) there is no simple way of predicting the value of p without resorting to detailed numerical experiments.

The attractions of this technique are its simplicity, the bounded range of p values, and that it can be used in 2-D and 3-D.

3.1.3. Renormalization

The so-called real-space renormalization technique, primarily developed for the study of critical phenomena in physics, such as percolation (Kirkpatrick, 1973; Wilson, 1979; shah and Ottino, 1986) was applied for the first time to the computation of block conductivities by King (1989). The technique is based on the calculation of the block conductivity of a very small block (as small as 2 by 2 cells in 2-D) and then successively upscaled using self-repetitive geometry until the final block size is reached. The technique is extremely fast and is not limited by the domain size or variance of the cell conductivities. The speed of the technique relies on an analytical expression of the block conductivity for a 2 by 2 block, which is borrowed from the expression of the electrical conductance of a 2 by 2 resistor network. Initially King

(1989) applied renormalization to 2-D grids of spatially uncorrelated values. Later Shah and Ottino (1986) extended the technique to 3-D and Mohanty and Sharma (1990) to correlated fields. The method provides excellent results (when comparing flow simulations at the measurement and block scales) for statistically isotropic, lognormal conductivity fields. For strongly anisotropic media (such as sand-shale formations) the method did not perform well due to the poor resolution of the successive upscaling around the edges of the shales.

Williams (1989) developed a large cell method based on renormalization for the calculation of block conductivities for strongly anisotropic media with a fraction of impermeable material.

The big advantage of renormalization is its speed. The major drawback is that, implicit to the calculation of electrical conductance for a 2 by 2 resistor network in 2-D, there are boundary conditions applied to the sides of each 2 by 2 block which may be unrealistic. Malick (1995) demonstrated that these possibly unrealistic boundary conditions, when repeatedly applied during the course of renormalization, may cause several error in the final block conductivity estimate. He compared block conductivities obtained using Eq. (1) after the solution of the flow equation at the measurement scale. The error is as large as 70% for a lognormal distribution of conductivities when the coefficient of variation reaches 3 and could be up to 200% for sand-shale distributions with shale density of 50%.

3.1.4. Stream-tube

The stream-tube method (Haldorsen and Lake, 1984; Begg and King, 1985; Haldorsen and Chang, 1986; Begg and Carter, 1987; Begg et al., 1985, 1989) is specially designed to calculate block conductivities in sand-shale formation, that is, for formations in which shale's are dispersed in a homogeneous matrix of sandstone, with a large contrast between the conductivities of sand and shale's, so that horizontal shale's can be regarded as barriers for vertical flow. The thickness of the shale's is assumed to be negligible and they are distributed within the sand in a uniform direction (say, horizontally). In the direction parallel to the shale's, given their negligible width, the block conductivity is equal to the sandstone conductivity. In the direction orthogonal to

the shale's, these act as barriers that increase the tortuosity of the streamlines proportionally to the length and frequency of the shale's.

The block conductivity orthogonal to the shale's is related to the streamline lengths through a tortuosity factor. Begg and King (1985) and Begg et al. (1985, 1989) derived an expression of vertical block conductivity as a function of shale proportion and the statistics of shale length. This functional relation provides a block vertical conductivity without knowledge of the exact geometry of the shales within the block.

The stream-tube method has been widely used in the petroleum industry and demonstrated to give good results. However Desbarats (1987) showed that the method overestimates vertical conductivity when shale density is large, that is, when flow paths become very tortuous.

3.1.5. Flow anisotropy

Of the methods presented before, the power average and the stream-tube approach assumed that block conductivity could be a tensor. In the power average approach, the principal directions of the block conductivity are supposed to be parallel to the block sides, and a different power p is used to determine each principal component. In the stream-tube approach, the principal directions of the block conductivity are supposed to be parallel and orthogonal to the shale orientation. In some cases, it is not possible to be sure which are the principal orientations of the block conductivity tensor, nor to assume that all blocks have the same orientation.

Kasap and Lake (1989) were interested in computing block conductivity tensors when cross-bedding is observed at the measurement scale. This is a case in which the directions of the principal components of block conductivity cannot be known a priori, and can vary from block to block. They developed an analytical technique for computing tensor block conductivities for the case of anisotropic conductivities at the measurement scale. Their method is based on the recurrent use of the block conductivity values obtained for a block-composed of two layers of homogeneous but anisotropic conductivities, under the assumption that flow lines are parallel. Equations were obtained for the tensor elements of the block conductivity and were validated using numerical simulations.

3.2. *Non-local techniques*

Local techniques derive block conductivities which are explicit functional relations of the cell conductivities within the block. However the dependence of the resulting values on some implicit boundary conditions indicates that the block conductivities are non-local, that is, they are not intrinsic to the block, they also depend on the flow conditions within the block, which, in turn, depend on the boundary conditions.

In the non-local techniques discussed next, block conductivity is not given as an explicit expression of the cell conductivities within the block; instead, Eq. (1) is applied directly after determining the vectors of specific discharge $\mathbf{q}_w$ and piezometric head gradient ∇h_w by solving the groundwater flow equation at the measurement scale. The techniques differ in the extent of the area within which flow is numerically solved at the measurement scale, and on the boundary conditions used for the solution. All of these methods are referred to as Laplacian since they are based on the solution of the Laplace equation.

3.2.1. *Simple Laplacian*

In the simple Laplacian technique, the block being upscaled is isolated from the rest of the blocks in the aquifer. The principal components of the block conductivity tensor are assumed to be parallel to the block sides, and each principal component is computed by numerically solving a flow problem with prescribed heads in the faces of the block orthogonal to the principal direction and impermeable otherwise. Fig. 2 shows the flow problem that has to be solved to determine the x-component of the block conductivity tensor in a two dimensional block. A similar problem has to be solved for the y-component after rotating the boundary conditions 90°.

Application of Eq. (1) to the solution of these problems yields a very simple expression for the components of the block conductivity as the ratio between the average specific discharge through any cross-section orthogonal to a principal direction, and the overall piezometric gradient between the opposite faces at which prescribed heads are applied (Gómez-Hernández, 1991; Sánchez-Vila, 1995).

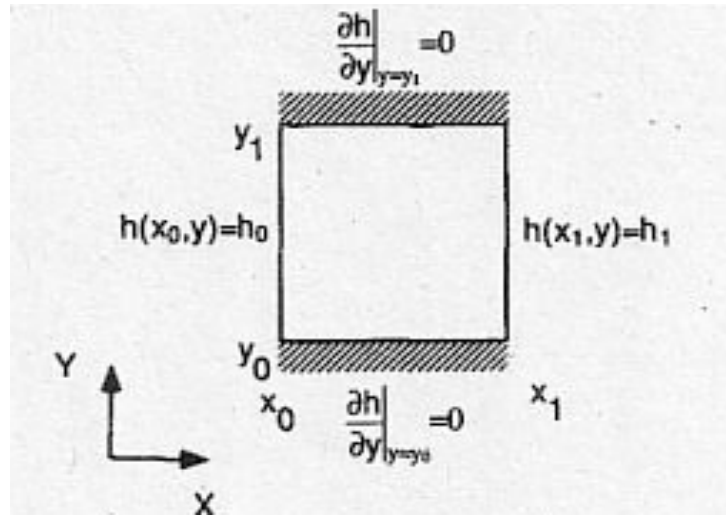


Fig. 2. Boundary conditions used in the simple Laplacian approach. These boundary conditions are used to determine the component $\mathbf{K}_{V,xx}$ of the diagonal block conductivity tensor. The same boundary conditions after rotation of 90° are used to determine the component $\mathbf{K}_{V,yy}$

For the 2-D example in Fig. 2, the expression for the component in the x-direction is

$$K_{V,xx} = - \left(\frac{Q}{y_1 - y_0} \right) \Bigg/ \left(\frac{h_1 - h_0}{x_1 - x_0} \right)$$

where:

Q is the total flow through any cross-section parallel to the y-axis

$y_1 - y_0$ is the block width

$h_1 - h_0$ is the piezometric head drop from face to face

$x_1 - x_0$ is the block length

Warren and Price (1961) were the first to use this approach. They analyzed random distributions of cell conductivities within the block, and found that the geometric mean was a good approximate of the block conductivities.

The Laplacian techniques suppose a big step towards accuracy in the estimation of block conductivities from the local approaches described previously. However, in this simple Laplacian approach we can criticize the assumption that block conductivity tensors are imposed to have principal components parallel to the block sides, and that the boundary conditions used to solve the flow problems at the measurement scale may be different from the boundary conditions actually existing at the faces of the block in the model.

3.2.2. Simple Laplacian extended

The simple Laplacian method discussed above requires the solution of a small flow problem for each block in the grid. Holden et al. (1989) tries to speed up the method using an iterative approach. If an iterative technique is used for the solution of the flow equation within each block, one could compute, after each iteration, an estimate of the block conductivity tensor components from the h_w and the q_w values at the current iteration. The key idea is to stop the iterations before the solution to the flow equation converges, under the conjecture that the block conductivity tensor components converge faster than the piezometric head distribution. In their example of 2-D rectangular blocks, they found that with many less iterations than needed for the convergence of piezometric heads, block conductivity tensors converge to a stable solution. Holden and Lia (1992) further extended this technique to calculate full block tensors in 3-D.

3.2.3. Laplacian using flow solution at the measurement scale over the entire aquifer

The boundary conditions used in the simple Laplacian approach are arbitrarily set to help compute directional conductivities in the directions parallel to the block sides. It would be better to use boundary conditions as close as possible to those existing around the block when the flow equation is solved at the measurement scale over the entire aquifer. But, knowledge of the boundary conditions around the block sides requires the solution of the flow equation at the measurement scale over the entire aquifer, defeating the purpose of upscaling, which is to obtain a coarse description of block conductivities to alleviate the cost of solving the flow equation at the measurement scale.

There is one justification for the solution of the flow equation at the measurement scale in order to obtain block conductivities: when block conductivities are to be used as input parameters for multiphase flow modelling. The advent of fast workstations, the computer resources available to petroleum engineers and their interest in accurate predictions of multiphase flow simulations prompted the development, in the petroleum literature, of a series of techniques for the computation of (saturated) block conductivities using the distribution of ∇h_w and $\mathbf{q}_w$ within the block resulting from the solution of the (single-phase) flow equation at the measurement scale over the entire aquifer.

In the quest for accurate block conductivities, it was understood that assuming the principal components of the block conductivity parallel to the block sides was not justified. Therefore, techniques to determine block conductivity tensors with arbitrary orientations of their principal directions had to be developed.

White (1987) and White and Horne (1987) were the first to propose a technique to determine full non-diagonal block conductivity tensors, and the first to suggest that Eq. (1) should be used with values of ∇h_w and $\mathbf{q}_w$ from the solution of the flow equation at the measurement scale over the entire aquifer. In their 2-D exercise, they propose to use the following equation to determine the block conductivity, for each block:

$$\begin{pmatrix} \bar{q}_{w,x} \\ \bar{q}_{w,y} \end{pmatrix} = - \begin{pmatrix} K_{V,xx} & K_{V,xy} \\ K_{V,yx} & K_{V,yy} \end{pmatrix} \cdot \begin{pmatrix} \nabla \bar{h}_{w,x} \\ \nabla \bar{h}_{w,y} \end{pmatrix}$$

where:

the overbar is used to indicate spatial average within the block

$q_{w,x}$, $q_{w,y}$, $\nabla h_{w,x}$ and $\nabla h_{w,y}$ are the respective components of vectors $\mathbf{q}_w$ and ∇h_w

$K_{V,xx}$, $K_{V,xy}$, $K_{V,yx}$ and $K_{V,yy}$ are the tensor components of $\mathbf{K}_V$

The problem with this approach is that the above linear system contains two equations and four unknowns, leaving the definition of the block conductivity undetermined. White and Horne suggested that the problem could be overcome by solving the flow

equation n times at the numerical scale, varying the boundary conditions applied to the entire aquifer. The resulting over-determined set of $2n$ linear equations is solved by least-squares. The need to use several boundary conditions detaches the computation of the block conductivity tensor from a specific regional flow pattern, thereby producing block tensors that perform well under different flow scenarios.

White and Horne's approach succeeds in obtaining full non-diagonal tensors, and in accounting for aquifer-scale boundary conditions. The major drawback is that it is computationally intensive and that for large aquifers it may be impractical, especially in 3-D.

Pickup et al. (1992) considered that it would be more convenient to try to determine the block conductivity tensor for specific boundary conditions existing at the aquifer scale, instead of producing tensors that are applicable to a wide range of flow conditions. Their argument is that such an approach should yield more accurate block conductivities for the specific flow scenario of interest, with the drawback that the upscaling should be repeated if aquifer conditions change. After solving the flow equation at the measurement scale over the entire aquifer, the boundary conditions at the sides of each block are determined. These boundary conditions are the ones that should be used to solve the flow equation within the block and, by application of Eq. (1), yield the block conductivity tensor. The problem is, as stated before, that solutions of the flow equation corresponding to at least two boundary conditions are necessary to determine uniquely the four components of a 2-D block conductivity tensor. Pickup et al. (1992) proposed solving two flow problems for each block, with boundary conditions derived from the correct boundary conditions by perturbing them enough to produce a different flow pattern within the block but without deviating too much from the correct values. The major drawback of this approach is the high sensitivity of the resulting block conductivities to the magnitude of the perturbation and the difficulty of selecting an appropriate perturbation value.

Another approach based on the solution of the flow equation at the measurement scale with global boundary conditions was developed by Yamada (1995) and will be discussed later in relation to block geometry definition.

3.2.4. Laplacian with skin

To reduce the computer time in White and Horne's method, Gómez-Hernández (1990, 1991) presented another Laplacian approach inspired by that of White and Horne (1987). His method also yields full block conductivity tensors, and attempts to impose realistic boundary conditions on the sides of the block to determine the cell-specific discharges and piezometric head gradients. Instead of solving the flow equation at the measurement scale over the entire aquifer, the flow equation is solved over an area (or volume in 3-D) comprising the block plus a "skin" region. The size of the skin region was arbitrarily set to one-half of the block size in each direction. As in White and Horne (1987), the flow equation must be solved for at least two sets of boundary conditions applied to the outer sides of the skin area in order to determine the block conductivity tensor components. Gómez-Hernández chose to use four sets of boundary conditions as shown in Fig. 3, forcing flow parallel to the block sides and the block diagonals. He showed that this method works well for a variety of heterogeneous formations (isotropic, anisotropic and sand/shale distributions). Holden and Lia (1992) extended this technique to 3-D.

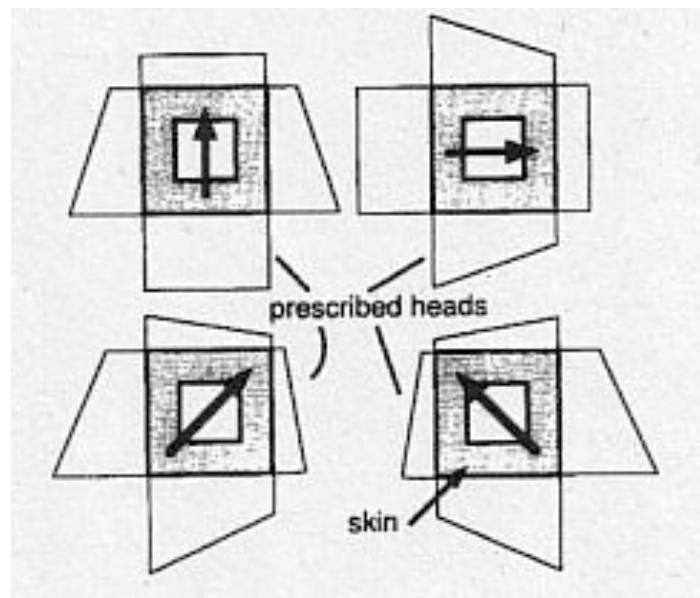


Fig. 3. Boundary conditions used in the Laplacian with skin approach. For each of the four sets of boundary conditions, flow is solved at the measurement scale within an area that contains the block and a "skin" around of half the block size in each direction

3.2.5. Laplacian with periodic boundary conditions

Neither White and Horne (1987) nor Gómez-Hernández (1990, 1991) constrain the block conductivity tensor to be positive-definite and symmetric. Conductivity tensors must be positive-definite, otherwise water could move in the direction of increasing piezometric heads. Whether block conductivity tensors must be symmetric is a subject of debate not yet resolved.

Durlofsky and Chung (1990) and Durlofsky (1991) present a Laplacian approach that always yields symmetric and positive definite block conductivity tensors. The novelty of their method is to use the type of boundary conditions that would result from a “periodic” aquifer made up by the repetition in space of the block being upscaled. The method is based on the assumption that the spatial heterogeneity of measurement-scale conductivities occurs at two scales, a large-scale variability that defines the long trends in conductivity variation and a small-scale variability that is periodic in space. The periodicity of the aquifer description implies full correspondence between heads and flows at opposite sides of the block.

The block equation within each block is solved for two orthogonal directions of the overall head gradient. Then, Eq. (1) is established for each solution, resulting in four equations with four unknowns. Durlofsky proves that the solution of these set of equations always yields a symmetric and positive-definite tensor (i.e. $K_{V,xy} = K_{V,yx}$, $K_{V,xx} K_{V,yy} - K_{V,xy} K_{V,yx} \geq 0$). This approach provides exact analytical results for $\mathbf{K}_V$ for truly periodic media. For non-periodic media, the method is theoretically valid if the block size is much larger than the scale of the heterogeneity at the measurement scale.

Comparisons made by Pickup et al. (1992, 1994) showed that Durlofsky’s approach is quite accurate and robust even for situations in which periodic boundary conditions do not strictly apply.

3.2.6. Non-parallel flow

The dependence of block conductivities on the boundary conditions applied to the block is evident at this stage. However, all the methods described up to this point use boundary conditions that impose parallel flow through the block. Desbarats (1992a)

studied the problem of determining block conductivities under radial flow. More precisely, he determined a scalar block conductivity to be assigned to a heterogeneous block with a constant-rate well at its centre when prescribed and constant piezometric heads are applied to the block boundaries.

Using an empirical approach he concludes that, in 2-D, a weighted geometric average of the cell conductivities, with weights proportional to the inverse of the squared distance to the well, yields good results for low to moderate variance of log-conductivity. Desbarats (1993) also studied the problem of computing block conductivities for blocks containing two wells in a dipole configuration. For this case, he found that the interwell conductivity approximates to the harmonic mean of the conductivities averaged over circular regions centered at each well.

3.2.7. Analytical approaches

Rubin and Gómez-Hernández (1990) derived, and validated numerically, an analytical expression for 2-D block conductivities for the case of a block embedded in a heterogeneous infinite aquifer with constant specific discharge specified at infinity. Cell conductivities were assumed to be a scalar with an isotropic spatial correlation. It was also assumed that, as a consequence of the latter, block conductivities were also scalar. Under these conditions block conductivity becomes:

$$K_v = K_g \left[1 + \overline{Y'} + \frac{\overline{Y'^2}}{2} + \frac{1}{j_a} (\overline{Y' j'_x} - \overline{Y'} \overline{j'_x}) \right] \quad (2)$$

where:

K_g is the geometric mean of conductivity over the entire aquifer

The overbar indicates spatial average values over the block V

Y' is the fluctuation of $Y = \ln(K_w)$ with respect to its mean

j_a is the magnitude of the mean piezometric head gradient (which is supposed to be parallel to the x-axis)

j'_x is the fluctuation of the x component of the gradient ∇h_w

This expression, which is only valid for small variances of Y , shows clearly the dependence of the block conductivity on the flow conditions within the block through the terms containing j'_x .

Sáez et al. (1989) also provided an analytical expression for block conductivities using the multiple scale method. They considered two observation scales. At the larger scale, the small scale heterogeneity is assumed to be non-detectable, and hydraulic conductivity varies smoothly. At the smaller scale, the heterogeneity of the medium is apparent and hydraulic conductivity varies rapidly and erratically in space. At any given location, the hydraulic conductivity is expressed as the sum of a large scale value plus a perturbation due to the heterogeneity at the smaller scale. Similarly, the hydraulic head is expressed as the sum of the large scale value plus a perturbation. Conductivity for a block much larger than the small scale of the heterogeneity is defined as the tensor $\mathbf{K}_V$ for which the large scale component of the hydraulic head satisfies a mass conservation equation:

$$\nabla \cdot (\mathbf{K}_V \cdot \nabla h^{(0)}) = 0$$

where:

$h^{(0)}$ is the large scale component of the hydraulic head.

Sáez et al. (1989) solved the above equation for the case of a periodic aquifer with unit period being the block for which the equivalent conductivity is sought. They obtained the following expression for block conductivity:

$$\mathbf{K}_V = \mathbf{K}_A + \mathbf{t} \quad (3)$$

that is, block conductivity is the sum of the arithmetic average $\mathbf{K}_A$ and a tortuosity tensor defined by the following spatial average:

$$\mathbf{t} = \frac{1}{V} \int_V \mathbf{K}_w \cdot \nabla \mathbf{g} dV$$

where the vector function $\mathbf{g}$ satisfies the boundary-value problem:

$$\nabla \cdot (\mathbf{K}_w \nabla \mathbf{g}) = -(\nabla \cdot \mathbf{K}_w) \quad (4)$$

with $\mathbf{g}$ periodic in the unit cell.

The problem with the analytical solution of block conductivity given by Sáez et al. is that it is limited to blocks larger than the scale of the erratic variability of cell conductivities. Furthermore, it requires the permeable medium to be periodic with period equal to the block size.

3.2.8. Method of moments

Kitanidis (1990) used a definition for block conductivity different from that of Eq. (1). His definition is based on the method of moments, first formulated by Aris (1956) and later generalized by Brenner (1980). In the method of moments the definition of block conductivity differs from that in Eq. (1). Instead of trying to find the block conductivity that relates average flow to average gradient, the objective is to find a block value that matches the spatial moments of the hydraulic head in the heterogeneous medium as explained below. This definition requires the solution of a transient problem as opposed to the steady-state solution on which Eq. (1) relies. The application of the method of moments is better understood with an example. Consider an infinite 2-D aquifer with constant hydraulic conductivity in which a Dirac pulse in the hydraulic head is introduced at time zero, at the origin. The solution of the transient dissipation of the pulse is given by a Gaussian bell:

$$h(\mathbf{x},t) = (2\pi)^{-3/2} |2\mathbf{D}t|^{-1/2} \exp(-\mathbf{x}\mathbf{D}^{-1}\mathbf{x}/4t)$$

where:

t is time

$\mathbf{D} = \mathbf{K}/S$ is called the diffusivity tensor

S is the specific storage coefficient

The second moment of the function $h(\mathbf{x},t)$ with respect to the origin is the “moment of inertia” and is given by

$$\Delta(t) = \int \mathbf{x} \cdot \mathbf{x} h(\mathbf{x},t) d\mathbf{x} = 2\mathbf{D}t$$

Note that half the rate of change of the second moment is given by $(1/2)d\Delta(t)/dt = \mathbf{D}$.

In the method of moments, the evolution of a Dirac pulse of piezometric head at the origin is solved in the heterogeneous block, and the rate of change of the second moment is identified with the diffusivity tensor of the homogeneous equivalent block conductivity value.

To solve for the evolution of the Dirac pulse some hypotheses are needed. First, the aquifer is assumed to be periodic with a period much larger than the scale of variability of $\mathbf{K}_w$. Second, the moments are defined at two scales (similarly to Sáez et al. (1989); only the moments at the larger scale are of interest. And third, only slowly varying flow is considered. Under these hypotheses the resulting expression for $\mathbf{K}_V$ is very similar to the expression obtained by Sáez et al. (1989). The block conductivity tensor is equal to its arithmetic spatial average plus an integral term equivalent to the tortuosity term in Eq. (3). This integral term is written in terms of a function g that must satisfy a boundary value equivalent to that in Eq. (4).

Dykaar and Kitanidis (1992a,b) discuss a numerical technique for the efficient solution of the boundary value problem (4), called the numerical spectral method. This method has the same drawbacks as the one by Sáez et al. (1989): it is limited to large blocks and requires the assumption that the medium is periodic with period equal to the block size.

3.2.9. Energy dissipation

Indelman and Dagan (1993a,b) and Bøe (1994) used the concept of energy dissipation to define block conductivity tensors. Energy dissipation is defined as the energy per unit time necessary to force the fluid through the porous medium. A necessary condition on the block conductivity value is that it should produce the same energy dissipation as the heterogeneous block. Bøe (1994) showed that with this definition, and periodic boundary conditions applied to the sides of the block, the resulting block conductivities coincide with those of Durlafsky (1991). Indelmann and Dagan (1993a,b) were more interested in obtaining the statistical properties of the upscaled blocks, than in the one-to-one relationship between each block and the cell conductivities within. Their approach is mentioned later when discussing the direct generation of block conductivities.

3.3. Block Geometry

All of the methods discussed above investigate upscaling of grids made up of rectangular blocks; none of them has been extended to the case of non-rectangular grids. Much effort has been devoted to computing block conductivities for heterogeneous blocks without paying much attention to the geometry of the blocks. One should not forget that upscaling is not an objective per se: the objective of upscaling is to use the block values for the simulation of (single or multiphase) flow and, possibly, mass transport. Some of the more elaborate Laplacian methods provide, for a fixed block geometry, the best block conductivity estimates one can get. In order to improve these estimates, we should try to optimize the geometrical definition of the blocks.

No matter how good an upscaling method is, it always involves an averaging of the flow problems that filters out some of the details of flow within the block. One can attempt to devise a technique to define the geometry of the blocks so that the averaging implicit in upscaling is minimal in the areas in which the details of flow behaviour are most consequential to the final objective. For instance, if the final objective is to simulate mass transport and early mass arrivals are most consequential, a geometry definition of the blocks trying to delineate fast channels will reduce the impact of the loss of resolution on the prediction of early mass arrivals (e.g. Durlofsky et al., 1994a,b).

Although gridding for flow simulation is an old subject, gridding techniques for flow simulation in conjunction with upscaling are relatively recent. In this section we describe four of these techniques.

3.3.1. Elastic grid

Garcia et al. (1990) introduced the concept of an “elastic grid”. They devised an algorithm that starts from an uniform square grid of the aquifer, and then displaces the corners of the blocks with the objective of minimizing the heterogeneity of the cell conductivities within the blocks. Each edge connecting two vertices is assigned an elasticity coefficient that is made a function of the cell conductivity variance of adjoining blocks. The potential energy of each edge is proportional to the square of its

length and its elasticity coefficient. The block vertices are adjusted in an iterative manner until the total potential energy is minimized. This approach results in an irregular grid with blocks that are mildly heterogeneous, and for which simple upscaling techniques should provide good results. A typical grid is shown in Fig. 4.

Farmer et al. (1991) devised a method similar to Garcia et al. in which the optimization is carried out by simulated annealing. Robey (1995) introduced an elastic gridding approach in which the objective to be met by the final grid was related to a global measure of heterogeneity, instead of a local measure as in the approach of Garcia et al.

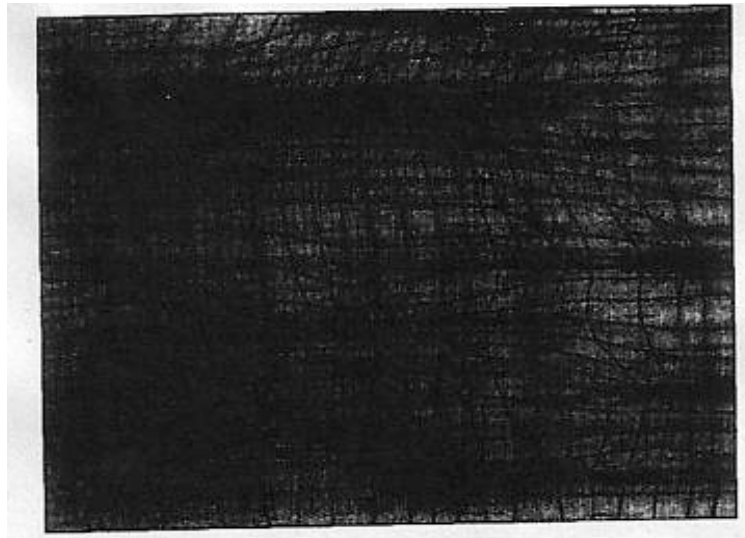


Fig. 4. Elastic grid. A typical elastic grid obtained using the Garcia et al. (1990) method, where the objective is to minimize the cell conductivity heterogeneity within each block. The grid at the measurement scale contains 200 by 150 cells. The grid at the numerical scale contains 30 by 30 blocks. Dark cells indicate high conductivity values

3.3.2. Elastic grid with flow variables

The elastic grid approaches discussed above do not incorporate flow variables for the determination of the block geometries. Tran (1995) and Tran and Journal (1995) realized that minimization of the variance of cell conductivities within the blocks does not ensure that fast flow paths are preserved in the upscaled model. There is a need to define the block geometry as a function of the flow variables. Tran and Journal proposed an extension of White and Horne's (1987) Laplacian method. After solution of

the flow equation at the measurement scale over the entire aquifer, the block geometries are determined by the Garcia et al. (1990) elastic gridding algorithm but applied to the stream function values. The coefficient of elasticity of any segment joining two vertices is now a function of the variance of the stream values at adjoining blocks. In this way, they ensure that the density of streamlines is approximately constant within each block. Consequently, blocks are small in regions of high flow velocity and large where flow velocity is small. From the point of view of flow and transport at the aquifer scale, Tran and Journal's approach gives better results than those of Garcia et al.

3.3.3. Simplified elastic grid with flow variables

The previous method, although superior to the original method of Garcia et al. (1990), has the same drawbacks as White and Horne's (1987): the flow equation has to be solved at the measurement scale over the entire aquifer, in order to know the streamline function in the cells. Tran's approach is computationally intensive and cannot be used for large aquifers. To solve these problems, Wen (1996) implemented a variation that does not require the solution of the flow equation at the measurement scale. He proposed an iterative approach in which both block conductivities and block geometries are updated at each iteration. His method starts with an elastic grid obtained using the Garcia et al. (1990) method in its original implementation, that is, minimizing the heterogeneity of cell conductivities within the blocks.

Then, an extension of Durlafsky's (1991) Laplacian method for irregular blocks is used to determine block conductivity tensors. The flow equation is solved at the numerical scale (not the measurement scale) using the geometry definition and the block conductivities from the previous iteration. With this solution, velocities are computed in each cell of the aquifer, and the Garcia et al. elastic gridding algorithm is used to redefine the block geometry, with the difference that the potential energy of edges is now proportional to the variance of flow velocity on adjoining blocks, instead of to the variance of cell conductivities. With the new geometry, a new iteration starts: block conductivities are re-computed, and flow is again solved at the numerical scale. The iterative process stops when neither the block geometries nor the block conductivities change substantially from one iteration to the next. This method gives results as good as

Tran's (1995) at a fraction of the cost. Its major drawback is that there is no theoretical proof of convergence of the technique, although for the cases in which it has been tested, convergence was always reached.

3.3.4. Potential-streamfunction space discretization

Yamada (1995) approached the upscaling process with a different perspective. He accepts that the boundary conditions of the simple Laplacian (Fig. 2) may depart from the actual boundary conditions around the perimeter of the blocks. However, instead of trying to refine the boundary conditions and make them closer to the ones that the blocks actually have when embedded within the aquifer, he searches for the block geometries for which the simple boundary conditions in Fig. 2 apply. These block geometries can easily be defined if the gridding is carried out in the potential streamfunction space. After solving the flow equation at the measurement scale, the results are mapped to the potential-streamfunction space. In this space, each block is defined as a rectangle, thus ensuring that in two opposite faces the streamfunction is constant, and in the other two opposite faces the fluid potential is constant. With this definition, the use of no-flow boundary conditions in two sides of the block, and prescribed head conditions in the other two sides, is completely justified. Furthermore, since flow cannot cross streamlines, there is no need to compute any component of the block conductivities in the direction orthogonal to the bounding streamlines (no-flow boundaries). Yamada found that flow simulations performed in the reshaped grid system successfully reproduce the single-phase head distributions and produce reasonable approximations for head and saturation on two-phase problems.

Although this technique is attractive, it has three major drawbacks:

- (i) it has been devised in 2-D and its extension to 3-D is not trivial owing to the difficulty of computing streamtubes in 3-D
- (ii) the reshaping done in the potential-streamfunction space requires that the streamfunction be single-valued at each location – if point sinks or sources are present, the streamfunction will be multi-valued at the well locations
- (iii) it requires the solution of the flow equation at the measurement scale over the entire aquifer

3.4. Direct block conductivity generation

Reconsidering again that the objective of upscaling is the solution of the flow equation at the numerical scale, some authors have concluded that the generation of grids at the measurement scale (Fig. 1(a)), with the sole purpose of upscaling them to produce a block conductivity model, is a waste of resources. The question that these authors have considered is: can block conductivities be generated directly from a few data at the measurement scale, thus avoiding the generation of the measurement scale grid values and the time consuming step of block upscaling, and yet displaying the same characteristics observed in the upscaled models obtained with the other techniques? Fig. 5 sketches this concept. In the top row, the so –called two-step approach (Gómez-Hernández, 1991) is depicted: from a set of measurements, a set of realizations of conductivities is generated at the measurement scale; these realizations are upscaled to the numerical scale, and flow is solved in each of them to arrive at a set of realizations of the spatial distribution of hydraulic conductivity within the aquifer. In the bottom row, the direct simulation approach is depicted: the initial and final points are the same as in the two-step approach, the difference is that the block values are generated directly from the measurements.

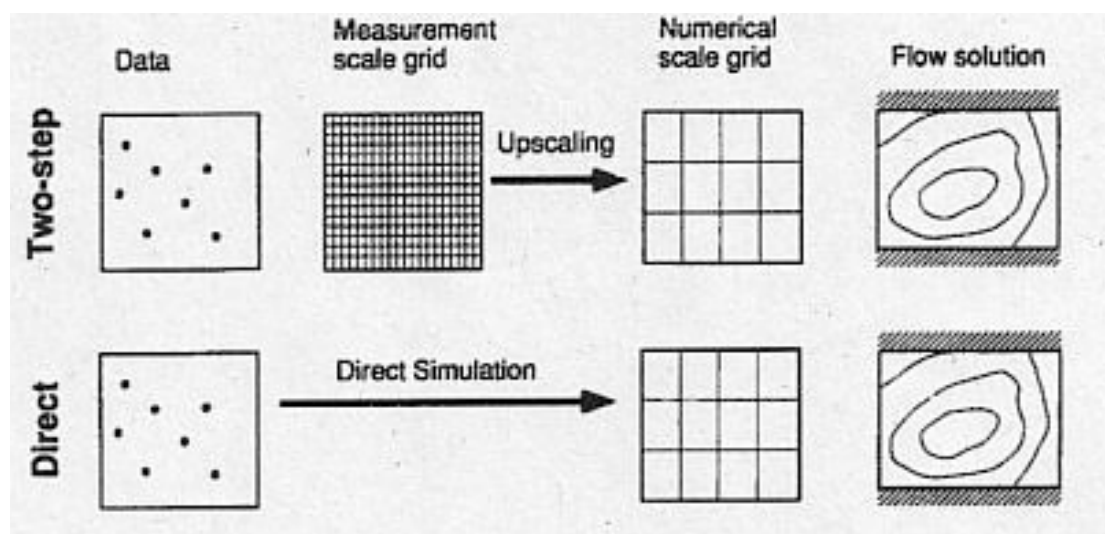


Fig. 5. Two-step versus direct simulation. In the top row, the two-step approach; at the bottom, the direct simulation approach.

3.4.1. Scalar block conductivities

Rubin and Gómez-Hernández (1990) were the first to approach this problem analytically. Taking as a starting point the analytical result of their upscaling technique (Eq. (2)), they computed what should be the expected value and covariance of block conductivities, as well as the cross-covariance between cell and block conductivity values. With these statistics and the hypothesis that the multilognormality assumed for the cell conductivities is preserved after upscaling, they could proceed to the generation of scalar block conductivities conditioned on cell measurements by any standard geostatistical technique. Their method is limited by the assumptions used to derive Eq. (2), namely the isotropic spatial variability of cell conductivities, small variability of log-conductivity, and the assumption that block conductivity is a scalar.

3.4.2. Training images

To overcome the problems of the previous approach, Gómez-Hernández (1990, 1991) proposed the inference of the cell to block covariance's through the use of a training image. The idea is to start by generating a "training grid" at the measurement scale, on which any of the upscaling methods described in the previous sections is used to determine the block conductivity tensors. At this stage, two realizations are available, one with cell conductivities and the other with the corresponding block conductivity tensors; from these two realizations, the cross- and auto-covariances among the cells and the components of the block conductivity tensors can be experimentally inferred. Once the training image has been used to infer these covariances, direct generation of the components of the block conductivity tensor is possible, without the need to resort to upscaling again.

The major disadvantage of this method is that too many auto- and cross- covariances have to be inferred. In 2-D, the number of variables involved, assuming that the block conductivity tensors are symmetric, is four: one for the cell conductivity and three for the block conductivity tensor (the components in the two principal directions and the orientation of the main principal direction). Consequently, the number of covariance's to estimate is nine. In 3-D, in which seven variables would be involved (one for the cells, and six for the tensor), the number of covariance's to infer is 27!

In order to reduce the number of covariances to infer, Tran (1995) proposed to infer the auto- and cross-covariances only for the components of the block conductivity; moreover, he assumed that the principal components of the conductivity tensor are parallel to the block sides, thereby reducing the number of variables to two in 2-D and the number of covariances to three. The conditioning to cell data (for which the cross-covariance cell-block would be required) is resolved through a heuristic approach.

3.4.3. Regularization

Desbarats (1989, 1992b) derived the expected value and variance of block conductivities when these are obtained by power averaging. He used a linear approximation of the log-conductivity obtained by power averaging together with standard regularization techniques (e.g. Journel and Huijbregts, 1978) to compute the expected value and variance of block values. Desbarats did not pursue the computation of the cell-block covariance, or the block-block covariances, but it would be simple to extend his results to determine these values. Once these covariances are also computed, the direct generation of block conductivities conditional to cell conductivity data is a trivial matter of stochastic co-simulation of multiple variables. The drawbacks of the approach are those stemming from the use of the power-average method to compute block conductivities and from the linearization of the log-conductivity.

3.4.4. Energy dissipation

Using an energy dissipation definition for block conductivity, Indelmann and Dagan (1993a, b) derived the expected value and covariance of the upscaled block values. They stated that imposing the preservation of energy dissipation to compute block conductivities is not enough to enable derivation of a one-to-one relationship between block conductivity and the cell conductivities within. However, they showed that identity between the energies dissipated at the measurement and the numerical scales could be satisfied in a statistical sense. Working under these premises, they proceeded to compute the expected value and covariance of the components of three-dimensional equivalent conductivity symmetrical tensors, arriving, for the most-general three-

dimensional case, at the expressions of six geometrical means and 15 cross-covariances of log-conductivity. These expressions are complex, and the authors indicate the the existence and uniqueness of a solution in the most general case is not proven. However, for the specific cases they analyze, good insight is obtained about the spatial variability of block conductivities. Among their conclusions, they stated that, except for blocks of circular or spherical shape, the block conductivity tensor is always anisotropic. Therefore, in all numerical methods, block conductivities have to be given as a tensor of anisotropic covariance since numerical blocks are never circular or spherical. In their papers, the authors also described the step-by-step procedure for the direct generation of block conductivities. Sánchez-Vila et al. (1995) showed that the method of Rubin and Gómez-Hernández (1990) results in block conductivities which are statistically very similar to those of Indelman and Dagan (1993a, b).

3.4.5. Disadvantages

The direct generation of block conductivities is very appealing since it puts the effort where it is needed, i.e. no time is spent in the generation of grids at the measurement scale and the later upscaling of each block, and block values are generated directly. The main problem of this method is that it can only be applied to blocks of uniform size and cannot benefit from any geometry definition algorithm. The reason is that if different block sizes are considered, conductivity must be considered as a different random variable for each block size. Introducing multiple block sizes would multiply the number of random variables involved and the number of covariances to determine. Only the analytical approaches of Rubin and Gómez-Hernández (1990) and Indelman and Dagan (1993a, b) which provide analytical expressions for block conductivity expressions, could be readily applied to multiple block sizes.

4. Summary

A review of the many existing techniques for conductivity upscaling has been presented. The emphasis of this review has been placed on the methods. An attempt has been made to refer to the seminal papers of each method, and, to the best of our knowledge, all the existing methods for upscaling have been reviewed.

Block conductivities are now understood as not being a material property but dependent on the flow conditions within the block. The observed current line of research in conductivity upscaling focuses on accuracy more than on speed, and on the inclusion of the geometry definition as an integral part of the upscaling process. The idea of direct simulation of block-conductivity, although attractive in concept, needs further testing and refinement.

References – Upscaling of Flow Parameters

Ababou, R. and Wood, E.F., 1990. Comment on “Effective roundwater model parameter values: Influence of spatial variability of hydraulic conductivity, leakage and recharge” by J.J. Gómez-Hernández and S.M. Gorelick, *Water Resour. Res.* 26(8): 1843-1846.

Aris, R., 1956. On the dispersion of a solute in a fluid flowing through a tube. *Proc. R. Soc. London. Ser. A*, 235: 67-77.

Bachu, S. and cuthiell, D., 1990. Effects of core-scale heterogeneity on steady state and transient fluid flow in porous media: Numerical analysis. *Water Resour. Res.*, 26(5): 683-874.

Begg, S.H. and King, P.R., 1985. Modelling the effects of shales on reservoir performance: Calculation of effective vertical permeability. Paper SPE 13529.

Begg, S.H., Chang, D.M. and Haldorsen, H.H., 1985. A simple statistical method for calculating the effective vertical permeability of a reservoir containing discontinuous shales. Paper SPE 14271.

Begg, S.H. and Carter, R.R., 1987. Assigning effective values to simulator grid-block parameter for heterogeneous reservoir. Paper SPE 16754.

Begg, S.H., Carter, R.R. and Dranfield, P., 1989. Assigning effective values to simulator gridblock parameters for heterogeneous reservoirs. *SPE Reservoir Engineering*, November: 455-463.

Bøe, Ø., 1994. Analysis of an upscaling method based on conservation of dissipation. *Transport in Porous Media*, 17(1): 77-86.

Bouwer, H., 1969. Planing and interpreting soil permeability measurements. *J. of the Irrigation and Drainage Division of the A.S.C.E.*, IE(3): 391-402.

Brenner, H., 1980. Dispersion resulting from flow through spatially periodic porous media. *Philos. Trans. R. Soc. London, Ser. A*, 297 (1498): 81-133.

Cardwell, W.T. and Parsons, R.L., 1945. Averaging permeability of heterogeneous oil sands. *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 160: 34-42.

Clifton, M.P. and Neuman, S.P., 1982. Effect of kriging and inverse modelling on conditional simulation of the Avra Valley aquifer in Southern Arizona. *W.R.R.*, 18(4): 1215-1234

Dagan, G., 1979. Models of groundwater flow in statistically homogeneous porous formations. *W.R.R.*, 15(1); 47-63.

Dagan, G., 1982a. Stochastic modelling of groundwater flow by unconditional and conditional probabilities, 1: Conditional simulation and the direct problem. *W.R.R.*, 18(4): 813-833.

Dagan, G., 1982b. Analysis of flow through heterogeneous random aquifers, 2: Unsteady flow in confined formations. *W.R.R.*, 18: 1571-1585.

- Dagan, G., 1985. Stochastic modelling of groundwater flow by unconditional and conditional probabilities, 2: The inverse problem. *W.R.R.*, 21(1): 65-72.
- Dagan, G., 1989. *Flow and Transport in Porous Formations*. Springer-Verlag, New York.
- Desbarats, A.J., 1987. Numerical estimation of effective permeability in sand-shale formation. *W.R.R.*, 23(2): 273-286.
- Desbarats, A.J., 1989. Support effect and the spatial average of transport properties. *Math. Geology*, 21(3): 383-389.
- Desbarats, A.J., 1992a. Spatial averaging of transmissivity in heterogeneous fields with flow toward a well. *W.R.R.*, 28(3):757-767.
- Desbarats, A.J., 1992b. Spatial averaging of hydraulic conductivity in three-dimensional heterogeneous porous media. *Math. Geology*, 24(3): 249-267.
- Desbarats, A.J., 1993. Geostatistical analysis of interwell transmissivity in heterogeneous aquifers. *W.R.R.*, 29(4): 1239-1246.
- Desbarats, A.J. and Dimitrakopoulos, R., 1990. Geostatistical modelling of transmissivity for two-dimensional reservoir studies. *SPE formation Evaluation*, Dic.: 437-443.
- Deutsch, C., 1989. Calculating effective absolute permeability in sandstone/shale sequences. *SPE Formation Evaluation*, September: 343-348.
- Deutsch, C. and Journel, A.G., 1992. *GSLIB: Geostatistical Software Library and User's Guide*. Oxford University Press, New York, 340 pp.
- Durlofsky, L.J. and Chung, E.Y., 1990. Effective permeability of heterogeneous reservoir regions. 2nd European Conference on the Mathematics of Oil Recovery, Paris, 1990, pp-57-64.
- Durlofsky, L.J., 1991. Numerical calculation of equivalent grid block permeability tensors for heterogeneous porous media. *W.R.R.*, 27(5): 699-708.
- Durlofsky, L.J., 1992. Representation of grid block permeability in coarse scale models of randomly heterogeneous porous media. *W.R.R.*, 28(7): 1791-1800.
- Durlofsky, L.J., Jones, R.C. and Milliken, W.J., 1994a. A new method for the scale up of displacement processes in heterogeneous reservoirs. 4th European Conference on the Mathematics of Oil Recovery, Roros, Norway, June, 1994.
- Durlofsky, L.J., Milliken, W.J., Dehghani, K. and Jones, R.C., 1994b. Application of a new scale up methodology to the simulation of displacement process in heterogeneous reservoirs. *SPE International Petroleum Conference & Exhibition of Mexico*, Veracruz, October 1994.
- Dykaar, B.B. and Kitanidis, P.K., 1992a. Determination of the effective hydraulic conductivity for heterogeneous porous media using a numerical spectral approach, 1: Method. *W.R.R.*, 28(4): 1155-1166.
- Dykaar, B.B. and Kitanidis, P.K., 1992b. Determination of the effective hydraulic conductivity for heterogeneous porous media using a numerical spectral approach, 2: Application. *W.R.R.*, 28(4): 1167-1178.

- Farmer, C.L., Heath, D.E. and Moody, R.O., 1991. A global optimization approach to grid generation. 11th SPE Symposium on Reservoir Simulation, Anaheim, CA, February 1991, pp. 341-350.
- Fayers, F.J. and Hewett, T.A., 1992. A review of current trends in petroleum reservoir description and assessment of the impacts on oil recovery. *Adv. In Water Resources*, 15(4): 341-365.
- Garcia, M.H., Journel, A.G. and Aziz, K., 1990. An automatic grid generation and adjustment method for modelling reservoir heterogeneities. Report 3, Stanford Center for Reservoir Forecasting, Stanford, CA.
- Garcia, M.H., Journel, A.G. and Aziz, K., 1992. Automatic grid generation for modelling reservoir heterogeneities. *SPE Reservoir Engineering*: 278-284.
- Gelhar, L.W. and Axness, C.L., 1983. Three-dimensional stochastic analysis of macrodispersion in aquifers. *W.R.R.*, 19(1): 161-180.
- Gómez-Hernández, J.J. and Gorelick, S.M., 1989. Effective groundwater model parameter values: Inference of spatial variability of hydraulic conductivity, leakance and recharge. *W.R.R.*, 25(3): 405-419.
- Gómez-Hernández, J.J., 1990. Simulation of block permeability conditioned upon data measured at a different scale. In: *ModelCARE 90: Calibration and Reliability in Groundwater Modelling*. IAHS Publ. no. 195, pp. 407-416.
- Gómez-Hernández, J.J., 1991. A stochastic approach to the simulation of block conductivity fields conditioned upon data measured at a smaller scale. Ph. D. thesis, Stanford University, CA.
- Gómez-Hernández, J.J. and Wen, X.H., 1994. Probabilistic assessment of travel times in groundwater modelling. *J. Stochastic Hydrology and Hydraulics*, 8(1): 19-55.
- Grindheim, A.O., 1990. An evaluation of homogeneization techniques for estimating effective absolute block permeability by use of a stochastic reservoir description simulator. Master thesis, Norwegian Institute of Technology (NTH).
- Gutjahr, A.L., Gelhar, L.W., Bakr, A.A. and MacMillan, J.R., 1978. Stochastic analysis of spatial variability in subsurface flows, 2: Evaluation and application. *W.R.R.*, 14(5): 953-959.
- Haldorsen, H.H. and Lake, L.W., 1984. A new approach of shale's management in field scale simulation models. *Soc. Of Petrol. Eng. Jour.*, 24 (August): 447-457.
- Haldorsen, H.H., 1986. Simulation parameters assignment and the problem of scale in reservoir engineering. In: Lake, L.W. and Carroll, H.B. (eds.), *Reservoir Characterization*. Academic Press, pp. 445-485.
- Haldorsen, H.H. and Chang, D.M., 1986. Notes on stochastic shale's; from outcrop to simulation model. In: Lake, L.W. and Carroll, H.B. (eds.), *reservoir Characterization*. Academic Press, pp-445-485.
- Hoeksema, R.J. and Kitanidis, P.K., 1984. An application of the geostatistical approach to the inverse problem in two-dimensional groundwater modelling. *W.R.R.*, 20(7): 1003-1020.

- Hoekssema, R.J. and Kitanidis, P.K., 1985. Comparison of Gaussian conditional mean and kriging estimation in the geostatistical solution of the inverse problem. *W.R.R.*, 21(6): 825-836.
- Holden, L., Hoiberg, J. and Lia, O., 1989. Homogeneization of absolute permeability. Norwegian Computer Centre (NCC) Report.
- Holden, L. and Lia, O., 1992. A tensor estimator for the homogeneization of absolute permeability. *Transport in Porous Media*, 8: 37-46.
- Indelman, P. and Dagan, G., 1993a. Upscaling of permeability of anisotropic heterogeneous formations, 1: The general framework. *W.R.R.*, 29(4): 917-923.
- Indelman, P. and Dagan, G., 1993b. Upscaling of permeability of anisotropic heterogeneous formations, 2: General structure and small perturbation analysis. *W.R.R.*, 29(4): 925-933.
- Journal, A.G., Deutsch, C. and Desbarats, A.J., 1986. Power averaging for block effective permeability. *SPE* 15128.
- Journal, A.G. and Huijbregts, C.J., 1978. *Mining Geostatistics*. Academic Press, London.
- Kasap, E. and Lake, L.W., 1989. An analytical method to calculate the effective permeability tensor of a grid block and its application in an outcrop study. *SPE* 18434.
- King, P.R., 1989. The use of renormalization for calculating effective permeability. *Transport in porous Media*, 4(1): 37-58.
- Kirkpatrick, S., 1973. Percolation and conduction. *Rev. Mod. Phys.*, 45(4): 574-588.
- Kitanidis, P.K., 1990. Effective hydraulic conductivity for gradually varying flow. *W.R.R.*, 26(6): 1197-1208.
- Lake, L.W., 1988. The origins of anisotropy. *J. of Petroleum Tech.*: 395-396.
- Malick, K.M., 1995. Boundary effects in the successive upscaling of absolute permeability. Master thesis, Stanford University, CA.
- Mantoglou, A. and Gelhar, L.W., 1987. Effective hydraulic conductivity of transient unsaturated flow in stratified soils. *W.R.R.*, 23(1): 57-67.
- Matheron, G., 1967. *Éléments pour une théorie des milieux*. Mason et Cie.
- Mohanty, S. and Sharma, M.M., 1990. A recursive method for estimating single and multiphase permeabilities. *SPE paper 20477 presented at the 65th Annual Technical conference and Exhibition in New Orleans, LA, September 23-26, 1990.*
- Muggeridge, A.H., 1991. Generation of effective relative permeabilities from detailed simulation of flow in heterogeneous porous media. In: Lake, L.W., carroll, H.B. and Wesson, T.C. (eds.), *Reservoir Characteriation II*. Academic Press, San Diego, pp. 197-225.
- Naff, R.L., 1991. Radial flow in heterogeneous porous media: An analysis of specific discharge. *W.R.R.*, 27(3): 307-316.
- Neumann, S.P. and Orr, S., 1993. Prediction of steady flow in nonuniform geologic media by conditional moments: Exact nonlocal formalism, effective conductivities, and weak approximation. *W.R.R.*, 29(2): 341-364.

- Pickup, G.E., Jensen, J.L., Ringrose, P.S. and Sorbie, K.S., 1992. A method for calculating permeability tensors using perturbed boundary conditions. In 3rd European Conf. on the Mathematics of Oil Recovery, Delft, The Netherlands, June 1992.
- Pickup, G.E., Ringrose, P.S., Jensen, J.L. and Sorbie, K.S., 1994. Permeability tensors for sedimentary structures. *Math. Geology*, 26(2): 227-250.
- Poley, A.D., 1988. Effective permeability and dispersion in locally heterogeneous aquifers. *W.R.R.*, 24(11): 1921-1926.
- Robey, T.H., 1995. An adaptive grid technique for minimizing heterogeneity of cells or elements. *Math. Geology*, 27(6): 706-729.
- Rubin, Y. and Gómez-Hernández, J.J., 1990. A stochastic approach to the problem of upscaling of conductivity in disordered media: Theory and unconditional numerical simulations. *W.R.R.*, 26(4): 691-701.
- Russo, D., 1992. Upscaling of hydraulic conductivity in partially saturated heterogeneous porous formation. *W.R.R.*, 28(2): 397-409.
- Sáez, A., Otero, C.J. and Rusinek, I., 1989. The effective homogeneous behavior of heterogeneous porous media. *Transport in Porous Media*, 4: 213-238.
- Sánchez-Vila, X., 1995. On the geostatistical formulations of the groundwater flow and solute transport equations. Ph. D. thesis, Universitat Politècnica de Catalunya, Barcelona, Spain.
- Sánchez-Vila, X., Girardi, J.P. and Carrera, J., 1995. A synthesis of approaches to upscaling of hydraulic conductivity. *W.R.R.*, 31(4): 867-882.
- Shah, N. and Ottino, J.M., 1986. Effective transport properties of disordered, multiphase composites: Application of real-space renormalization group theory. *Chem. Eng. Sci.*, 41(2): 283-296.
- Tran, T.T., 1995. Stochastic simulation of permeability field and their scale-up for flow modelling. Ph. D. thesis. Stanford University, CA.
- Tran, T.T. and Journel, A.G., 1995. Automatic generation of corner-point-geometry flow simulation grids from detailed geostatistical descriptions. *Adv. of Water Resour.*
- Warren, J.E. and Price, H.H., 1961. Flow in heterogenous porous media. *Society of Petroleum Engineering Journal*, 1: 153-169.
- Wen, X.H., 1996. Stochastic simulation of groundwater flow and mass transport in heterogenous formations: Conditioning and problem of scales. Ph. D. thesis, Universidad Politècnica de Valencia, Spain.
- White, C.D., 1987. Representation of heterogeneity for numerical reservoir simulation. Ph. D. thesis, Stanford University, CA.
- White, C.D. and Horne, R.N., 1987. Computing absolute transmissivity in the presence of fine-scale heterogeneity. *Paper SPE 16011*, pp. 209-221.
- Williams, J.K., 1989. Simple renormalization schemes for calculating effective properties of heterogeneous reservoirs. In: 1st European Conf. on the Mathematics of Oil recovery, Cambridge, UK, July 1989, pp. 281-298.



Wilson, K.G., 1979. Problems in physics with many scales length. Sci. am. 241 (August): 158-179.

Yamada, T., 1995. A dissipation-based coarse grid system and its application to the scale-up of two phase problems. Ph. D. thesis, Stanford University, CA.

Yeh, T.C., Gelhar, L.W. and Gutjahr, A.L., 1985. Stochastic analysis of unsaturated flow in heterogenous soils, 1: Statistically isotropic media. W.R.R., 21(4): 447-456.



PART 2

UPSCALING OF TRANSPORT PARAMETERS

PART 2 – UPSCALING OF TRANSPORT PARAMETERS

A - Upscaling transport parameters under the Fickian Approach

1. Basic definitions and transport processes

Before starting any developments, it is good practice to provide the reader with a clear view of the context of the study and general definitions of the key terms that will be used. The problem of interest is the movement (or transport) of solutes in natural soils. While the general concept of soil is well established, the definition of soil varies, hinging on the perspective of the discipline employing it as a resource. In this work, soil will be defined as an inert material, made of aggregated solid particles in-between which gas and liquids are present.

A solute is a chemical substance that dissolves in the liquid soil water phase. In this study, only ideal inert solutes that do not undergo decay will be considered. Furthermore, the solute will be assumed to be present in sufficiently low concentration for density effects to be neglected. No chemical process such as hydrolysis, oxydation or interaction with other dissolved species will be considered, nor will biological processes (biodegradation, biotransformation, ...). The solute will be assumed to move in a saturated porous medium, i.e. the presence of air as a third phase will not be considered neither.

Basically, three main physical processes control solute transport in the soil : advection, diffusion and mechanical dispersion.

Firstly, advection is mass transport caused by bulk movement of flowing groundwater.

If no other process occurs, then contaminant plumes are simply translated at groundwater velocity. The driving force is the hydraulic gradient and the average transport velocity can be calculated as the Darcy flux divided by the volumetric proportion of mobile fluid in the soil also called effective porosity.

The advective solute mass flux in direction i can be written as

$$q_i^A = v_i C$$

where C [g/m³] is the solute concentration. This process will play an important role in heterogeneous formations, where velocity fluctuations cannot be neglected.

As spatial concentration gradients exist, diffusion is the net flux of solutes from zones of higher concentration to zones of lower concentration. Diffusion does not depend on any bulk movement of the solution and will occur even if pore water is at rest. The diffusive solute mass flux in direction i [g/m²/s]) can be described by Fick's first law of diffusion

$$q_i^d = -D^d \frac{\partial C}{\partial x_i}$$

where x_i is the coordinate in direction i and D^d [m²/s] is an effective diffusion coefficient being related to the molecular diffusion coefficient in liquid phase. At low pore-water velocities, such as in clayey soils, solute transport is dominated by diffusion.

Finally, there is a tendency for solutes to spread out from the flow lines that it would be expected to follow according to the advective hydraulics of the flow system, leading to apparent diffusion coefficients that are higher by several orders of magnitude. This spreading phenomenon is usually called mechanical dispersion and is caused entirely by differential microscopic velocities in the pore space (due, for example, to the non-uniform velocity profile within a pore and to variations in pore diameter and in pore length.

Dispersive solute flux is classically represented using a diffusion-like or Fickian law

$$q_i^D = -\sum_j D_{ij} \frac{\partial C}{\partial x_j}$$

where q_i^D [g/m²/s] is the dispersive solute mass flux in direction i and D_{ij} [m²/s] is a second-order tensor called mechanical dispersion.

This Fickian assumption may, most of the time, be questioned. Afterwards some questions about non-Fickian transport are presented.

The solute mass transport equation can be set up by writing the mass balance on a representative elementary volume (R.E.V.) of soil (according to Bear's definition) Combining advective, diffusive and dispersive fluxes leads to

$$\frac{\partial C}{\partial t} = - \sum_i \frac{\partial}{\partial x_i} (q_i^A + q_i^d + q_i^D)$$

Diffusion and dispersion are usually combined in a single tensor $D_{ij}^H = D^d + D_{ij}$ called hydrodynamical dispersion. Substituting yields

$$\frac{\partial C}{\partial t} = - \sum_i v_i \frac{\partial C}{\partial x_i} + \sum_i \sum_j \frac{\partial}{\partial x_i} \left(D_{ij}^H \frac{\partial C}{\partial x_j} \right)$$

which is usually called the advection-dispersion equation (ADE). In this study, this equation will also be referred to as the classical or Fickian model of solute transport in porous media. In a one-dimensional framework, it reads

$$\frac{\partial C}{\partial t} = -v \frac{\partial C}{\partial x} + D_L \frac{\partial^2 C}{\partial x^2}$$

where $v = v_1$ and $D_L = D_{11}^H$ [m^2/s] called longitudinal hydrodynamical dispersion coefficient, is assumed to be constant. The coefficient of mechanical dispersion is found to depend strongly on the advective velocity. The exact relationship between these two parameters can however only be obtained from theoretical considerations for simple or hypothetical pore systems. Except in the case of very simple conceptual models, one can generally find that the coefficient of mechanical dispersion is linearly related to velocity

$$D_{ij} = \sum_k \sum_l \alpha_{ijkl} \frac{v_k v_l}{\|v\|}$$

where α_{ijkl} [m] is a fourth-order tensor called dispersivity assumed to depend only on soil properties and $\|v\|$ is the norm of the velocity vector. In the case of an isotropic homogeneous medium, owing to symmetry properties, the dispersivity tensor can be fully described by two parameters α_L and α_T , respectively called longitudinal and transverse dispersivity, both expressed in length units. In a uniform flow field, if the principal directions of the dispersion tensor are aligned with the principal directions of the velocity flow field, one can write

$$\begin{aligned} D_L &= \alpha_L v + D^d \\ D_T &= \alpha_T v + D^d \end{aligned}$$

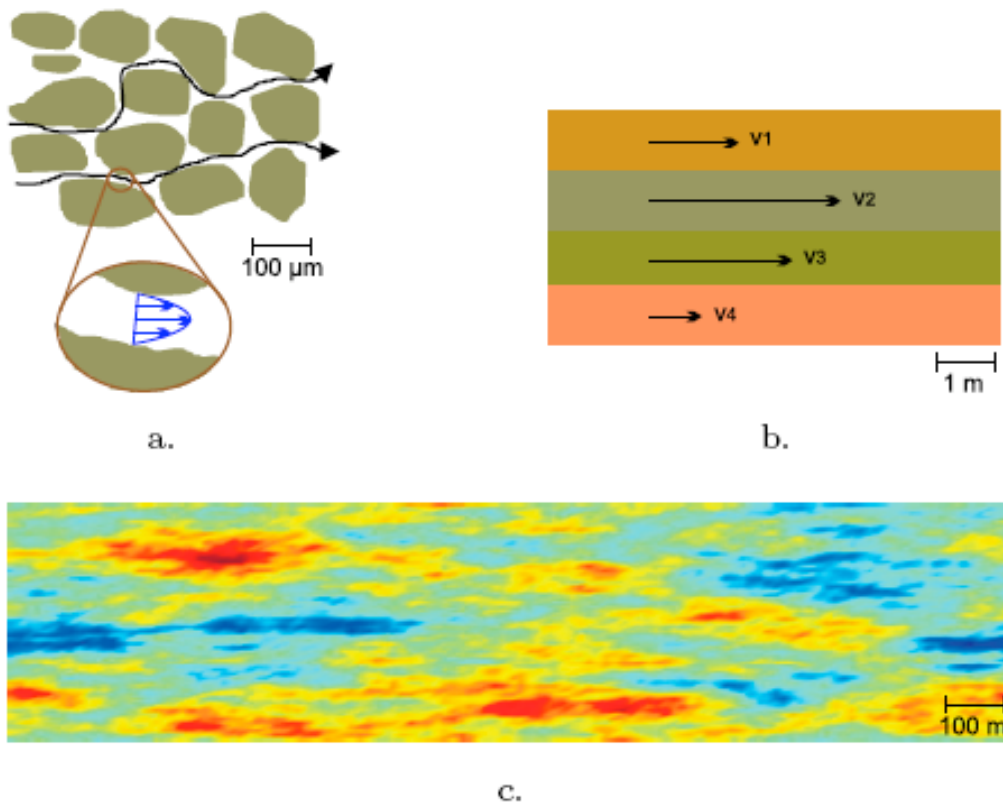
where $D_T = D_{22}^H = D_{33}^H$ quantifies mechanical dispersion in a direction transverse to flow.

Extensive experimental validation of this equation has been performed. Reference books usually provide plots of the longitudinal dispersion versus velocity and show that in the laboratory, when diffusion can be neglected, this approximation is valid under typical groundwater flow conditions. Other studies were also conducted at larger scale. Klotz et al. investigated in the laboratory and in the field a more general relation $D_L = \alpha_L v^B + D^d$ and found that parameter B should be close to one. They also showed the dependency of longitudinal dispersivity to soil sedimentological properties.

Although supported by several theoretical models and verified under well-controlled laboratory conditions, the Fickian model of dispersion has shown difficulties in predicting solute transport under certain other conditions. Dispersion is basically an advective process, as it is caused by variations in fluid velocity. However, this process does not only take place at the pore scale, but also occurs at larger scales, ranging from macroscopic to megascopic. At the field scale, commonly encountered geological structures influence contaminant transport drastically, leading to velocity variations over several orders of magnitude. This includes the effects of stratification and the presence of lenses with higher or lower permeability. At the megascopic scale, differences between geologic formations also cause non-ideality in solute transport. As the flow path increases in length, a solute cloud can encounter greater and greater variations in the aquifer, causing the variability of the velocity field to increase. Because dispersivity is related to the variability of the velocity, neglecting or ignoring the true velocity distribution (i.e. by replacing the heterogeneous medium by an equivalent homogeneous one) must be compensated for by a corresponding higher apparent (or effective) dispersivity, leading to what is commonly called the scale effect of dispersion.

This scale effect first arose from the comparison of laboratory and field values of dispersivity. Whereas typical values of dispersivity from column experiments range between 0.01 and 0.1 m, values of macroscopic dispersivity (or macrodispersivity) are in general three to four orders of magnitude larger. It has also been widely observed that field-scale dispersion coefficients increase with distance and with time.

However, it must be underlined that field dispersivity values reported in the literature are not always reliable. Inverse modelling is the usual tool to determine dispersivity.

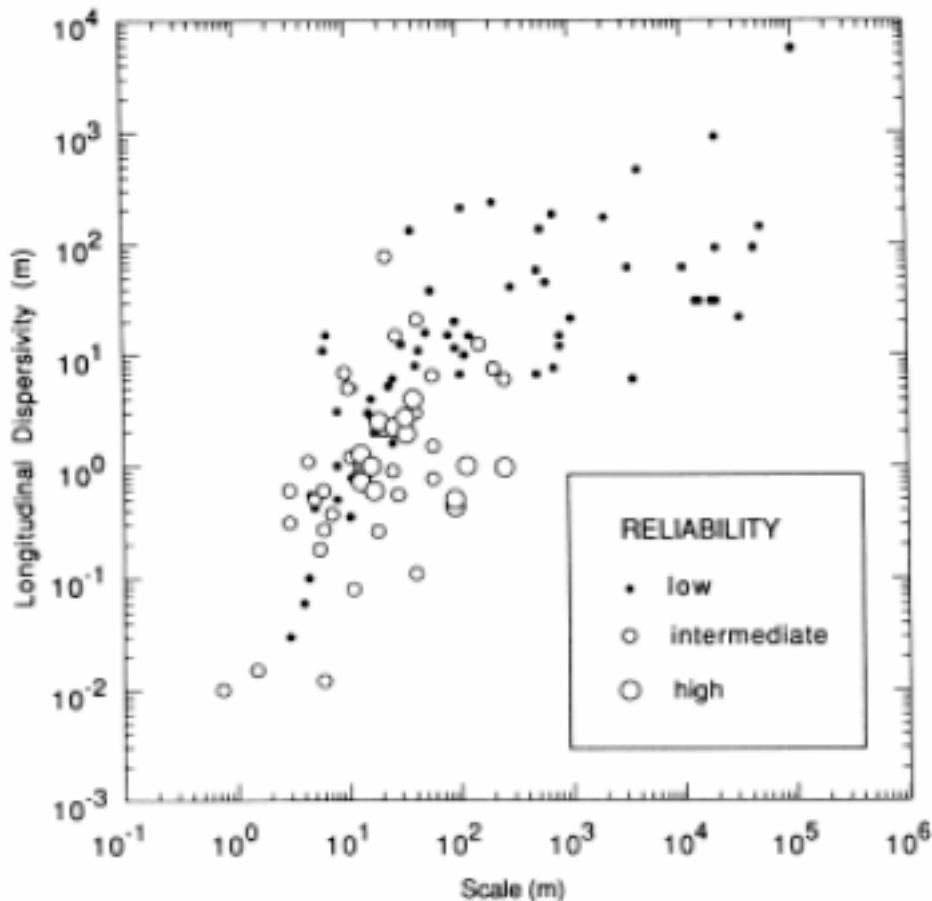


Velocity fluctuations at different scales. a. Pore-to-pore variations. b. Stratification as a cause of variation. c. Randomly heterogeneous two-dimensional anisotropic medium.

The latter is adjusted so that the experimental curve fits a given theoretical solution to the solute transport problem. When interpreting field observations of concentration, numerous factors, such as actual injection conditions, solute density effects or even temporal variations of the advective flow regime or biased interpretation techniques, are likely to be interpreted as dispersion. For example, Domenico and Robbins (1984) showed that interpreting the two- or three-dimensional spreading of a tracer with a one-dimensional model requires a spatially increasing dispersivity, whereas the use of a dimensionally correct model does not show any dispersion scale-effect.

In studies with insufficient data, the lack of field data is hidden in the dispersion term of the governing transport equation. This was mostly highlighted by Gelhar et al. [1992] who classified results from field studies using a reliability criterion. Despite this criterion, they produced an experimental curve for longitudinal dispersivity versus measurement scale, reprinted on Fig. 1.2, clearly establishing the trend for dispersivity

to increase with distance. Finally, this scale effect was demonstrated using controlled laboratory experiments.



Experimental longitudinal dispersivity values versus measurement scale with data classified by reliability. From Gelhar et al. [1992]

In this chapter, it will be shown how transport parameters and in particular, the longitudinal dispersivity, can be upscaled based on different characterization methods for heterogeneous permeability fields. The major assumption that has to be drawn in this framework is that the classical Fickian transport model remains valid at every scale of interest, provided flow and transport parameters of the medium are properly adapted. Basically, this approach is equivalent to considering a macroscale R.E.V. and deriving equivalent macroscale flow and transport parameters.

Three main approaches for the upscaling of solute transport will be reviewed in this chapter. First, the stochastic theory will be introduced. As the literature in this domain is relatively abundant, we will mainly focus on the general derivation by Gelhar and Axness (1983). Basically, this theory shows how fluctuations in permeability results in an increased spreading of solute plumes.

Then, it will be shown how fractal geometry can give an insight into macrodispersivity. Finally, inclusion models. They allow one to deal with a medium composed of inclusions of given shapes and permeabilities and solve transport considering advection only.

It must be noted that the upscaling of longitudinal dispersivity is always possible in a deterministic framework. Assuming that the heterogeneous permeability field is fully determined, the corresponding transport problem can be solved at a local scale and apparent properties (i.e. effective transport properties of an equivalent homogeneous medium) are obtained by subsequent averaging at a larger scale. In the case of a perfectly stratified aquifer (i.e. where the permeability only depends on the elevation with respect to an arbitrary datum), semi-analytical methods have been developed, based either on moment analysis (Güven et al., 1984) or on modal analysis (Güven et al., 1986).

2. The stochastic approach

Hydraulic properties of subsurface materials, such as hydraulic conductivity, will generally vary in complicated ways in space. It cannot therefore be objectively fully characterized in a deterministic way. However, as subsurface heterogeneity usually results from formation processes (such as e.g. sedimentation), it is not fully random neither, and (geo)statistical methods can be used to identify and characterize its spatial structure. Stochastic analysis enables then the variability in flow and transport to be related to variability and spatial structure associated to hydraulic properties of the heterogeneous medium considered.

In this section several results from stochastic theories applied to solute transport in heterogeneous porous media will be presented. As an introduction, basics of geostatistics and stochastic modelling will be reviewed, and the main assumptions required by the method will be presented. Furthermore, tools to characterize the spatial structure of heterogeneous permeability fields will be presented. Then, the analytical expression of macrodispersivity obtained by Gelhar and Axness will be derived, based on an Eulerian description of the velocity field. Afterwards, a few analytical solutions to be used in the next chapters will be provided.

2.1. Definitions and fundamental assumptions

In a stochastic framework, the hydraulic properties of a heterogeneous medium are treated as random variables. A random variable R can be described in terms of its cumulative probability distribution function (CDF) $F_R(r) = P[R \leq r]$, which denotes the probability that R is less than some specified value r . For a continuous random variable, the probability density function (PDF) can also be used to describe it, and is linked to the CDF using $f_R(r) = dF/dr$. The mean or expected value and the variance of the variable R are

$$\mu_R = E[R] = \int_{-\infty}^{+\infty} r f_R(r) dr$$
$$\sigma_R^2 = E[(R - \mu_R)^2] = \int_{-\infty}^{+\infty} (r - \mu_R)^2 f_R(r) dr$$

μ_R is a measure of the central tendency of the random variable and σ_R^2 is a measure of the variability associated with the variable. The squareroot of the variance is called standard deviation.

A normal or Gaussian random variable is described by the PDF

$$f_R(r) = \frac{1}{\sqrt{2\pi\sigma_R^2}} \exp\left[-\frac{(r - \mu_R)^2}{2\sigma_R^2}\right]$$

A normal variable is thus entirely characterized by its mean and variance. A log-normal random variable R is such that $\ln(R)$ is a normal random variable. In subsurface hydrology, and more particularly in the stochastic approach of transport in heterogeneous formations, hydraulic conductivity is usually assumed to be log-normally distributed. Therefore, one defines $Y = \ln(K)$, where the permeability K is expressed in [m/s] and $\ln$ is the natural logarithm. This hypothesis has the advantage that negative values are excluded, which is consistent with the physical requirement that permeability is positive.

When we are dealing with more than one variable, it is necessary to consider how the variables are interrelated probabilistically. The joint CDF of two random variables R and S is $F(r,s) = P[R \leq r, S \leq s]$ and the corresponding joint density probability function is $f(r,s) = \partial^2 F(r,s) / \partial r \partial s$. The degree of linear relationship between R and S is quantified by the covariance

$$\text{cov}(R,S) = E[(R - \mu_R)(S - \mu_S)] = \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} (r - \mu_R)(s - \mu_S) f(r,s) dr ds$$

If R and S are independent, then the covariance is zero. However, the inverse statement is not correct : if the covariance is zero, then the random variables are not necessarily independent. They are said to be uncorrelated. Another useful tool to quantify the correlation of two random variables is the variogram

$$\gamma(R,S) = 1/2 E[(R - S)^2] = \sigma_R \sigma_S - \text{cov}(R,S)$$

A random function (also called random field or stochastic process) can be viewed as a random variable with an infinite number of components. For instance, hydraulic conductivity of soils can be considered as a spatial multidimensional stochastic process $K(x)$, where x is a vector of spatial coordinates. For a fixed x , the random field is a

random variable, and is completely characterized by its joint PDF to any arbitrary order. A particular record of a stochastic process (e.g. the measured permeability field in a given situation) is referred to as a realization of the stochastic process, whereas the ensemble refers to the collection of all possible realizations of the stochastic process.

In applications related to flow through porous formations, the concept of ensemble is relatively abstract, as one only encounters one single realization of the process. The ensemble then reflects uncertainty in the depiction of the spatial structure of the formation, rather than a set of existing similar formations.

Moreover, this representation relies on a finite-length record composed of discrete values of data measured at some interval. The statistical characterization of the random structure is then based on spatial averages over the single realization available, rather than over ensemble averages. This might not induce a high bias if the ergodic hypothesis prevails and the single realization considered contains the whole information available in each realization of the ensemble.

Because a stochastic process is defined as a random variable at each point (in time or in space), the mean, the variance and the covariance are functions that may vary (in time or in space). In the case of the log-permeability field Y of soils, one could calculate

$$\mu_Y(x) = E[Y(x)] = \int_{-\infty}^{+\infty} y f_Y(y, x) dy$$

$$\sigma_Y^2(x) = E[(Y(x) - \mu_Y(x))^2] = \int_{-\infty}^{+\infty} (y - \mu_Y(x))^2 f_Y(y, x) dy$$

where y are specified values of log-permeability. An important particular class of stochastic processes is that of stationary (or homogeneous) random functions for which both mean and variance are constant (in time or in space). One will thus have $\mu_Y(x) = \mu_Y$ and $\sigma_Y^2(x) = \sigma_Y^2$. For a second-order or weakly stationary random field, the covariance (which is then a function) is moreover only dependent on the separation (in time or in space) of the two random variables considered.

2.2. Covariance function and spectral representation

Assuming two zero-mean weakly stationary random spatial fields $f(x)$ and $g(x)$, their covariance function is noted $C_{fg}(\mathbf{h})$ and only depends on the separation gap $\mathbf{h}$ (where a vector notation was adopted as the covariance can be dependent on the orientation, in

the case of a macroscopically anisotropic random field). f and g could be either permeabilities, heads, velocities, concentrations or any variable of interest. C_{fg} is either called the autocovariance or the crosscovariance, depending on f and g being representative of a same random field or not. The covariance function cannot take any arbitrary parametric shape. It must meet several properties, some of them being difficult to verify. One found therefore convenient to adopt a set of simple covariance models that are known to be valid. One of the most used model is the exponential covariance model, expressed in the one-dimensional case as

$$C_{fg}(h) = \sigma_f \sigma_g \exp\left(-\frac{|h|}{\lambda}\right)$$

where λ is called correlation length or integral scale. Intuitively, λ is a measure of the separation required for two random variables to become uncorrelated. Other one-dimensional covariance models are, among others, the Gaussian and the hole-effect covariance function.

$$C_{fg}(h) = \sigma_f \sigma_g \exp\left(-\left(\frac{h}{\lambda}\right)^2\right)$$

$$C_{fg}(h) = \sigma_f \sigma_g \exp\left(-\frac{|h|}{\lambda}\right) \left(1 - \frac{5|h|}{3\lambda} + \frac{1}{3} \frac{h^2}{\lambda^2}\right)$$

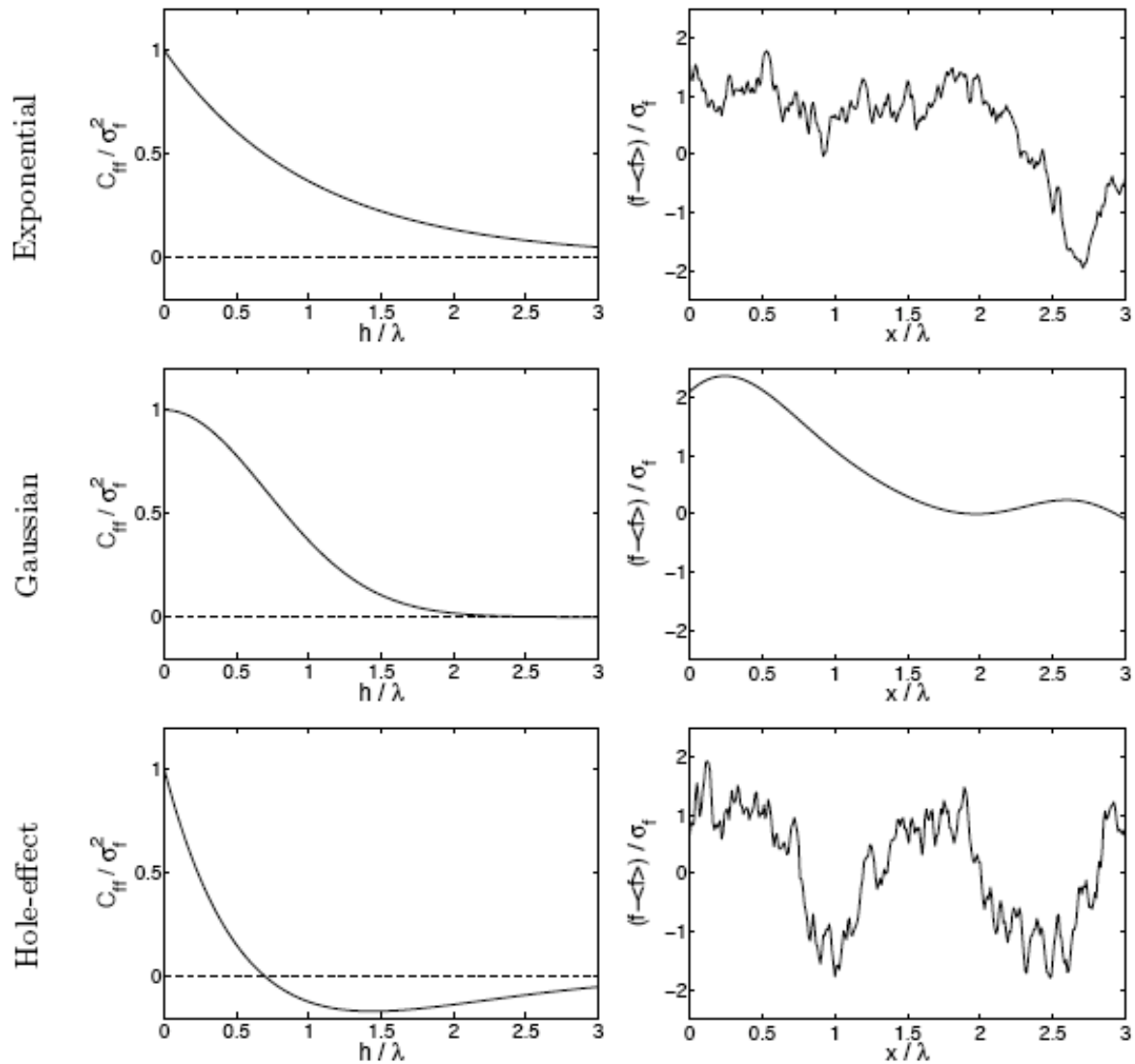
Next figure illustrates these different models (in the case of autocovariance C_{ff}) and shows one realization of a corresponding stochastic process. Basically, the exponential model can be used to model small-scale sharp variability, whereas the Gaussian model produces softer variations and mild transitions. The hole effect model can be used to represent alternating sequences, such as stratification. If a process is stationary, it is virtually always possible to describe it in terms of its frequency content, which is accessible through a Fourier-transform of this process. The Fourier-transform of the covariance function is called the power density spectrum (or spectral density function), is noted S_{fg} , and is evaluated according to

$$S_{fg}(s) = \tilde{f}(s) \tilde{g}^*(s) = \int_{-\infty}^{+\infty} C_{fg}(\mathbf{h}) \exp(-2\pi i \mathbf{h} \cdot \mathbf{s}) d\mathbf{h}$$

where s is the wave number (that has the same number of dimensions as x), $\tilde{f}(s)$ is the Fourier-transform of function $f(x)$ and $\tilde{g}^*(s)$ is the complex conjugate of the Fourier-

transform of function $g(x)$. Inversely, the covariance function can be obtained from the inverse Fourier-transform of the spectral density function

$$C_{fg}(\mathbf{h}) = \int_{-\infty}^{+\infty} S_{fg}(s) \exp(2\pi i \mathbf{h} \cdot \mathbf{s}) ds$$



Models of covariance and one realization of a corresponding random field

2.3. Eulerian derivation of macrodispersion

In this section, the general three-dimensional derivation of macrodispersion performed by Gelhar and Axness will be shortly summarized, following the lines of Gelhar and

Cirpka. The starting point is the advection-dispersion equation, expressed with a constant local hydrodynamical dispersion tensor D_{ij}^H and assuming that concentration and migration velocity are stationary random functions.

$$C = \langle C \rangle + C'$$

$$\mathbf{v} = \langle \mathbf{v} \rangle + \mathbf{v}'$$

where bold symbols are vectors. $\langle C \rangle, \langle \mathbf{v} \rangle, C'$ and $\mathbf{v}'$ are respectively mean concentration, mean velocity, concentration fluctuation and velocity fluctuation. Fluctuations are assumed to have a zero mean $\langle C' \rangle = \langle \mathbf{v}' \rangle = 0$. Substituting these expressions, taking expected values and dropping higher-order terms, yield the governing equation for the mean concentration

$$\frac{\partial \langle C \rangle}{\partial t} = - \sum_i \langle v_i \rangle \frac{\partial \langle C \rangle}{\partial x_i} - E \left[\sum_i v_i' \frac{\partial C'}{\partial x_i} \right] + \sum_i \sum_j \frac{\partial}{\partial x_i} D_{ij}^H \frac{\partial \langle C \rangle}{\partial x_j}$$

Considering the classical advection-dispersion equation, a new term arises here. It reflects additional mass transport due to correlation between specific discharge and concentration fluctuations. It produces a large-scale dispersion effect and can be approximated using a Fickian-like law

$$E \left[\sum_i v_i' \frac{\partial C'}{\partial x_i} \right] = \sum_i \frac{\partial}{\partial x_i} \langle v_i' C' \rangle \approx - \sum_i \sum_j \frac{\partial}{\partial x_i} \left(D_{ij}^* \frac{\partial \langle C \rangle}{\partial x_j} \right)$$

D_{ij}^* is the macrodispersion tensor and is assumed to be proportional to the absolute value of migration velocity, as for the local dispersion tensor. It can be evaluated using the governing equation of concentration perturbations. The latter is obtained by

$$\frac{\partial C'}{\partial t} + \sum_i \left(v_i' \frac{\partial \langle C \rangle}{\partial x_i} + \langle v_i \rangle \frac{\partial C'}{\partial x_i} \right) - \sum_i \sum_j \frac{\partial}{\partial x_i} \left(D_{ij}^H \frac{\partial C'}{\partial x_j} \right) = \sum_i \frac{\partial}{\partial x_i} (v_i' C' - \langle v_i' C' \rangle) \approx 0$$

This approximation is of crucial importance. Basically, it implies that velocity fluctuations are sufficiently small for second-order products to be neglected. For a log-normal permeability field, it can be shown based on a similar stochastic analysis of the flow equation that this condition on velocity perturbation requires a small variance of the Y field, so that it can be linearized. Typically, these developments are assumed to be valid for $\sigma_Y^2 < 1$

In general, these equations must be solved simultaneously. However, a decoupling can be accomplished provided that concentration fluctuations occurs at a much smaller scale than variations associated to the mean concentration. It is then possible to solve it to evaluate the macrodispersive flux and subsequently substitute it in the equation. Assuming that the mean flow occurs in direction $i=1$ and using the notations introduced simplifies to

$$\frac{\partial C'}{\partial t} = -v_1' |\nabla \langle C \rangle| - \langle v_1 \rangle \frac{\partial C'}{\partial x_1} + D_L \frac{\partial^2 C'}{\partial x_1^2} + D_r \frac{\partial^2 C'}{\partial x_2^2} + D_r \frac{\partial^2 C'}{\partial x_3^2}$$

where the notation $|\nabla \langle C \rangle|$ indicates that the gradient of the mean concentration is assumed to be constant in time and in space. This assumption may not be very realistic. But a mean gradient hardly varying over several correlation lengths of the hydraulic conductivity field may be achieved in the large-time limit under ordinary flow conditions, allowing one to apply the theory derived here in field conditions.

Las equation may be transferred into the Fourier-space. Using some basic properties of the Fourier-transform, one obtains

$$\left(\frac{d}{dt} + b \right) \tilde{C}'(s) = -\tilde{v}_1'(s) |\nabla \langle C \rangle|$$

where $\sim$ indicates the Fourier-transform and where

$$b = 2\pi i \langle v_1 \rangle s_1 + 4\pi^2 D_L s_1^2 + 4\pi^2 D_r (s_2^2 + s_3^2)$$

This is a linear non-homogeneous first-order time differential equation. Since the concentration gradient is taken as a constant and assuming as initial condition a concentration distribution equal to the mean concentration (i.e. a concentration perturbation $C' = 0$), one obtains

$$\tilde{C}'(s, t) = -\tilde{v}_1'(s) |\nabla \langle C \rangle| \int_0^t \exp(b(\tau - t)) d\tau = -\frac{\tilde{v}_1'(s) |\nabla \langle C \rangle|}{b} (1 - \exp(-bt))$$

To compute the longitudinal apparent dispersion coefficient it can be used

$$D_L^* = -\frac{1}{|\nabla \langle C \rangle|} \langle C' v_1' \rangle$$

As $\langle C'v_1' \rangle$ is the integral of the cross-spectral density of concentration and longitudinal velocity fluctuations S_{Cv_1} , last equation can be transformed into

$$\alpha_L^*(t) = \frac{1}{\langle v_1 \rangle} \int_{-\infty}^{+\infty} \frac{1 - \exp(-bt)}{b} \tilde{v}_1'(s) \tilde{v}_1^*(s) ds = \frac{1}{\langle v_1 \rangle} \int_{-\infty}^{+\infty} \frac{1 - \exp(-bt)}{b} S_{v_1 v_1}(s) ds$$

This equation establishes the link between velocity fluctuations and macrodispersivity. As the velocity spectrum is linked to log-permeability variations, macrodispersivity is basically found to be dependent on the permeability field. Moreover, macrodispersivity is also proved to be time-dependent and vanishes for large time, macrodispersivity converges to a constant asymptotic value.

Similar derivations have been performed by Dagan and by Neuman et al. Dagan used a Lagrangian framework, but had to use an approximate relationship between the Eulerian and the Lagrangian velocity covariance. Neuman et al. used a more abstract mathematical analysis based on semigroup theory. Basically, these derivations all require an assumption of relatively small perturbations, leading to little discrepancy among them and a domain of validity $\sigma_Y^2 < 1$.

2.4. A few analytical solutions

Most of available analytical solutions are based on exponential covariance models and assume that local dispersivities are negligible compared to correlation lengths. The asymptotic value of longitudinal dispersivity in an isotropic medium is given by

$$\alpha_L^*(\infty) = \sigma_Y^2 \frac{\lambda}{\gamma^2}$$

where γ is a flow factor accounting for the dependence of effective permeability on dimensionality. In the two-dimensional case, $\gamma = 1$, whereas in the three-dimensional case, $\gamma = \exp(\sigma_Y^2/6)$. It must be noted that Dagan obtained a similar result using a Lagrangian framework, but with $\gamma = 1$ in the three-dimensional case. Dagan states that taking into account a value $\gamma \neq 1$ is not consistent with first-order approximations adopted, as it introduces a term of order σ_Y^4 .

Fig. 2.2 depicts the influence of the variance of the log-permeability field on the asymptotic value of longitudinal apparent dispersivity.

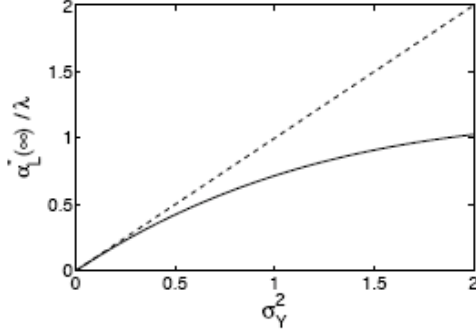


Figure 2.2: Asymptotic longitudinal dispersivity in the isotropic case. 3D (solid line) and 2D (dashed line) case. The solution by Dagan [51] in the 3D case corresponds to the dashed line.

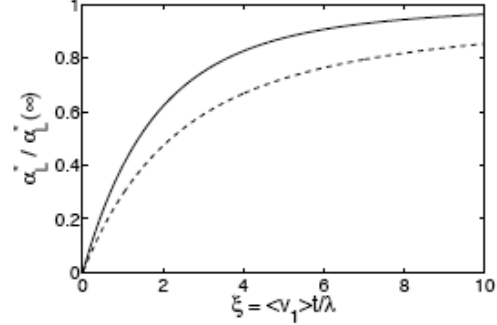


Figure 2.3: Convergence of longitudinal dispersivity in the isotropic case. 3D (solid line) and 2D (dashed line) cases.

The three-dimensional isotropic solution for intermediate times is given by Gelhar, based on an expression derived by Dagan

$$\frac{\alpha_L^*(t)}{\alpha_L^*(\infty)} = 1 - \frac{4}{\xi^2} + \frac{24}{\xi^4} - 8 \left(\frac{1}{\xi^2} + \frac{3}{\xi^3} + \frac{3}{\xi^4} \right) \exp(-\xi)$$

where $\xi = \langle v_1 \rangle t / \lambda$. In a two-dimensional isotropic aquifer, it is given by

$$\frac{\alpha_L^*(t)}{\alpha_L^*(\infty)} = 1 - \frac{3}{2\xi} + \frac{3}{\xi^3} - \frac{3}{\xi^2} \left(1 + \frac{1}{\xi} \right) \exp(-\xi)$$

Basically, these results express that the convergence to the asymptotic behavior is only controlled by the ratio of mean travel distance to correlation length.

In the two-dimensional case, as the number of available paths to bypass low permeability zones is lower than in the three-dimensional case, convergence is less rapidly reached (Fig. 2.3).

In the case of a two-dimensional anisotropic situation with flow occurring in a direction at an angle θ with respect to the bedding of the permeability field, asymptotic dispersivity is given by

$$\alpha_L^*(\infty) = \sigma_Y^2 \frac{\lambda_1 \lambda_2}{\gamma^2 \sqrt{\lambda_1^2 \sin^2 \theta + \lambda_2^2 \cos^2 \theta}}$$

where the flow factor is obtained from

$$\gamma = \frac{\exp[\sigma_Y^2(1/2 - g_{22})]}{\sin^2 \theta + B \cos^2 \theta}$$

with $B = \exp[\sigma_Y^2(g_{11} - g_{22})]$, $g_{11} = \lambda_2/(\lambda_1 + \lambda_2)$ and $g_{22} = \lambda_1/(\lambda_1 + \lambda_2)$.

Fig. 2.4 shows the effect of anisotropy on asymptotic longitudinal dispersivity. For high variance and high anisotropy, flow is mainly directed in the longitudinal direction and little transverse mixing can occur, leading to lower values of longitudinal dispersivity. As anisotropy decreases, transverse mixing increases, leading to higher apparent longitudinal dispersivities. Fig. 2.5 shows that, globally, when flow is not aligned with the main principal direction of the permeability field, apparent dispersivity tends to decrease. No analytical solution for transient apparent dispersivity in two-dimensional anisotropic situation could be found.

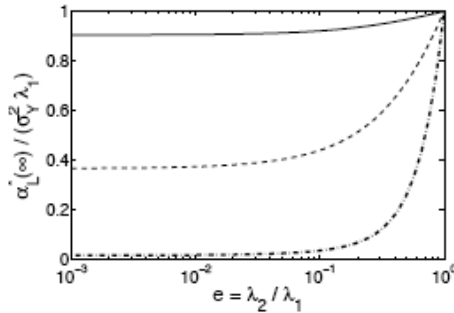


Figure 2.4: Influence of the anisotropy on asymptotic longitudinal dispersivity for $\theta = 0$. $\sigma_Y^2 = 0.1$ (solid line), $\sigma_Y^2 = 1$ (dashed line) and $\sigma_Y^2 = 4$ (dot-dashed line).

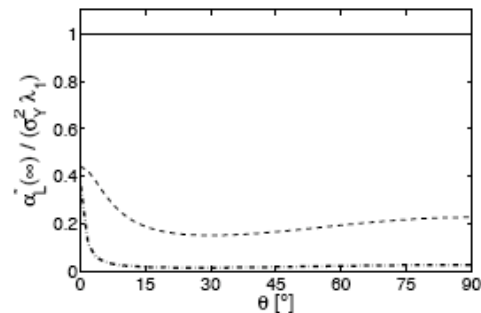


Figure 2.5: Influence of the flow direction on asymptotic longitudinal dispersivity for $\sigma_Y^2 = 1$. $e = 1$ (solid line), $e = 0.1$ (dashed line) and $e = 0.01$ (dot-dashed line).

The perfectly stratified case could be obtained under appropriate conditions ($\lambda_1 \rightarrow \infty, \lambda_2 \rightarrow \infty$ and finite λ_3). However, a separate but similar analysis was conducted by Gelhar et al. They assumed a normal permeability distribution (instead of a log-normal one) and obtained

$$\alpha_L^* = \int_{-\infty}^{+\infty} \frac{S_{KK}(s)}{\langle K \rangle^2} \frac{1 - e^{-\alpha_T v s^2}}{\alpha_T s^2} ds$$

in which $S_{KK}(s)$ is the power density spectrum of the hydraulic conductivity field, characterized by an integral scale λ .

Three different regimes can be identified. At early times, transverse spreading has not caused any mixing yet and solute particles remain on their initial flow line. The concentration distribution behaviour is fully controlled by longitudinal advection and apparent longitudinal dispersivity varies linearly in time

$$\alpha_L^* \rightarrow \frac{\sigma_K^2}{\langle K \rangle^2} vt \quad t \rightarrow 0$$

After some time, spatial concentration gradients appear due to transverse velocity variations, causing diffusion and dispersion of particles from their initial flow line. Particle velocities then change according to their new flow line, and new concentration gradients appear, causing new transfers of particles between flow lines. For intermediate times, transverse transport processes have ensured mixing over the respective layer thicknesses (or over the integral scale λ), but not over the overall aquifer thickness. In this case, it can be shown that longitudinal dispersivity increases according to the square-root of time. The third regime corresponds to full mixing of the solute plume over the aquifer thickness. This regime was first investigated by Taylor and Aris for laminar flow through a tube, with a deterministic velocity distribution.

They showed that in this regime, commonly referred to as the Taylor dispersion regime, the dispersive flux is Fickian with a constant asymptotic apparent dispersivity. In the stochastic approach of solute transport in perfectly layered soils, this regime only exists provided the covariance function of the permeability field is properly chosen. Using a hole-effect covariance model, Gelhar et al. obtained

$$\alpha_L^*(\infty) = \frac{1}{3} \frac{\sigma_K^2}{\langle K \rangle^2} \frac{\lambda^2}{\alpha_T}$$

Asymptotic apparent longitudinal dispersivity is directly proportional to the variance of the $\ln(K)$ field (as $\sigma_K^2 / \langle K \rangle^2 \approx \sigma_Y^2$) but depends on the square of the correlation length. Moreover, its value is inversely proportional to the magnitude of transverse mixing.

3. Fractal models of heterogeneity

The main feature of a fractal object is that its degree of irregularity is independent of the scale. As long as one watches it closer and closer, new small-scale irregularities appear, although it is not possible to detect them from a larger-scale point of view. In normal Euclidian geometry, the length L of a line can be calculated with

$$L = n\varepsilon$$

where n is the number of length units ε . If the size of ε is diminished by 2, then the number of measuring units n increases by 2, keeping the length constant.

Many natural objects do not behave according to this simple relationship. It has been found that, in the case of fractal lines such as coastal lines,

$$F = n\varepsilon^d$$

where F is a measure of the fractal line length (which, contrary to L , is not expressed in [m] but in [m^d]) and d is the dimension in which one has to measure the line length in order to obtain a constant value for F . d is called the fractal dimension. In the case of a line, this parameter may vary from 1 to 2. If $d = 1$, the measured line is geometrically simple, whereas if $d = 2$, the line is so irregular that it completely fills a plane. Combining equations leads to

$$L(\varepsilon) = F\varepsilon^{1-d}$$

which describes the dependence of a measured length with the measurement unit ε , according to fractal length F and fractal dimension d .

3.1. Application to solute transport

Fractal geometry was first introduced by Wheatcraft and Tyler to describe solute particle travel paths in heterogeneous media. However, as the Euclidian length of a fractal line increases without bounds as long as the measurement unit decreases, particle travel path cannot be fully fractal. Indeed, water flow does not exactly follow the shape

of the soil grains, otherwise some particules would have an infinite travel time. A cutoff limit ε_c was then introduced for the measurement unit, this limit being comprised between a mean pore size and the size of the R.E.V. for the smallest heterogeneity.

In a single fractal streamtube, if x_F is the actual distance travelled by a particle (in [m]) and if x_S is the longitudinal straight-line distance travelled by this same particle (also expressed in [m]), one has

$$F = x_S^d$$

where the measurement unit is equal to the straight-line path. Substituting this relationship and measuring at the fractal cutoff limit leads to

$$x_F = \varepsilon_c^{1-d} x_S^d$$

which can be viewed as a scaling relationship between measurement scale x_S and real particle travel path x_F . This is illustrated in Fig. 2.6. If measurement scale is divided by 2, if particle travel path is fractal, it is not divided by 2 but by 2^d .

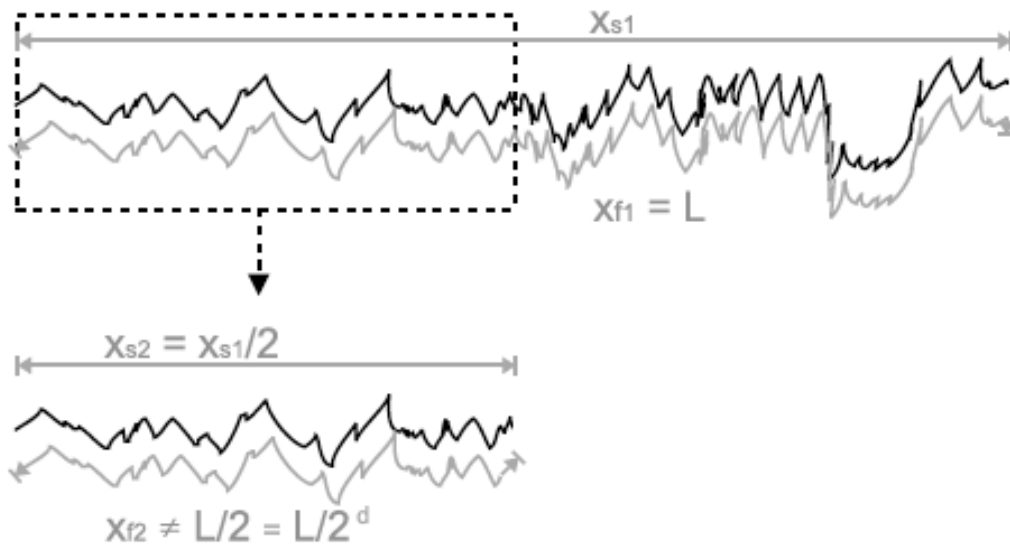


Figure 2.6: Schematic illustration of a fractal particle path.

Provided the Fickian model is valid at some local scale, the spreading of a dissolved particle cloud in space, expressed as the variance of the particle position $\sigma_C^2 = E[(X - \langle X \rangle)^2]$, is given by

$$\sigma_C^2 = 2\alpha_L x_F$$

where α_L is the local longitudinal dispersivity. This variance can also be expressed in terms of measured variables

$$\sigma_C^2 = 2\alpha_L^* x_S$$

where α_L^* is the measured (apparent or effective) longitudinal dispersivity. Using this expression we obtain

$$\alpha_L^* = \alpha_L \varepsilon_C^{1-d} x_S^{d-1}$$

which allows the upscaling of longitudinal dispersivity based on a fractal description of the heterogeneous medium. For an homogeneous non-fractal medium ($d = 1$), field-scale dispersivity remains equal to local dispersivity. Wheatcraft and Tyler and Zhou and Selim extended this latter equation to transport in a soil composed of a set of fractal streamtubes. However, this approach is rather conceptual, and one could expect a real aquifer to behave somehow differently than a set of disconnected fractal streamtubes. Zhan and Wheatcraft proposed another approach, combining fractal geometry and spectral analysis, that could be more adapted to real field-scale situations.

3.2. Fractal geometry and spectral analysis

Whereas classical stochastic approaches involve $\ln(K)$ covariance functions that have a finite correlation length, in order to have a rapid decrease of hydraulic conductivity autocorrelation this assumption is not necessary anymore when using concepts of fractal geometry. Zhan and Wheatcraft proposed to use a power-law covariance model $C_{YY} = |h|^{2H}$ where $0 < H < 1$ is called Hurst coefficient and link with the fractal dimension according to $H = 1 + e_u - d$ (e_u being the Euclidian dimension). $H=1$ corresponds thus to a non-fractal medium.

For this type of heterogeneity, Fickian behaviour will never be achieved if the aquifer is not bounded, and longitudinal macrodispersivity will monotonically increase with plume scale to infinity. However, for most geological formations, physical boundaries always exist. A generally encountered situation is that no-flow boundaries enclosing the fractal porous medium define the field scale at which contaminants will disperse. Zhan and Wheatcraft then introduced a macroscale cutoff limit L_m , having the same role as the correlation length used in classical stochastic analysis, but being linked to a physical boundary rather than to the structure of the permeability field.

Zhan and Wheatcraft showed that, in the case of a stratified fractal aquifer, asymptotic macrodispersivity can be computed from

$$\alpha_L^*(\infty) = \frac{\sigma_Y^2}{\alpha_T} \frac{2-d}{3-d} \left(\frac{L_m}{2\pi} \right)^2$$

where $1 < d < 2$ and L_m is representative of the aquifer thickness.

Relative macrodispersivity can be computed according to

$$\frac{\alpha_L^*}{\alpha_L^*(\infty)} = 1 - \exp\left[-\frac{\xi}{(2\pi)^2}\right] + \frac{1}{2-d} \frac{\xi}{(2\pi)^2} \exp\left[-\frac{\xi}{(2\pi)^2}\right] - \frac{1}{2-d} \left[\frac{\xi}{(2\pi)^2} \right]^{3-d} \Gamma\left(d-1, \frac{\xi}{(2\pi)^2}\right)$$

where $\gamma = 1$ and $\gamma = 1 + \sigma_Y^2/6$ in two and three-dimensional cases respectively.

Fig. 2.7 shows the dependency of asymptotic dispersivity on Hurst coefficient for two- and three-dimensional problems. These results are qualitatively consistent with results from stochastic theories, as an increase in the correlation of the medium (i.e. an increase of the Hurst coefficient or an increase of the correlation length) results in a higher asymptotic longitudinal apparent dispersivity and that an increase in the Euclidian dimension of the problem results in a decrease of the dispersivity. It should be noted that a totally fractal medium ($H = 0$) yields a macroscopic dispersivity equal to zero, which is again consistent with stochastic theories ($\alpha_L^* = 0$ for $\lambda = 0$) but contradictory with results of streamtubes models developed in the previous section.

Fig. 2.8 shows the transient development of apparent longitudinal dispersivity in the case of a perfectly stratified aquifer.

In the anisotropic case, Zhan and Wheacraft also developed two and three-dimensional analytical solutions for asymptotic apparent dispersivity.

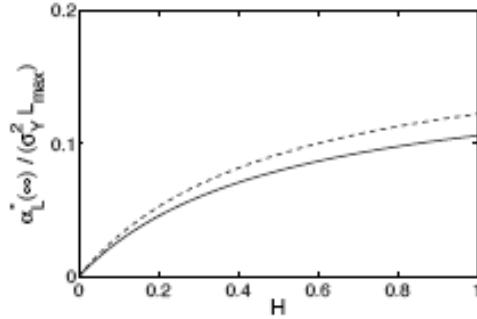


Figure 2.7: Influence of Hurst coefficient on asymptotic dispersivity for two-dimensional (solid line) and three-dimensional (dashed line) medium. $\sigma_Y^2 = 1$.

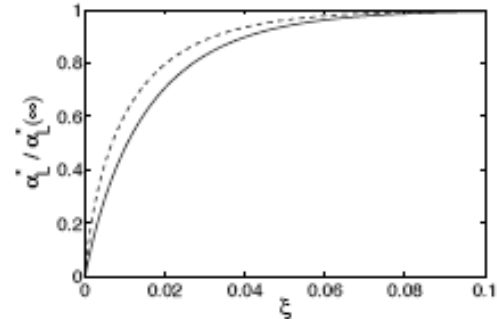


Figure 2.8: Influence of fractal dimension on the transient behavior of apparent longitudinal dispersivity in a perfectly stratified aquifer. $d \rightarrow 1$ (solid line) and $d \rightarrow 2$ (dashed line).

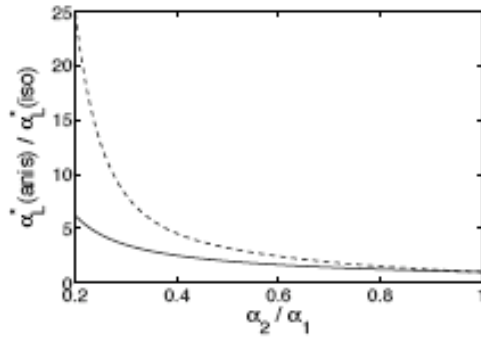


Figure 2.9: Influence of the anisotropy ratio on apparent longitudinal dispersivity in a two-dimensional aquifer for flow parallel to the bedding. $H \rightarrow 0$ (solid line) and $H \rightarrow 1$ (dashed line).

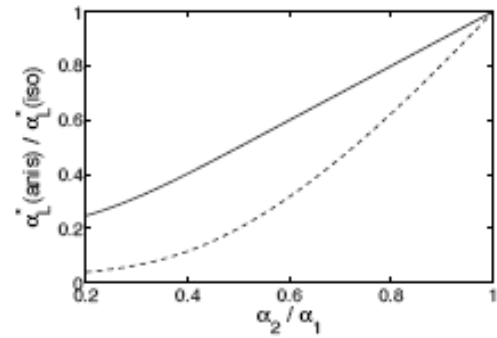


Figure 2.10: Influence of the anisotropy ratio on apparent longitudinal dispersivity in a two-dimensional aquifer for flow perpendicular to the bedding. $H \rightarrow 0$ (solid line) and $H \rightarrow 1$ (dashed line).

4. Inclusion models

Transport in aquifers made of inclusions of highly contrasted permeabilities has only been very recently investigated. Desbarats performed pioneering numerical simulations using a binary medium with inclusions of low permeability and showed that permeability contrast and inclusion volumetric proportion were the main controlling parameters for transport. Rubin proposed a first-order stochastic approach and derived analytical results in the case of bimodal isotropic media. Like other results from stochastic theories, Rubin's results are only valid for low permeability contrasts. Eames and Bush and later Dagan and Lessoff and Lessoff and Dagan studied transport properties of two- and three-dimensional bimodal fields composed of inclusions of fixed size and of constant permeability, disposed at random in an homogeneous matrix. Their developments were conducted under the assumption of low volumetric proportion of inclusions (i.e. in the dilute system limit) so that advective transport could be solved by isolating one inclusion and the dispersive effect of a collection of lenses was determined subsequently in a simple additive manner. Dagan et al. and Fiori et al. further refined the analysis by considering distributions of ellipses of different size and of different permeabilities, and by computing the transient development of apparent dispersivity.

They released the dilute system approximation by considering instead the selfconsistent approach, in which the flow and transport problems are solved for a single inclusion embedded in a equivalent homogeneous medium replacing the neighbouring inclusions. However, they limited their analysis to isotropic media and compared the results with numerical simulations. Dagan and Fiori and Fiori and Dagan studied transport properties of media with composite inclusions, that allowed them to derive results without relying neither on the dilute system nor on the self-consistent approach. However, they also conducted their analysis in the isotropic case. Fiori et al. and Jankovic et al. performed extensive numerical simulations on bimodal isotropic medium for different volumetric proportions of inclusions (ranging from 5 to 40%) and for different permeability ratios (ranging from 0.01 to 10). They found that the self-consistent approach could be reasonably adopted in each of their tested case.

In this section, it is thus proposed to further study the model suggested by Dagan et al. developed under the self-consistent approximation, and to extend it to anisotropic formations using the results proposed by Dagan and Lessoff and Lessoff and Dagan.

4.1. Conceptual model

Dagan et al. have suggested to model heterogeneous formations as multiphasic ones, made up of M types of block geometry and of N different types of material. Blocks are assumed not to overlap (Fig. 2.11 a.). A point of the medium lies in the block i, j of shape i ($i = 1 \dots M$) and of material j ($j = 1 \dots N$) with a known probability p_{ij} . p_{ij} thus denotes the volumetric proportion of blocks of size i and of material j in the medium. Centroid positions of blocks x_{ij} are however not known and are treated as random variables.

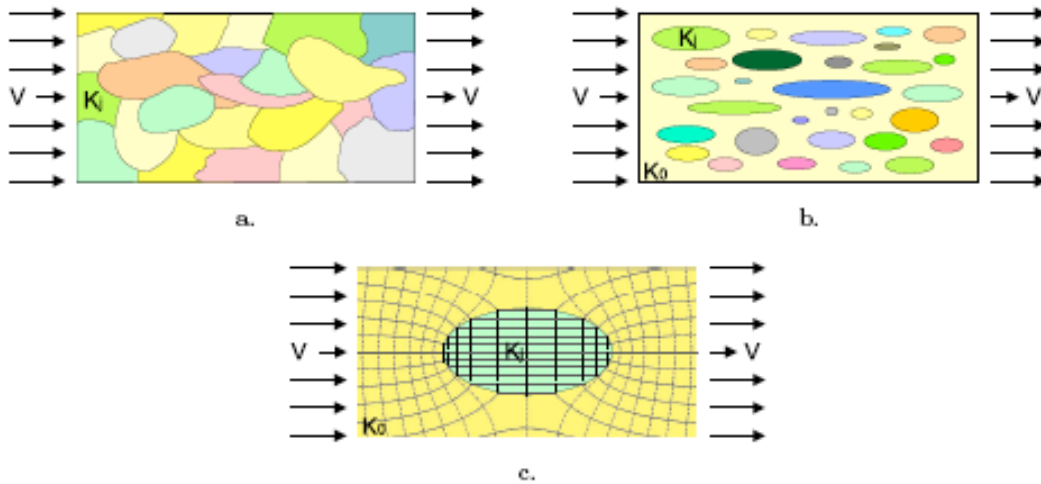


Figure 2.11: Conceptual model and the self-consistent approximation. a. Statistically homogeneous but anisotropic heterogeneous permeability field. b. Model of inclusions of regular shape disposed at random in a matrix. c. Single inclusion embedded in a matrix. *Adapted from Dagan et al. [55].*

If K_j is the permeability of material j , the overall conductivity field is given by

$$K(x) = \sum_i \sum_j K_i I(x - \bar{x}_{ij})$$

where the indicator function $I(x - \bar{x}_{ij})$ is equal to 1 for x belonging to the inclusion (i, j) and is equal to zero otherwise. It is emphasized that permeabilities of two neighbouring blocks remain uncorrelated. Mean and variance of the log-permeability field can be computed from

$$\ln(K_g) = \sum_i \sum_j p_{ij} m_j$$

$$\sigma_Y^2 = \frac{1}{2} \sum_i \sum_j \sum_{k \neq j} (m_j - m_k)^2 p_{ij} p_{ik}$$

where $m_j = \ln(K_j)$. The variance of such media can be very high, well above the classical limit $\sigma_Y^2 < 1$ established for the validity of first-order stochastic theories.

To further simplify the model, Dagan et al. propose to represent blocks as inclusions of regular size, such as ellipses or spheroids, and to assume that they are submerged in a matrix of arbitrary conductivity K_0 to be determined below (Fig. 2.11 b.). Dagan et al. state that, despite these limitations and provided the distribution of sizes and permeabilities is properly chosen, this type of permeability field can properly mimic any given permeability distribution and any two-point anisotropic covariance function.

In a given heterogeneous formation of this geometry, the solution of the flow field can be represented as a distribution of singularities of source type, each source corresponding to a given block. The self-consistent approach proceeds by isolating one inclusion of shape i and permeability K_j and by suppressing the remaining ones in the matrix of permeability K_0 (Fig. 2.11 c.). The flow and transport problems are then solved assuming there is no interaction between each block. As K_0 could be any reference permeability somehow linked to the effective permeability K_e of the medium, the self-consistent approach assumes $K_0 = K_e$ and K_0 reflects the presence of neighbourings blocks that have been suppressed. The derivation of K_e for two- and three-dimensional isotropic media is given by Dagan and extended to three-dimensional anisotropic media.

4.2. Advective transport by the Lagrangian approach

Under ergodic condition, the spatial moments of a solute plume can be computed from the statistical moments of the trajectory of a single particle. One will then consider a solute particle injected at time $t = 0$ and at position x_0 .

The trajectory of this particle is $x = X(t, x_0)$ and is given by

$$\mathbf{X}(t, x_0) = x_0 + \mathbf{V}t + \sum_i \sum_j \mathbf{X}'_{ij}$$

where $\mathbf{V}$ is the far field velocity and $\mathbf{X}'_{ij}$ is the trajectory fluctuation caused by block (i,j). Trajectory second moments are given by

$$X_{ms}(t) = \sum_i \sum_j E \left[X'_{ij,m}(x_0 - \bar{x}_{ij}) X'_{ij,s}(x_0 - \bar{x}_{ij}) \right]$$

where m and s refer to the components of the vectors of the trajectory fluctuations.

Details of the computation method are given by Lessoff and Dagan and by Fiori et al.

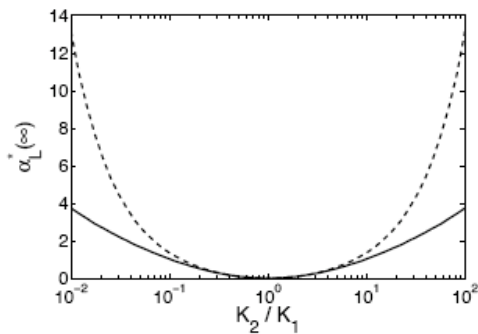


Figure 2.12: Influence of permeability contrast on apparent longitudinal dispersivity. Proportions of inclusions are $p_1 = p_2 = 0.5$. $e = 1$ (solid line) and $e = 1/4$ (dashed line).

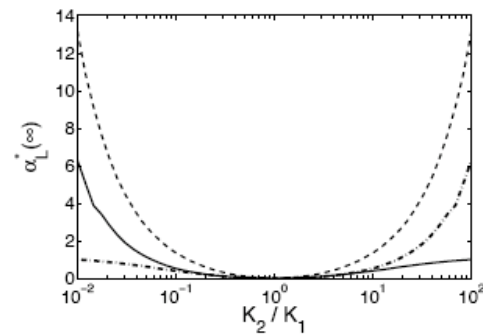


Figure 2.13: Influence of permeability contrast on apparent longitudinal dispersivity. Anisotropy ratio is $e = 1/4$ and proportions of inclusions are $p_2 = 0.1$ (solid line), $p_2 = 0.5$ (dashed line) and $p_2 = 0.9$ (dot-dashed line).

Figs. 2.12 to 2.15 show the behaviour of the asymptotic dispersivity for a two-facies permeability field (facies 1 and 2) of varying permeability contrast, anisotropy ratio and volumetric proportion. Each point on these figures requires computation of effective permeability and computation of asymptotic dispersivity. It appears that for equal volumetric proportion of facies, curves are symmetric. For higher anisotropy ratio,

apparent longitudinal dispersivity increases, which is in accordance with results obtained by Lessof and Dagan under the dilute assumption. When the medium is mainly composed of a low-permeability facies, apparent dispersivity increases when permeability decreases. However, as discussed qualitatively by Dagan and Lessoff and Dagan et al., the behaviour for low permeability inclusions is altered by transverse dispersivity and molecular diffusion, which provide a cutoff in asymptotic longitudinal macrodispersivity.

When the medium is predominantly composed of high permeability inclusions, apparent dispersivity converges to a constant value for increasing permeability. Apparent dispersivity is maximum for a volumetric proportion of inclusions close to 50 %.

5. Conclusion

In this chapter, three methods for the upscaling of longitudinal dispersivity in heterogeneous media were detailed. These methods allow one to compute apparent (or effective) values of longitudinal dispersivity to be used in the ADE for an equivalent homogeneous medium.

The stochastic method is relatively popular but is bound to a strong limitation of low permeability variability. The other limitation of this method is that it is based on a statistical characterization of the permeability field. This characterization ideally requires vast amounts of data, that are generally not available in field-scale problems.

The fractal method that has been presented does not require an assumption low variability. However, it basically requires similar characterization methods as the stochastic approach, as the transport problem is parametrized using a covariance function for the permeability field and a large scale cutoff distance. Finally, the self-consistent approach allowed one to derive apparent dispersivity values in the case of highly heterogeneous media. The main limitation of this approach is that diffusive and local-scale dispersive transport are not considered, which might induce a serious bias when considering media with relatively low permeabilities.

The basic approach for modelling large-scale solute transport consists then to use the upscaled dispersion coefficients in the classical advection-dispersion equation and solve it at the scale of interest. However, as the time needed to reach the asymptotic large-scale Fickian behavior turns out to be extremely long, the assumption of a constant macrodispersion coefficient can still be questionable in most of the case. The remaining solution consists in solving the ADE with time- or space-dependent dispersion coefficients, either numerically or analytically.

Upscaling transport parameters under the non-Fickian Approach

1. Introduction

The question of how to quantify contaminant transport in porous soils and rock has been the focus of research over several decades in hydrology, as well as in the closely related disciplines of soils science and petroleum engineering. Landmark tracer breakthrough experiments, dating mostly from the 1950s and 1960s, formed the basis for theoretical developments and analyses that considered almost exclusively the classical advection-dispersion equation (ADE). The ADE, and variants thereof, have continued to be used to this day as the principal means for considering and quantifying tracer transport in porous media.

However, just how suitable is the ADE framework for describing tracer transport in porous media? Even early pioneering experiments reported the occurrence of systematic errors in fitting breakthrough curves (BTCs) using the classical ADE. In a series of careful and well-documented column experiments, Scheidegger (1959) observed that deviations in fits of the ADE to the BTCs could not be explained simply by the usual variability (error) in experimental measurements. Scheidegger (1959, p.103) stated: "The deviations are systematic which appears to point toward an additional, hitherto unknown effect." Aronofsky and Heller (1957) also analyzed published tracer experiments and reported that systematic deviations arise between measurements and predictions using the ADE. Indeed, over the last 4 decades several other studies have pointed out some specific and serious inadequacies in the applicability of the classical ADE, even with small-scale laboratory experiments on homogeneous samples. Silliman and Simpson (1987) demonstrated convincingly in laboratory experiments the scale dependency of the dispersivity coefficient; this is in a stark contrast to the fundamental assumption that the dispersivity is a constant derived from the microgeometry of the porous medium. Such scale-dependent behaviour is typical of "non-Fickian" or "anomalous" transport. These issues are by no means limited to laboratory-scale experiments. Deviations from the classical ADE behaviour are even more significant in natural systems.

While the ADE can treat “homogeneous” porous media under some conditions, such homogeneity rarely, if ever, exists. The heterogeneity of natural geological formations at a wide range of scales necessitates consideration of more sophisticated transport theories. Why is the conceptual picture underlying the classical ADE formulation limited? What is missing from this picture describing the transport behaviour of a contaminant in a natural porous medium? The answers to these questions lie in the basic recognition that in all geological formations, heterogeneities are present at all scales, from the submillimeter pore scale to the basin scale itself. We emphasize that the term “heterogeneities” can refer to variations in the distribution of the geometrical properties (e.g., porosity and hydraulic conductivity), as well as to variations in the biogeochemical properties of the medium, all of which can affect tracer transport.

Three points of conceptual understanding can be drawn immediately from this fact:

- (1) The high degree of variability in these heterogeneities rules out, a priori, the possibility of obtaining complete knowledge of the pore space in which fluids and contaminants are transported
- (2) The paths travelled by a contaminant in an aquifer are strongly influenced by the heterogeneities of the geological formation, as well as by the initial and boundary conditions (BCs), which determine the underlying flow field.
- (3) Tracer migration is sensitive to heterogeneities at all scales, so that we should not be surprised that small-scale heterogeneities can significantly affect large-scale behaviour.

The key consequence of these points is a critical consideration of the idea of “homogeneity” of the medium for the purposes of modelling transport and/or defining “effective” transport parameters. It has been shown that even carefully packed, laboratory-scale flow cells and columns containing porous media contain “heterogeneities”. Studies using magnetic resonance imaging to visualize flow conditions within “homogeneous” geological materials in laboratory-scale, column experiments report the existence of preferential flow paths, which strongly influence both water flow and tracer transport (e.g., Hoffman et al., 1996; Oswald et al., 1997). These

paths occur because of the presence of macrostructures (caused, e.g., from bridging effects) as well as by microstructures that reflect grain-size heterogeneities.

At the field scale the issue of “homogeneization” of course arises. Do the above mentioned laboratory-scale heterogeneities simply average out and become insignificant at large scales? If so, how large is “large”? As already noted above, heterogeneities are present at all scales. Thus, for example, the existence of preferential flow paths has been reported even in apparently “structureless” soils at the field scale (e.g., Ghodrati and Jury, 1992).

The nature of contaminant transport in geological materials is thus linked inextricably to the extent and scale dependence of heterogeneities. The transport that is anomalous, or non-Fickian, occurs when the contaminant encounters, at each scale, a sufficiently broad spectrum of velocities and stagnant areas resulting from the heterogeneities. In addition to the strong influence of preferential flow paths and slow flow or diffusion-dominated regions, tracers can, in many cases be affected by biogeochemical heterogeneities; these heterogeneities enable a wide range of reaction processes that (temporarily or permanently) delay the advance of a tracer. Non-Fickian behaviour is fundamentally different from Fickian transport, which is the usual assumption invoked, explicitly or implicitly, for application of the classical ADE and many of its variants. These other treatments, and many stochastic approaches, focus on definition of an effective “macrodispersion” parameter at any given scale of interest. This issue is discussed in detail below.

The concept of anomalous transport was first introduced by Montroll and Scher (1973) and Scher and Montroll (1975) and has subsequently been shown to have ubiquitous applicability to transport and diffusion in disordered systems. The original application of the concept and its quantitative predictions (Scher and Montroll, 1975) was in the field of electronic transport in amorphous semiconductors (Tiedje, 1984) and in polymeric media (Bos and Burland, 1987) where it was well confirmed by an extensive number of experimental studies. Subsequent use of these ideas expanded into many

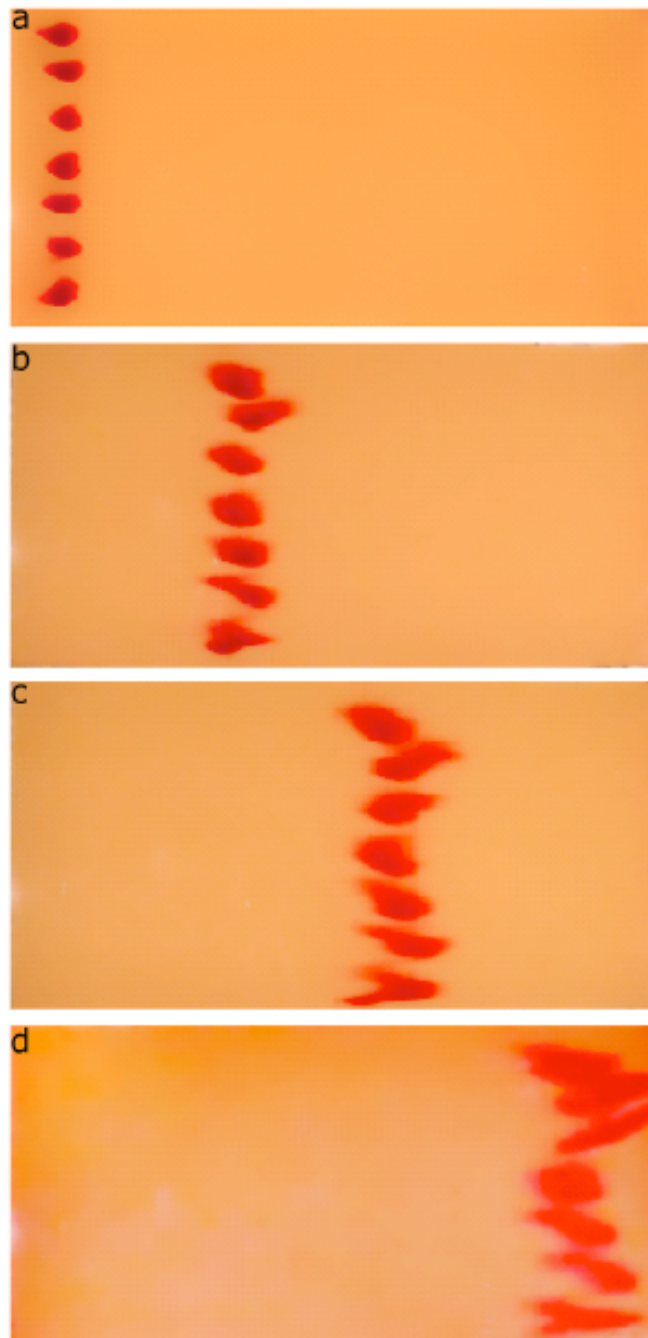


Fig. 1.- Photographs of a homogeneous, saturated sand pack with seven dye tracer point injections being transported, under constant flow of 53 mL/min, from left to right. Times at (a) $t=20$, (b) $t=105$, (c) $t=172$ and (d) $t=255$ min after injection.

Internal areas, e.g., the anomalous diffusion of defects as a basis for the universal stretched exponential relaxation behaviour in a diverse number of materials (Shlesinger, 1988). The present application to contaminant transport in geological formations is a uniquely rich example, as the full chemical plume and BTCs can be measured directly; this application has represented a new level of confirmation and further development of the theory.

Here and throughout, we use the term “anomalous” and “non-Fickian” interchangeably to denote any transport which differs from that described by the classical ADE. The ADE describes Fickian behaviour in the sense that mechanical dispersion is assumed to be quantifiable by a macroscopic form of Fick’s law, and the resulting temporal and spatial concentration distributions of an initial pulse are equivalent to a normal, otherwise known as a Gaussian, distribution.

To illustrate just how frequently non-Fickian transport occurs, consider tracer migration through an “homogeneous”, fully saturated sand pack. As indicated above, preferential paths for fluid flow and tracer transport are present even in these conditions, as shown, for example in Figure 1.

dimensions of the flow cell are 86 cm (length), 45 cm (height) and 10 cm (width).
Reprinted from Levy and Berkowitz (2003)

Contrary to Fickian transport the individual dye plumes are not symmetrical ellipses, nor are the different plumes identical to each other. Moreover, measurements of tracer BTCs in such “homogeneous”, meter-length flow cells have been shown to display “anomalous” early time arrivals (i.e., later than Fickian) and late time tails [Levy and Berkowitz, 2003]. Detailed analysis (see section 3.4.2) shows that the motion and spreading of these chemical plumes are characterized by distinct temporal scaling; that is, the time dependence of the spatial moments does not correspond to a normal (or Gaussian) distribution. In sections 2–5 we discuss the Continuous Time Random Walk (CTRW) approach to these transport phenomena, and in sections 6 and 7 we contrast it with other approaches that have been fully discussed in the literature.

2. Continuous Time Random Walk Framework

Two well-studied, generic geological media that possess heterogeneities on a very wide range of spatial scales are porous sedimentary rock and “random” fracture networks (RFN) in low-permeability rock. At the field scale a reasonable definition of the macroscopic characteristics (e.g., individual facies) of these geological formations can be feasible, thus enabling, at a sufficiently coarse resolution, modeling of flow and transport conditioned on these features.

However, in practice, there is always some scale, λ , below which ($y < \lambda$) heterogeneities are unresolved. The omnipresent question is, Can one justify the use of average local properties (e.g., mean velocity and dispersion) at the scale λ , or does the range of unresolved heterogeneities $y < \lambda$ have a key influence on overall transport behaviour? The answer is very often a practical one, not an intrinsic one, depending on the width of the distribution of material properties for $y < \lambda$.

To account for the effect of a sufficiently broad (statistical) distribution of material properties (e.g., of permeabilities) on the overall transport, one must consider a probabilistic approach that will generate a probability density function (pdf) describing key features of the transport.

This pdf, denoted $\psi(\mathbf{s}, t)$, is discussed thoroughly starting in section 2.3. The effects of multiscale heterogeneities on contaminant transport patterns are significant, and consideration only of the mean transport behaviour, e.g., the spatial moments of the concentration distribution, is not sufficient.

An essential input to the calculation of the field-scale transport is the plume motion and/or BTC across the λ scale. The CTRW is a probabilistic approach for calculating the latter based on a pdf of transition times (see section 2.1) generated by the range of heterogeneities. The nature of the transport, non-Fickian or Fickian, is determined by the functional shape of the pdf.

2.1. Conceptual Picture. Tracer Transitions

Contaminant motion in geological formations can be treated by considering particles (which represent, e.g., dissolved solutes) undergoing various types of transitions. These transitions encompass both the displacement due to structure and heterogeneity as well as the time taken to make the particle movement between, e.g., pores or fracture intersections. We conceptualize transport as a series of such particle transitions with a focus on retaining the full distribution of the transition times.

The variability in the hydraulic and geochemical properties of the geological domain cause a variety of particle transitions at velocity changes within the flow field, between flowing and stagnant zones, between mobile and immobile states, between macropores and micropores, between fractures and adjacent host rock, and by changes in advective paths at fracture and macropore intersections. This picture of motion by transitions will be referred to as “CTRW theory”, whereas the mathematical formalism used to implement the motion will be called the “CTRW framework.”

Each transition can be quantified as $w(\mathbf{s}, \mathbf{s}')$, the rate of particle transfer to position $\mathbf{s}$ from $\mathbf{s}'$, and can be considered on any spatial scale, e.g., on a pore scale between pore positions through an interpore throat (i.e., a “tube”). A multiple rate approach considers the range of these rates $\{w\}$. At this point one can see the basic problem in working with average rates in some representative region or volume, traditionally referred to as a “representative elementary volume” (REV). A particle “encounter” with a sparsely distributed, very small rate w_0 can have a large impact on the overall transport, but w_0 can be entirely absent in a REV average of $\{w\}$; other problems with the REV have been pointed out previously in the literature.

Thus the details of the distribution of $\{w\}$, or as we will show the ensemble average of the $\{w\}$ over all the configurations of a specific system, are key to the nature of the transport. The variation in spatial displacements in the distribution of $w(\mathbf{s}, \mathbf{s}')$ is small in the type of transport typically encountered in geological formations. For example, the “tube” lengths in the pore-scale model above have a narrow distribution. However, the variation in rates (i.e., values of $w(\mathbf{s}, \mathbf{s}')$), which is governed by the velocity spectrum of the flow field, is very large for highly disordered media; for example, the fluid flow

distribution in the “tubes” governs the transit time between pore sites (see section 3.8).

Hence the temporal distribution of the pdf (i.e., the range of $[w(\mathbf{s}, \mathbf{s}')]^{-1}$) discussed at the beginning of section 2 dominates the nature of the transport. The emphasis on temporal aspects of particle transport, induced by the spatial heterogeneity, is a key feature of the CTRW approach. We consider the significance of this emphasis further when we contrast CTRW to the usual ADE framework in section 6.1.

For now, we picture tracer transport as a series of discrete (in space) transitions. These can be defined naturally, for example, as transitions through a fracture network between fracture intersections. If we carefully retain the temporal distribution of these transitions, this picture can be expanded easily to a continuous-in-space formulation.

2.2. Basic Formulation of Transport

Our point of departure is a general framework that can encompass all of the processes enumerated above as special cases and reduce to the ADE for a “perfectly homogeneous” medium. Defining this overarching framework is a transport equation incorporating the full range of $\{w\}$ for any given realization of the domain,

$$\frac{\partial C(\mathbf{s}, t)}{\partial t} = - \sum_{\mathbf{s}'} w(\mathbf{s}', \mathbf{s}) C(\mathbf{s}, t) + \sum_{\mathbf{s}'} w(\mathbf{s}, \mathbf{s}') C(\mathbf{s}', t) \quad (1)$$

where $C(\mathbf{s}, t)$ is the normalized particle concentration or probability at point $\mathbf{s}$ and time t in a specific realization of the domain and the dimension of $\sum_{\mathbf{s}} w$ is reciprocal time.

Equation (1) expresses a conservation of mass at each site $\mathbf{s}$ and describes the rate of concentration change at $\mathbf{s}$ as a function of the distribution of probabilities of moving from $\mathbf{s}$ to $\mathbf{s}'$ and from $\mathbf{s}'$ to $\mathbf{s}$. This equation is known as the “master equation” (ME) [Oppenheim et al., 1977; Shlesinger, 1996]. It has been utilized widely in the physics and chemistry literature, e.g., electron hopping in random systems [e.g., Klafter and Silbey, 1980a]. In most of the applications considered here, the transition rates describe the effects of the velocity field on the particle motion. It is important to point out that the transport equation (1) does not separate the effects of the varying velocity field into an advective and dispersive part of the motion.

Specification of $w(\mathbf{s}, \mathbf{s}')$ involves detailed knowledge of the system, i.e., characterization of the heterogeneities on all length scales that influence the calculation of the flow field. Below the λ scale we must resort to a statistical description of this subdomain and hence to a distribution of $\{w\}$. To realize this probabilistic approach, we consider the ensemble average of (1), which can be shown [Klafter and Silbey, 1980b] to be of the form

$$\frac{\partial c(\mathbf{s}, t)}{\partial t} = - \sum_{\mathbf{s}'} \int_0^t \phi(\mathbf{s}' - \mathbf{s}, t - t') c(\mathbf{s}, t') dt' + \sum_{\mathbf{s}'} \int_0^t \phi(\mathbf{s} - \mathbf{s}', t - t') c(\mathbf{s}', t') dt' \quad (2)$$

where $c(\mathbf{s}, t)$ is the mean, ensemble-averaged, normalized concentration and $\phi(\mathbf{s}, t)$ is defined in (7).

The form of (2) is a “generalized master equation” (GME) which in contrast to (1) is nonlocal in time, that is, (2) contains an integral over time requiring knowledge of the past state of the concentration.

The ensemble average of a set of local (in time) kinetic equations (e.g., equation (1)) for a disordered system leads to a nonlocal transport equation, because all of the $\{w\}$ are made available to each site and the role of $w(\mathbf{s}', \mathbf{s})$ is replaced by a function of time which depends on a distribution of transit times between sites. Hence the ensemble average of any set of equations describing the dynamics of a physical model of a disordered system will lead to a nonlocal equation. (For a simple example see section 7.1 (especially (90) and (91)).)

The various nonlocal transport equations often have similar form, but there is no intrinsic relation between them as each depends on the physical model that generated them (see section 6.2). In fact, the use of nonlocal equations for a broad class of transport problems has a long history [e.g., Zwanzig, 1960; Mori, 1965, and references therein].

Applications more specifically related to the present ones include those of Kenkre et al. [1973], Montroll and Scher [1973], Scher and Lax [1973a], Shlesinger [1974], Scher and Montroll [1975], and Klafter and Silbey [1980a].

The transition rates in (2) are time-dependent but stationary, depending only on the difference $\mathbf{s}-\mathbf{s}'$. Hence, depending on available knowledge of the system, λ can range from meters to tens and hundreds of meters. As in (1), note that in (2) there is no separation between an advective and dispersive part of the motion.

2.3. CTRW Transport Equations

Using the Laplace transform, it can be shown [Kenkre et al., 1973; Shlesinger, 1974] that the GME (2) is completely equivalent to a CTRW (see Appendix A)

$$R(\mathbf{s}, t) = \sum_{\mathbf{s}'} \int_0^t \psi(\mathbf{s} - \mathbf{s}', t - t') R(\mathbf{s}', t') dt' \quad (3)$$

where $R(\mathbf{s}, t)$ is the probability per time for a walker to just arrive at site $\mathbf{s}$ at time t and $\psi(\mathbf{s}, t)$ is the probability per time for a displacement $\mathbf{s}$ with a difference of arrival times of t .

The initial condition for $R(\mathbf{s}, t)$ is $\delta_{\mathbf{s},0} \delta(t - 0^+)$, which can be appended to (3). The $\psi(\mathbf{s}, t)$ is the basic pdf discussed at the beginning of section 2; $\psi(\mathbf{s}, t)$ determines the nature of the transport, as will be considered in applications below.

A random walk with continuous time was introduced by Montroll and Weiss [1965] using a distribution $\psi(t)$ (see (5)) for the step time. The generalization of the formalism, i.e., the appearance of equation (3) with the joint distribution $\psi(\mathbf{s}, t)$ and labeled “CTRW”, and the physical application to transport, was first given by Scher and Lax [1973a]. Equation (3) describes a semi-Markovian process, Markovian in space but not in time, which accounts for memory in particle transitions. The CTRW reduces to a Markovian random walk for a single rate.

The correspondence between (2) and (3) is

$$c(\mathbf{s}, t) = \int_0^t \psi(\mathbf{s}, t - t') R(\mathbf{s}, t') dt' \quad (4)$$

where

$$\psi(t) = 1 - \int_0^t \psi(t') dt' \quad (5)$$

is the probability for a walker to remain on a site,

$$\psi(t) \equiv \sum_s \psi(s, t) \quad (6)$$

$$\tilde{\phi}(s, u) = \frac{u \tilde{\psi}(s, u)}{1 - \tilde{\psi}(u)} \quad (7)$$

where the Laplace transform (L) of a function $f(t)$ is denoted by $\tilde{f}(u)$.

Equations (3)–(5) are in the form of a convolution in space and time and can therefore be solved using Fourier (F) and Laplace transforms [Scher and Lax, 1973a]. The general solution, for periodic BCs in a lattice of size N (with site positions

$\mathbf{s} = \sum_{j=1}^3 s_j \mathbf{a}_j$, $s_j = 1, 2, 3, \dots, N$ and $\mathbf{a}_j$ = lattice constant), is

$$C(\mathbf{k}, u) = \frac{1 - \bar{\psi}(u)}{u} \frac{1}{1 - \Lambda(\mathbf{k}, u)} \quad (8)$$

Where $C(\mathbf{k}, u)$ and $\Lambda(\mathbf{k}, u)$ are the Fourier transforms of $\tilde{c}(s, u)$ and $\tilde{\psi}(s, u)$ respectively, where for each component of $\mathbf{k}$ the range of k values is $k_i = 2\pi l_i / N$, and l_i is an integer, $-(N-1)/2 \leq l_i \leq (N-1)/2$, for odd N .

An input of $\psi(s, t)$ in Λ in (8) leads to the determination of $c(s, t)$, which represents the tracer plume concentration after a F and L inversion. Because N is considered to be very large, the solution (8) is regarded as being in the infinite domain, vanishing at infinity.

Solutions for a bounded domain and for more general boundary conditions can also be developed. Note also that as N is very large, the lattice constant can be arbitrarily small and, for example, $\psi(s, t)$ can have a range of many lattice sites. The lattice thus acts as a “scaffold” to determine the solution (8) and does not confine the spatial distribution of the plume.

In addition to the determination of the concentration plume (8), another key function in CTRW is the first passage time distribution $F(\mathbf{s}, t)$, the probability density for a walker starting at the origin to reach $\mathbf{s}$ for the first time.

The solution in (8) is for periodic BCs; experiments and observations often call for an absorbing BC or exit plane. The main measurement for these experiments is the BTC, which is equivalent to the $F(\mathbf{s}, t)$ evaluated on a plane (e.g., $s_1=L$).

The implicit relation for $F(\mathbf{s}, t)$ is

$$R(\mathbf{s}, t) = \delta_{\mathbf{s},0} \delta(t - 0^+) + \int_0^t F(\mathbf{s}, t') R(0, t - t') dt' \quad (9)$$

Which states that the walker arrives at $\mathbf{s}$ for the first time at time t' and in the remaining time $t-t'$, the walker can visit and leave $\mathbf{s}$ an arbitrary number of times but ends at $\mathbf{s}$.

Equation (9) contains a convolution in time, and so in Laplace space the relation becomes an algebraic one that is solved easily:

$$\tilde{R}(\mathbf{s}, u) = \delta_{\mathbf{s},0} + \tilde{F}(\mathbf{s}, u) \tilde{R}(0, u) \quad (10)$$

thus:

$$\tilde{F}(\mathbf{s}, u) = \frac{\tilde{R}(\mathbf{s}, u) - \delta_{\mathbf{s},0}}{\tilde{R}(0, u)} \quad (11)$$

To obtain a BTC, we first consider that the walk starts from a plane, e.g. $s_1=0$, and evaluate $F(\mathbf{s}, t)$ at a fixed distance $s_1=L$ by summing over the other s_i directions ($i>1$),

$$f_B(t) \equiv \sum_{s_2, s_3} F(s_1 = L, s_2, s_3, t) \quad (12)$$

2.4. Numerical Inversion of Laplace Transforms

The analytical solutions developed in section 2.3, are of limited use in their Laplace space form. We therefore need to invert these solutions to the time domain. The inversion for the L involves finding the solution $g(t)$ of an integral equation of the first kind [Krylov and Skoblya, 1977]:

$$\int_0^{\infty} g(t)e^{-ut} dt = G(u) \quad (13)$$

where $G(u)$ is a given function of the complex parameter u .

In a few important cases we can develop $G(u)$ in an asymptotic form, for small u behavior, and solve for $g(t)$ for large t by analytic means. In general, we must resort to numerical means. We use the de Hoog et al. [1982] Laplace inversion algorithm, which makes use of complex-valued Laplace parameters.

The algorithm works as follows: Suppose that one is interested in the solution for a range of times spanning from $t_{\min}$ to $t_{\max}$. This range of times is then discretized in a time vector of arbitrary length N . It was observed that simultaneous inversion for times covering several orders of magnitudes gives inaccurate results for the small times.

Therefore the algorithm splits the time vector for which we want to obtain the concentrations into sections of the same order of magnitude (usually a logarithmic cycle), and the individual sections are inverted at a given time. So if the time vector spans n orders of magnitude, the inversion process will run n times. It is often a good idea to discretize the time vector in such a way that its values are equally spaced on a logarithmic scale.

The solution of the complex-valued partial differential equation (pde) must be known for a series of u values determined by the expression

$$u_{k,j} = \frac{1}{2T_k} \left(-\log_{10} \varepsilon + j2\pi\sqrt{-1} \right) \quad (14)$$

where T_k is the maximum time for the k th piece of time vector ($k=1, \dots, n$), and $j=1, \dots, m$. The ε parameter is typically of the order of 10^{-9} , and m is the number of terms in the Fourier series expansion (obtained from the inversion integral using the trapezoidal rule), typically in the range of 20 to 40. Note that, for each of the n pieces, the complex-valued $u_{k,j}$ in the above formula have an invariant real part and a variable imaginary part where the Fourier series expansion is calculated (with the use of an accelerated convergence method of the algorithm [de Hoog et al., 1982]). Practically, the user provides the full range of times and the numerical inversion subroutine will call

the pde solver $n \times m$ times, one for each of the $u_{k,j}$ values determined by the above procedure. The output is a series of concentration values at the discretized times in the time vector.

On the basis of the solutions discussed herein and the work of Dentz et al. [2004] and Cortis et al. [2004b], a CTRW “toolbox” has been developed [Cortis and Berkowitz, 2005] that provides a collection of easy-to-use MATLAB scripts and functions to calculate the full temporal and spatial behavior of a migrating tracer. The CTRW toolbox is freely available at <http://www.weizmann.ac.il/ESER/People/Brian/CTRW>.

2.5. Critique of the CTRW Approach

The applicability of the CTRW approach to a range of experiments was shown in section 3, and the numerical simulations of transport in nonstationary domains demonstrate further applicability of CTRW to field situations.

These features indicate that the interactions between the transporting particle and the medium can be mapped effectively onto an appropriate choice of $\psi(s, t)$. Furthermore, a few characteristics of the $\psi(s, t)$ are very often sufficient to capture completely the particle dynamics. This description begs the immediate question of how one obtains $\psi(s, t)$. A considerable effort may be required, but one can proceed in a hierarchy of levels of approximation. Here we suggest five possible approaches:

- (1) Fit the measurements with a simple form of $\psi(s, t)$, e.g., (45), and use β as a fitting parameter.
- (2) Develop a “library” of $\psi(s, t)$ for different types of geological formations and flow conditions.
- (3) Obtain the velocity histogram for a RFN [Scher et al., 2002a], a porous medium [Bijeljic and Blunt, 2006], or permeability field [Di Donato et al., 2003] and model $\psi(s, t)$.
- (4) Perform a numerical simulation on part of a complex system, e.g., an array of intersecting fracture platelets, and determine $\psi(s, t)$ in terms of variables such as platelet size and aperture and then use a pdf of these variables to develop $\psi(s, t)$ for the entire system.

(5) Determine the $w(s, s')$ and calculate the ensemble average. Also, in the case of a multiple trapping scenario, constraints on $\psi(s, t)$ can be obtained by using its specific connection to mass transfer.

Explicit and analytical linking or conditioning of $\psi(s, t)$ to known physical information, such as the heterogeneity of the hydraulic conductivity field, is certainly a key area to develop. A step in this direction is given by Dentz and Berkowitz [2005], who demonstrate a $\psi(s, t)$ that is based explicitly on the underlying heterogeneity distribution, for the case of transport under spatially random adsorption. On the other hand, it should be recognized that there naturally are limitations to full determination of $\psi(s, t)$, or for that matter any such effective transport description, from purely theoretical considerations.

However, to reiterate, on a practical level such full determination of $\psi(s, t)$ is not crucial. The remarkable feature documented in this paper is that a very few parameters capturing the important features of $\psi(s, t)$ are sufficient to account quantitatively for a host of observations. Even the well-known determination of the macrodispersion coefficient given by Gelhar and Axness [1983], as used in the ADE, is predicated on the assumption of Fickian transport but also on ignoring completely the dependence of this parameter on the cutoff (transition) time between non-Fickian and Fickian transport.

Moreover, a priori prediction of this transition is not trivial, being dependent on, e.g., the velocity distribution, the particle residence time, the heterogeneity scale of the hydraulic conductivity, and the boundary conditions. Thus full specification of a transport equation and parameter values must ultimately rest on site-specific measurements. As noted in the preceding paragraph, several approaches can be taken to obtain this information. In particular, because the underlying permeability distribution of a domain gives rise to the velocity distribution, which thus includes naturally all correlations affecting transport, the velocity distribution can be used to define the actual particle distributions. Treatment of many sorption and other multiple trapping pictures is straightforward and shown by, e.g., Margolin et al. [2003]. Further extension of the CTRW formulation, i.e., specification of either a $\psi(s, t)$ and/or modifications to account explicitly for biogeochemical reactions such as precipitation/dissolution or other, often nonlinear (feedback), reactions is another area for future research.

Another important area for further development focuses on methods of solving the transport equation. While the mathematics are somewhat more extended than those involved with the familiar ADE, CTRW solutions are accessible, and the pde formulation enables adaptation of many existing solution techniques. This review has focused on the methodology of Laplace transforms, but one can work directly in the time domain, if desired.

Because CTRW results from an ensemble average, the concentration distribution in CTRW is also an ensemble-averaged quantity, which we usually assume to be sufficient for a system size large compared to the scale of heterogeneity. The variation in the concentration, at a specific location, among different realizations of the underlying random fields is thus not quantified explicitly; that is, the average concentration is an ensemble average. In other words, if the system size L is much greater than the scale of heterogeneity l , then the rearrangement of the heterogeneity disorder from one realization to the next will result in a small change in a given neighborhood. Hence the variation from the ensemble-averaged $C(s, t)$ is expected to be small. Furthermore, the dynamics of $c(s, t)$ are governed by $\psi(s, t)$, which is a pdf based on the flow field (and thus heterogeneity distribution) of the entire system; this feature enhances the sampling of each locale to the heterogeneity distribution of the whole system. In contrast, if $L \approx l$, then the variations in realization-to-realization configurations can lead to large heterogeneity differences in a given locale and therefore large variations in concentration. For systems with $L \approx l$ it is best to use the hybrid approach; the ensemble average is then used for the small-scale residual heterogeneities. Thus the issue of variations is closely tied to the comparison between L and l . On a physical basis the ensemble average is best utilized when $L > l$.

On a formal basis, “predictive uncertainty” in the CTRW can be considered on two levels. The first level involves the GME (2), which is an equation for the ensemble-averaged $C(s, t)$. In principle, an equation for the variance of this function can also be developed from the master equation itself. The second level is a practical one: How sensitive are the results to variations in the parameters that one inputs into $\psi(s, t)$? In any application with a model $\psi(s, t)$ one can easily use Monte Carlo simulations to compute the effects of these variations on final predictions and hence assess the “predictive uncertainty.” It remains to examine these issues in detail.

3. Advection-Dispersion Equation and Upscaling

In section 1 we discussed the intensive efforts to model transport in porous media over the last decades. Many of these efforts are basically tied to the ADE. Afterwards we have discussed in detail the ramifications of the ADE approach and related modeling frameworks. We then contrast them to the CTRW framework with a particular emphasis on the different methods of averaging of the disorder-induced fluctuations of transport quantities.

The ADE is used extensively in all the natural sciences; for example, in semiconductor physics it describes the flow of electrons due to an applied voltage and allows for diffusive motion driven by spatial variations of the electron density. In liquid transport the ADE is used, e.g., to calculate Taylor dispersion (molecular diffusion of particles in a flowing fluid in a pipe). The ADE is

$$\frac{\partial c(\mathbf{s}, t)}{\partial t} = -\mathbf{v} \cdot \nabla c(\mathbf{s}, t) + \mathbf{D} : \nabla \nabla c(\mathbf{s}, t)$$

which is the same as the equation for constant fluid velocity $\mathbf{v}$ and dispersion $\mathbf{D}$. Hence one derivation of the ADE applied to porous media can be based on the kinetics described by the master equation (1) with a Taylor expansion of $C(\mathbf{s}, t)$, and $w(\mathbf{s}, \mathbf{s}')$ [Berkowitz et al., 2002].

The classical derivation of the ADE for porous media [e.g., Bear, 1972] is based on the assumption of the existence of a representative elementary volume (REV), i.e., on the assumption that at some scale $x \gg y$ the variations of the porous medium at the x scale can be considered homogeneous. The other required assumptions are that

- (1) the porous medium is fully saturated;
- (2) Darcy's law applies;

- (3) transport of a tracer can be split a priori into an advective part and a mechanical dispersion part;
- (4) mechanical dispersion obeys Fick's law, where the coefficient D is assumed to be composed of a molecular diffusion part, D_m , and a velocity-dependent part, which in one-dimensional form is written $D = D_m + v\alpha$, with α the so-called dispersivity usually assumed to be a characteristic length of the pores inside the REV
- (5) the transport velocity equals the fluid velocity; and
- (6) the spatial variation of the fluid velocity inside the REV can be neglected.

The historical motivation for the REV stems from the need to use a continuous mechanistic approach for porous media, i.e., media which are inherently discontinuous at the scale of the pores. For some quantities this is a very useful notion, as in defining geometrical properties like porosity, specific surface, and permeability as an average over the REV. These quantities can in some sense be considered “local quantities.” Averaging over the REV to define other quantities such as dispersivity is more limited and is a point of departure from the CTRW approach.

It must be recognized that use of the ADE, at a variety of different scales, is a key aspect of the vast majority of transport theories. The dispersivity then takes on the role of a “scaling” parameter in the sense that varying its magnitude is the basis for fitting ADE solutions to BTC measurements ranging over several orders of magnitude. A major drawback of the approach is that, in contrast to the fundamental assumption that α is an intrinsic porous medium constant, “force fitting” the ADE to measurements over scales from the small laboratory column to the large field scale demonstrates an ad hoc “space dependence” or “time dependence” of α [e.g., Lallemand-Barres and Peaudecerf, 1978; Gelhar et al., 1992].

A number of approaches have been made to connect the different scales with D or α as a fitting parameter. All of these approaches start from the assumption that the ADE equation holds at some microscopic scale and then assume further that some kind of

macrodispersion parameter can be found starting from the information contained at a microscopic scale. In many approaches it is also assumed that the ADE form holds at each scale with upscaled coefficients. The two main approaches, which to some degree overlap, we denote for brevity as “averaging” and “stochastic” methods.

3.1. Volume Averaging

3.1.1. Methods

The aim of averaging is to start with the ADE at the microscopic scale and move to a larger scale to obtain an ADE with modified coefficients. The challenge is to account for the deviation from the mean, due to the microscopic fluctuations, of the velocity and dispersion. We will highlight a few of these different approaches.

In “volume averaging,” moving up from one scale to another in a porous medium necessitates the use of some kind of average operator on the microscopic fields at the scale L_y to obtain fields which are significant at the macroscopic scale L_x . This average operator acts on some volume of the porous medium and assigns a macroscopic value to it. Therefore, unlike the microscopic fields, the macroscopic fields are smeared over space.

The question then arises: What is the “correct” size of the averaging volume? The usual answer is to define a REV as the smallest volume of integration for which there are no fluctuations in the averages of one or more of the characteristic features of the porous medium; for example, Bear [1972] defines the REV in terms of porosity. The size of the REV, L_x , must be intermediate between a characteristic microscopic length and a characteristic macroscopic length scale of the sample, L_R , i.e., $L_y \ll L_x \ll L_R$.

Sometimes these length scales depend not only on the microstructure of the porous medium but also on the physical process under study. It is also possible that porous media with clear separations of the geometric scales do not have a REV for a particular physical process. We argue that this is the case for the dispersion problem in porous media.

Moreover, Berkowitz and Bachmat [1987] showed that a REV-like dispersion tensor is necessarily scale (REV size) dependent when deviations of the macroscopic velocity are taken into account. A general definition of the volume average operator, indicated by angle brackets, can be made in terms of convolution products of spatial distribution functions [Cushman, 1984; Quintard and Whitaker, 1994]. An important result relating the gradient of some quantity φ at the microscales and macroscales is represented by a theorem that states that the average of the gradient of φ , $\langle \nabla \varphi \rangle$, at the microscopic scale y equals the gradient at the macroscopic scale x of the averaged physical quantity $\langle \nabla \varphi \rangle$ plus a fluid-solid surface average contribution.

A modified accounting for the role of deviations from average values, which arise from the same upscaling framework, is to use the “volume averaging with closure” method. Here the term “closure” refers to a particular integrodifferential problem, which determines definition of the deviations of the quantities of interest from their mean value using a pde. This method thus attempts to assign coefficients that prescribe the functional dependence of deviations from average quantities on the basis of a physically meaningful microscopic process. A detailed account of the approach is given by Whitaker [1999].

The basic requirements of this method are

- (1) separation of the microscopic and macroscopic length scales (see discussion below);
- (2) periodicity on the boundaries of the REV;
- (3) a phenomenological (postulated) relationship between the deviations of the quantities of interest from the average value and the gradient of the average quantity itself;
- (4) a coefficient of proportionality in requirement 3 that usually satisfies an integrodifferential problem that is similar to, or can be mapped onto, the original microscopic equations; and
- (5) a starting microscale equation that is invariably an ADE.

A typical definition of the macrodispersion coefficient (for constant porosity n and dropping the bold notation for vectors) is given by

$$\frac{\partial \langle c \rangle}{\partial t} + \langle v \rangle \frac{\partial \langle c \rangle}{\partial s} - \frac{\partial}{\partial s} \left(D \frac{\partial \langle c \rangle}{\partial s} \right) = 0$$

$$D = D_m + D_m \frac{1}{V_f} \int_{A_{fs}} (b_f - b_s) n_{fs} dA - \langle (v - \langle v \rangle) b \rangle,$$

$$(c - \langle c \rangle) = b \frac{\partial \langle c \rangle}{\partial s},$$

where the vector b is given by the problem

$$v \frac{\partial b}{\partial t} - \frac{\partial}{\partial s} \left(D_m \frac{\partial b}{\partial s} \right) = -(v - \langle v \rangle)$$

$$\frac{\partial b}{\partial s} = -I \quad \text{on} \quad A_{fs}$$

$$b = 0, \quad \text{for} \quad t = 0,$$

where, I is the identity tensor, A_{fs} denotes the fluid-solid surface, V_f is the fluid volume, n_{fs} is the normal vector to the fluid-solid surface, and the subscripts f and s denote fluid and solid phases, respectively. Thus the uncertainty in the fluctuations from the mean is mapped onto the quantity b , which, in turn, solves a microscopic ADE problem. The requirement of periodicity at the scale of the REV is key to this method. Bhattacharya and Gupta [1990] proved that to derive the ADE (in a central limit theorem framework, for instance), the requirement of periodicity (or quasiperiodicity) on the fluid velocity v is needed.

“Homogenization theory” [see, e.g., Rubinstein and Mauri, 1983; Bourgeat et al., 1988] and the “renormalization group” are upscaling techniques that have been used in the context of volume averaging. These approaches require an underlying REV at some scale for which a significant average concentration can be defined locally. Locality is enforced by the specification of periodic BCs on the relevant quantities over the local cell (REV).

In these theories an important parameter for the upscaling of the equations is $\epsilon = L_y/L_x$, where L_x is the length scale of the macroscopic variations and L_y is the length scale corresponding to the local variations.

The homogenization method establishes a hierarchy of equations based on an expansion of the original transport problem in ϵ . A closure hypothesis is needed to truncate the hierarchy; the usual one chosen is a Fickian one [see, e.g., Bourgeat et al., 1988]. Rigorous derivation of a stochastic homogenization method that does not require periodic BCs is given by Auriault and Adler [1995] and Lunati et al. [2002].

“Renormalization group” techniques have been used in the context of subsurface hydrology to determine macrodispersion coefficients for solute transport in random flow fields [e.g., Koch and Shaqfeh, 1992; Zhang, 1995; Jaekel and Vereecken, 1997]. Starting from an ADE with random advection, the macrodispersion coefficients are expanded into a perturbation series in the fluctuations of the random flow field. The renormalization group represents in this context a tool to systematically sum up certain contributions of the perturbation series (and in its simplest application a so-called one-loop renormalization is used).

The resulting macrodispersion coefficients are beyond second-order perturbation theory in the random field fluctuations, similar to the results obtained from the application of “Corrsin’s conjecture” [e.g., Dagan, 1994b; Zhang, 1995]. The latter, however, has been shown to be inconsistent in two dimensions [Dagan, 1994b; Dentz et al., 2003; Attinger et al., 2004].

3.1.2. Length-Scale and Timescale Separation. A Critical Discussion of the ADE and Averaging

At the start of this section we noted basic assumptions required for applicability of the ADE. The assumptions that a porous medium can be considered homogeneous at the relevant scale of measurement and that transport mechanisms can be separated a priori into components of advection and hydrodynamic dispersion are highly restrictive. However, as discussed in section 1, illustrated in the “homogeneous” medium shown in Figure 1, the key underlying assumption that small fluctuations can be neglected is clearly inadequate. Thus ADE-type descriptions of tracer transport and use of, e.g., REV approaches are rarely fully correct even on local scales of several centimeters.

At best, ADE-type descriptions usually capture only the average properties of tracer migration. Only when the transport length is orders of magnitude larger than the heterogeneity scale does homogenization occur, with the result that Fickian transport is indeed present in the system. For real domains with a finite hierarchy of heterogeneity scales, but also finite (and usually limited) domain lengths, i.e., for the vast majority of field-scale transport problems of interest, a REV-like homogenization limit does not exist. To make matters more complex, determination of the “cutoff” at which Fickian transport descriptions are correct is far from rigorous.

Let us consider these issues further, recognizing that an efficient and meaningful upscaling to large spatial and temporal scales is required of any practical transport theory. As shown by Levy and Berkowitz [2003], analysis of solute transport in “macroscopically homogeneous” media indicates that flow and transport do not “homogenize” on the same temporal and spatial scales. The fundamental importance of time and length scales relative to the scales of heterogeneity and domain size were also examined in the context of the two column experiments in section 3.5. The transition from non-Fickian to Fickian behavior as the column length increased showed that the difference in residence time was the determining factor. In other words, the validity of Darcy’s law on certain spatial scales does not automatically imply that transport of a passive solute can be described by the standard Fickian theory.

A consequence of this fact is that the effects of transport processes cannot simply be separated into “independent” mechanisms. Because the timescale changes as the overall flow rate changes, the transport parameters (e.g., β or equivalent parameters for other forms of $\psi(t)$ in the CTRW framework) are not “intrinsic” and constant. This result is in stark contrast to the specification of precisely these assumptions for, e.g., the dispersivity α in the ADE. This behavior accounts also for the intertwining of the two dispersion mechanisms in the CTRW-based FPME formulation in contrast to the usual ADE or stochastic approaches, which attribute the spreading of the BTC only to the second spatial moment of the tracer distribution. The memory function is indicative of a nonlocal-in-time dispersion, whereas the $D\psi$ parameter, required to fit the entire BTC, provides a measure of the local-in-space dispersion.

Traditional transport theories have focused on spatial heterogeneity. A key feature of the CTRW approach, on the other hand, is the emphasis on temporal aspects of particle transport, induced by spatial heterogeneity. Shifting the focus to work within the CTRW framework therefore represents a change in paradigm.

As discussed in section 6.1.1, some of the averaging techniques require that the porous medium be periodic (i.e., the hypothesis of periodicity is a crucial one in the argument of Brenner [1980], together with the hypothesis of ergodicity). While assuming periodicity is a convenient idealization for small-scale fluid flow applications [see, e.g., Dorfman and Brenner, 2002, and references therein], specification of natural geological structures as periodic is not an appropriate starting point for modeling contaminant migration. Another consequence of the periodicity requirement should also be recognized: Brenner [1980] showed that for periodic porous media the “fluid velocity” v is necessarily identical to the “transport velocity” $v\psi$ and traced the difference between the two velocities only to some particle-size dependent exclusion effect. While this is certainly an important factor, for instance, in colloidal transport (where dispersion generally plays a minor role), other mechanisms are present as well.

CTRW theory, on the other hand, is not limited by the assumption of periodicity (nor of ergodicity). Periodicity is, in fact, strictly forbidden at a local scale, because the structure of the master equation (1) requires, in general, an accounting of all jumps in the domain. Relaxing these assumptions in a CTRW framework leads to the correct physical picture that the fluid velocity v is, in general, different from the tracer transport velocity v_{ψ} . In the CTRW picture the relative weights of each jump, and therefore the possibility for a tracer to explore different positions in space, are governed by the transition times w^{-1} .

3.2. Stochastic Approach

Rather than give a comprehensive review, in this section we highlight two important aspects of the stochastic approach to subsurface hydrology that are of relevance in the present context:

- (1) non-Fickian transport and
- (2) effective transport descriptions and their relation to CTRW. We emphasize that the term “stochastic approach” is a general one and can, in principle, include a wide variety of formulations (including CTRW) and solution methods. However, we shall use the term as it has been identified in recent years, namely, with the particular framework outlined below.

The stochastic approach has been considered extensively in subsurface hydrology and applied to a wide variety of transport situations ranging from passive and reactive solute transport to the study of seawater intrusion in spatially heterogeneous environments. For thorough overviews of stochastic modeling in hydrology we refer the interested reader to the textbooks by, e.g., Dagan [1989], Gelhar [1993], Dagan and Neuman [1997], Zhang [2002], and Rubin [2003]. Critical reckoning of the current position of stochastic modeling in subsurface hydrology can be found in a series of papers [Christakos, 2004; Dagan, 2004; Freeze, 2004; Ginn, 2004; Molz, 2004; Neuman, 2004; Rubin, 2004; Sudicky, 2004; Winter, 2004; Zhang and Zhang, 2004].

In a stochastic approach, spatially and temporally fluctuating system parameters such as hydraulic conductivity, porosity, and chemical properties of the medium, for example, are modeled as random fields characterized by specific, experimentally accessible statistical properties. The effective transport behavior of a solute can then be obtained by ensemble averaging of the observables of interest over all realizations of the respective random fields.

3.2.1. Transport Coefficients and Non-Fickian Behaviour

The influence of medium heterogeneities on largescale transport can be quantified in terms of effective transport coefficients such as the effective center of mass velocity and effective dispersion coefficients, which are derived from the first and second moments of the normalized concentration $c(s, t)$, respectively.

In the stochastic approach, large-scale transport coefficients are defined as averages over all possible realizations of the respective random fields. We focus here on “ensemble dispersion” coefficients $D_{ij}^{ens}(t)$ [e.g., Kraichnan, 1959; Roberts, 1961; Gelhar and Axness, 1983; Neuman et al., 1987; Dagan, 1984, 1988], which are derived from the ensemble-averaged concentration distribution, $c(s, t)$:

$$D_{ij}^{ens}(t) = \frac{1}{2} \frac{d}{dt} \left[\int s_i s_j c(s, t) d^d s - \int s_i c(s, t) d^d s \int s_j c(s, t) d^d s \right]$$

Note that the $D_{ij}^{ens}(t)$ characterize the spreading of the average solute distribution and not necessarily solute spreading in a typical heterogeneity realization, as opposed to “effective” dispersion coefficients [e.g., Batchelor, 1949; Kitanidis, 1988; Dagan, 1990, 1991; Rajaram and Gelhar, 1993; Zhang and Zhang, 1996; Attinger et al., 1999; Dentz et al., 2000]. The $D_{ij}^{ens}(t)$ is independent of time if, e.g., the concentration distribution is Gaussian. We focus on $D_{ij}^{ens}(t)$ because it is related to the dispersive flux in an effective upscaled transport equation for the average solute concentration.

A principal result of the stochastic approach is that of Gelhar and Axness [1983], who expressed the heterogeneity- induced solute spreading by means of a longitudinal macrodispersion coefficient $D_L^{mac}(t)$ related to the variance σ_{ff}^2 and correlation length l of the log-hydraulic conductivity field $f(s)$ and the mean, ensemble-averaged, groundwater flow velocity $[[v]]$,

$$D_L^{mac}(t) \equiv \lim_{t \rightarrow \infty} D_{ll}^{ens}(t) \propto \sigma_{ff}^2 l [[v]].$$

Frequently, large-scale transport is modeled by advective-dispersive transport with local-scale dispersion substituted by the (constant) macrodispersion coefficients. The assumptions underlying this approach are that

- (1) large-scale transport obeys the same dynamic equation as transport on a local scale and
- (2) (constant) local-scale transport coefficients can simply be substituted by their (constant) large-scale counterparts given as suitably defined ensemble averages.

However, the $D_{ij}^{ens}(t)$ are, in general, functions of time or transport distance, as discussed, e.g., in section 6.1 [e.g., Koch and Brady, 1987, 1988; Dagan, 1988; Neuman and Zhang, 1990; Koch and Shaqfeh, 1992], i.e.,

$$D_{ij}^{ens} = D_{ij}^{ens}(t)$$

which implies that large-scale solute dispersion is, in general, non-Fickian.

Here we review briefly aspects of non-Fickian dispersion as a consequence of the correlation structure of the loghydraulic conductivity. We note for comparison, the CTRW theory also relates the statistical properties of the hydraulic conductivity, through determination of the statistical distribution of $1/v$, directly to the $\psi(t)$ and the memory function $M(t)$. A related treatment based on analysis of transport in streamlines is given by Di Donato et al. [2003].

3.2.2. Discussion

Most stochastic approaches to subsurface transport model local-scale transport by a spatially and temporally local transport equation that is characterized by spatially and temporally varying transport parameters. Thus nonlocal effects caused by small-scale heterogeneities are not taken into account in the “traditional” stochastic approaches.

While not a prerequisite, a local-scale ADE-like equation is almost invariably chosen as the starting point for development of an upscaled transport equation. As discussed in section 6, the application of (74) to describe local-scale transport in a saturated aquifer assumes that transport is Fickian in an homogeneous region. However, in real aquifers the “homogeneous” regions are restricted in size. As pointed out by, e.g., Levy and Berkowitz [2003] and Cortis et al. [2004a], tracer transport even over small domain sizes is not necessarily Fickian, and flow and transport do not “homogenize” on the same temporal and spatial scales. The effect of non-Fickian transport characteristics at the local scale remains to be explored within the framework of the stochastic approach.

A closely related problem arises: In terms of defining a local-scale equation one must ask, How local is “local”? The heterogeneity of the conductivity field is often used to fix the heterogeneity of the velocity field (through Darcy’s law), neither of which is well defined at the pore scale. As such the assumed local transport equation can be considered applicable only at some scale larger than that of the pores. In the same sense the relevant stochastic field is thus not the conductivity field but rather the velocity field.

Discussion of a number of issues related to the very existence and definition of “macrodispersion” is in order. First, expressions for the macrodispersion, are valid only in a large time, Fickian regime for transport. This limit is rarely, if ever, reached in practice. Second, the cutoff at which macrodispersion is reached is not well defined because of memory effects. Thus the classical “macrodispersion” parameter is not necessarily an “absolute” quantity. Another interesting perspective that questions whether macrodispersion coefficients exist is given by Lowe and Frenkel [1996].

Furthermore, conceptual questions that remain to be fully addressed refer to the issue of self-averaging [e.g., Bouchaud and Georges, 1990; Clincy and Kinzelbach, 2001; Eberhard, 2004], i.e., determining the length and timescales over which the ensemble average “observables” are representative (and not artifacts of the statistical ensemble) of the corresponding observables in a single realization; that is, their sample to sample fluctuations become small. Examples for when this self-averaging property does not apply are transport in a stratified medium [Clincy and Kinzelbach, 2001; Eberhard, 2004] and transport in a randomly fluctuating transient velocity field in an homogeneous medium [Dentz and Carrera, 2003]. Neuman [1993] and [Guadagnini and Neuman, 2001] developed moment equations for the ensemble moments of the solute concentration to study the uncertainty of the average solute concentration due to the sample-to-sample fluctuations of the solute concentration from realization to realization of the underlying random fields.

Practical application of the stochastic approach to quantify the full evolution of a migrating contaminant plume remains a key issue. The overwhelming emphasis of such studies has focused on spatial moment characterizations of tracer plume migration and/or determination of the macrodispersion parameter.

It is unfortunate, and somewhat perplexing, that with the intense efforts of the last decades on stochastic analyses, consideration of full, measured BTCs and efforts to fit them has rarely been attempted. Clearly, for real applications we must consider the full spatial and temporal evolution of a migrating tracer plume. A criticism to this effect was voiced by Gelhar [1997, p. 174], who stated that the emphasis of the “stochastic approach” over the previous decade had been on “... theoretical refinements of practically insignificant, but conveniently solvable, problems”

To conclude, both the CTRW approach and the effective transport description resulting from a stochastic transport model describe effective solute transport in terms of nonlocal transport equations. The basic difference between the CTRW approach and the others discussed in this section lies in the basic starting point to quantify transport and in the method to account for the impact of fluctuations present in disordered systems.

In each chosen locale the CTRW model incorporates a full pdf of the range of transition rates composing the transport. A good illustration of this difference is given by Bijeljic and Blunt [2006]. The excellent comparison they obtained for the experimentally measured macrodispersion as a function of Pe required quantification of the b , derived from the full pdf of the inter pore transit times. This key information is suppressed by the averaging over a locale to obtain coefficients for the ADE. The correct determination of macrodispersion requires full knowledge of the entire time dependence of the spatial moments of the plume (i.e., a solution of a nonlocal-in-time equation) together with the cutoff time.

4. Alternative Effective Transport Formulations

Recent attention has been focused on two alternative formulations to treat solute transport, based on the multirate mass transfer (MRMT) approach [Pfister and Scher, 1978; Roth and Jury, 1993; Harvey and Gorelick, 1995; Haggerty and Gorelick, 1995; Haggerty et al., 2000; Carrera et al., 1998] and on the use of fractional differential equations (FDE) [Benson et al., 2000; Metzler and Klafter, 2000; Baeumer et al., 2001; Schumer et al., 2003].

We note, parenthetically, that two other oft quoted formulations to quantify solute transport are based on transfer functions [Jury, 1982; Jury et al., 1986] and stochastic convective [Dagan and Bresler, 1979; Sposito et al., 1986] concepts.

The transfer function approach is a general descriptive method to characterize solute flux in heterogeneous media; a medium is treated as a black box, and heterogeneity-induced effective transport mechanisms are not specified. Transport of a solute is thus characterized by a transfer function (Green's function), which represents the solute arrival time distribution at a control plane in response to an instantaneous pulse at an input plane.

The stochastic convective model is essentially a specific implementation of the transfer function approach, which assumes that solute transport takes place in independent stream tubes with constant flow velocity. There is no mass exchange between stream tubes by local dispersion. The influence of a broad range of flow velocities on solute arrival is then taken into account by averaging the solution of the one-dimensional ADE [Dagan and Bresler, 1979; Sposito et al., 1986].

Determination of the number and properties of the stream tubes is ill-defined and nonunique, and the method provides only a purely empirical fit to existing measurements. Another drawback with these approaches is that parameters fit for a specific BTC are not generally relevant for BTC fits or predictions at other times or distances.

4.1. Multirate Mass Transfer

The MRMT approach distinguishes mobile and immobile solute fractions. MRMT thus models the effect of medium heterogeneities on effective solute transport by a distribution of typical mass transfer (exchange) times between mobile and immobile solute phases. The discussion of MRMT includes naturally multiporosity and mobile-immobile models, matrix diffusion, multiple trapping, and transport under linear first-order reactions. MRMT has been applied to quantify transport of linearly sorbing solutes [Sardin et al., 1991; Roth and Jury, 1993], and transport in media characterized by regions of fast and very slow solute transport. In the latter context one encounters multiporosity and, as a special case, double porosity models [Feehley et al., 2000] and mobile-immobile [Nkedi-Kizza et al., 1984] and matrix diffusion models [e.g., Glueckauf, 1955; Neretnieks, 1980; Rao et al., 1980; Cunningham et al., 1997; Carrera et al., 1998]. These are all summarized under the name MRMT models [Pfister and Scher, 1978; Haggerty and Gorelick, 1995; Haggerty et al., 2000] because they describe linear mass transfer from mobile to immobile solute phases.

In MRMT the total solute concentration $c(\mathbf{s}, t)$ is decomposed into a mobile (subscript m) and an immobile (subscript im) fraction:

$$c(\mathbf{s}, t) = c_m(\mathbf{s}, t) + c_{im}(\mathbf{s}, t)$$

The temporal change in the total concentration is balanced by the divergence of advective and dispersive flux in the mobile phase, which yields together with the equation presented the transport equation [Roth and Jury, 1993; Haggerty and Gorelick, 1995]

$$\frac{\partial c(\mathbf{s}, t)}{\partial t} = -\mathbf{v} \cdot \nabla c_m(\mathbf{s}, t) + \nabla \cdot D \nabla c_m(\mathbf{s}, t)$$

This equation is closed by a linear relation between the mobile and immobile concentrations, [Pfister and Scher, 1978] or [Carrera et al., 1998; Haggerty et al., 2000; Dentz and Berkowitz, 2003].

To better understand this relation between $c_m(s, t)$ and $c_{im}(s, t)$, we first start with a multiple trapping process, which is a specific case of MRMT that involves first-order transitions into and out of immobilizing sites (traps).

This was the first example of MRMT shown to be a subset of CTRW [Schmidlin, 1977; Noolandi, 1977; Pfister and Scher, 1978]. It can therefore be shown that MRMT is a special case of CTRW

4.1.1. Diffusive Mass Transfer

For diffusive mass transfer the trapping rate $\omega(t_r) = \theta/t_r$, where θ denotes the volume ratio between the mobile and immobile regions. In this case, $P(t_r)$ denotes the distribution density of typical diffusion times in the immobile regions. For diffusion into spherical immobile regions the transfer function is given by [Haggerty and Gorelick, 1995; Dentz and Berkowitz, 2003]

$$R(t/t_r) = t_r L^{-1} \left\{ \frac{3}{\sqrt{ut_r}} \left[\coth(\sqrt{ut_r}) - \frac{1}{\sqrt{ut_r}} \right] \right\}$$

while for diffusion into layered immobile regions one finds

$$R(t/t_r) = t_r L^{-1} \left[\frac{1}{\sqrt{ut_r}} \tanh(\sqrt{ut_r}) \right]$$

4.1.2. “First Order” Mass Transfer

For “first-order” mass transfer between mobile and immobile regions (e.g., the trapping case above [Pfister and Scher, 1978; Haggerty et al., 2000]) and for linear kinetic adsorption [Roth and Jury, 1993] the transfer function is given by

$$R(t/t_r) = \exp(-t/t_r)$$

The functional form of $\omega(t_r)$ depends on the particular trapping mechanism. For purely advective trapping, $\omega(t_r) = \omega_0$ is constant; for “diffusive” trapping, i.e., if diffusive

mass transfer is to be mimicked by a first-order mechanism, then $\omega(t_r) = \theta/t_r$ [Dentz and Berkowitz, 2003].

4.1.3. Synthesis

The main point is that CTRW encompasses MRMT as a special case. The relation between MRMT and decoupled CTRW on the basis of this expression has been studied in detail by Pfister and Scher [1978] and Dentz and Berkowitz [2003].

The representation of different functions in a MRMT form, although formally possible, is not a physically meaningful MRMT process.

4.2. Fractional Derivative Equations

FDE formulations to quantify transport have received attention in recent years [e.g., Benson et al., 2000; Metzler and Klafter, 2000; Baeumer et al., 2001; Schumer et al., 2003; Zhang et al., 2005]. A detailed treatise is given by Metzler and Klafter [2000]. It should be recognized that the term “fractional” can refer to fractional order differentiation in time or space or both. Moreover, a number of definitions for fractional operators exist [Metzler and Klafter, 2000]. In principle, one can derive both temporal and spatial FDEs from a limiting form of the CTRW solution (8) by expanding $\Lambda(\mathbf{k}, u)$ in (8) for small values of u and $\mathbf{k}$, rearranging the equation, and using appropriately defined operators. FDEs have also been demonstrated to be special cases of other transport formulations [e.g., Cushman and Ginn, 2000]. Here we demonstrate that the “usual” temporal fractional derivative equation for transport is a specialized, asymptotic limit of the CTRW formulation. We also discuss other limitations of using the temporal and spatial FDEs for transport modeling in porous media systems. It is interesting to note that while the (temporal) FDE is usually written phenomenologically, as a “generalized analog” to the ADE, its underlying physical and mathematical picture is elucidated when seen as a limited subset of the CTRW formulation.

The temporal FDE can be written as [Metzler and Klafter, 2000]

$$\frac{\partial c(\mathbf{s}, t)}{\partial t} = -\frac{\partial^{1-\beta}}{\partial t^{1-\beta}} \left\{ \mathbf{v}'(\mathbf{s}) \cdot \nabla c(\mathbf{s}, t) - \nabla \cdot [\mathbf{D}'(\mathbf{s}) \cdot \nabla c(\mathbf{s}, t)] \right\}$$

with the definition of the operator

$$\frac{\partial^{-\gamma}}{\partial t^{-\gamma}} c(\mathbf{s}, t) \equiv \frac{1}{\Gamma(\gamma)} \int_0^t \frac{c(\mathbf{s}, t')}{(t - t')^{1-\gamma}} dt'$$

The primes on $\mathbf{v}'$ and $\mathbf{D}'$ indicate that these quantities do not have the same dimensions as usual; that is, $\mathbf{v}'$ has dimensions $[L]/[t^\beta]$. Another advantage of the CTRW transport equations, is that we can define a dimensionless time $\tau \equiv t/\bar{t}$, where $\bar{t}$ is a time unit determined by the physical model for $\psi(t)$. The comparison between FDE and CTRW must include this difference in time units. The operator shown before was constructed to possess the important relation of its L,

$$L[\partial^{-\gamma} c(\mathbf{s}, t)/\partial t^{-\gamma}; u] = u^{-\gamma} \tilde{c}(\mathbf{s}, u)$$

One apparent attraction of the FDE to some proponents is its pde form which is similar to the familiar ADE. More significantly, the pde form of the CTRW transport equation contains the FDE as a particular case, and its evaluation for a range of BCs is straightforward.

In contrast to the temporal FDE a spatial FDE assumes a transition time distribution $\psi(t)$ with a finite first moment and a transition length distribution $p(\mathbf{s})$ with a diverging second moment. This latter condition is unphysical, implying that some particles must execute long jumps instantaneously. This case can be shown to be a Markovian process (rather than a temporally based semi-Markovian one) called a Lévy flight. It is important to recognize that a Lévy flight refers to a random movement in space, where the length of the transitions is considered over discrete steps, but time is not involved. Lévy walks, on the other hand, attach a time “penalty” by assigning a velocity to each transition in space. In the simplest case this velocity is constant; relaxation of this condition leads back to the more general CTRW formulation [Klafter et al., 1987; Shlesinger et al., 1993]. Lévy walks cannot be described in terms of simple fractional transport equations [Metzler, 2000].

Application of a spatial FDE to tracer migration in geological formations demands a domain that contains “streaks” of high and low hydraulic conductivity, arranged so as to lead to particle transitions of high and low velocity. In other words, the physical picture of a Lévy flight requires a wide distribution of streak lengths to obtain a non-Fickian distribution of particle transitions. Recall though that non-Fickian patterns arise even without the clear presence of such a conductivity distribution. Moreover, even within a long streak, particle scatter will reduce or eliminate the number of long excursions.

The spatial FDE thus uses the power law form $p(\mathbf{s}) \approx |\mathbf{s}|^{-1-\varsigma}$, $0 < \varsigma < 2$, for the transition length, which is the characteristic function of a centered and symmetric Lévy distribution.

For $\varsigma \geq 2$ one recovers the usual Gaussian behavior. With an asymptotic (small $\mathbf{k}$) form for $p(\mathbf{s})$ one can obtain [Metzler et al., 1998] a spatial FDE

$$\frac{\partial}{\partial t} c(\mathbf{s}, t) + \nabla \cdot \mathbf{D}^\varsigma \nabla c(\mathbf{s}, t) = D^\varsigma \nabla^\varsigma c(\mathbf{s}, t)$$

where here D is a generalized diffusion parameter.

In terms of the CTRW framework a power law $p(\mathbf{s})$ can be considered in a decoupled form of $\psi(\mathbf{s}, t)$ or, alternatively, directly in a coupled $\psi(\mathbf{s}, t)$. With regard to the former a power law $p(\mathbf{s})$ is not generally required.

We conclude this section by pointing out also that the FDE approach, both temporal and spatial, does not recognize the transport velocity to be fundamentally different from the fluid velocity. Thus the FDE places the mechanism for non-Fickian behavior entirely on the value of the exponent controlling the (spatial or temporal) power law distribution.

We stress once again that in contrast the CTRW formulation is more comprehensive: The memory function accounts for the nonlocal-in-time dispersion, whereas $\mathbf{D}_\psi$ provides a measure of the local-in-space dispersion.

5. Conclusions

Quantification of contaminant transport in geological formations has been a long-standing problem. The difficulty in capturing the complexities of tracer plume migration patterns suggests that local, small-scale heterogeneities cannot be neglected; we have shown that these unresolvable heterogeneities contribute significantly to the occurrence of non-Fickian transport. Indeed, BTCs of passive tracers in even macroscopically “homogeneous” granular materials exhibit non-Fickian features: Early and late arrival times are observed to differ systematically from theoretical predictions based on solution of the ADE for uniform porous media. Even in these small-scale, “homogeneous” domains, subtle and residual pore-scale disorder effects can account for these observations.

We have reviewed a recent, different approach to this problem based on a CTRW framework. The theory developed within this framework is structured by a conceptual picture of transport as a sequence of particle transfer rates. The starting point to arrive at the CTRW is the master equation, which describes the kinetics of the probability of site occupancy, incorporating these rates, for a single realization of an heterogeneous medium. The ensembleaveraged ME is the GME, which we show is equivalent to the CTRW, and serves as the transport equation. A particularly convenient approximation of this equation is the pde “similar” in form, in Laplace space, to the well-known ADE.

On this basis we can state that the CTRW framework represents a powerful and effective means to quantify transport in a wide range of porous and fractured media. It enables calculation of both BTCs and the full temporal and spatial evolution of contaminant plumes, covering both the premacrodispersion and macrodispersion regime time ranges. Further, as the calculation does not resort to using perturbation theory, the results are valid for strongly heterogeneous formations (e.g., log hydraulic conductivity variance >10). The CTRW theory can be extended naturally to treat transport in nonstationary domains with specific conditioning information.

References – Upscaling of transport parameters under the Fickian Approach

- [1] Anderman, E. R., and Hill, M. C. Modflow-2000, the U.S. Geological Survey modular ground-water model. Documentation of the advective-transport observation (ADV2) package, version 2. Tech. Rep. 01-54, U.S. Geological Survey, 2001.
- [2] Anderman, E. R., and Hill, M. C. Modflow-2000, the U.S. Geological Survey modular ground-water model. Documentation of effective porosity parameters in the advective-transport observation (ADV2) package. Tech. rep., U. S. Geological Survey, 2003.
- [3] Anderson, M. P. Using models to simulate the movement of contaminants through groundwater flow systems. *Critical Reviews in Environmental Control*, 2 (1979), 97–156.
- [4] Aral, M. M., and Liao, B. Analytical solutions for two-dimensional transport equation with time-dependent dispersion coefficients. *Journal of Hydrologic Engineering* 1, 1 (1996), 20–32.
- [5] Aris, R. On the dispersion of a solute in a fluid flowing through a tube. *Proc. Royal Soc. London A* 235 (1956), 67–77.
- [6] Baeumer, B., Benson, D. A., and Meerschaert, M. M. Advection and dispersion in time and in space. *Physica A* 350 (2005), 245–262.
- [7] Baeumer, B., Benson, D. A., Meerschaert, M. M., and Wheatcraft, S. W. Subordinated advection-dispersion equation for contaminant transport. *Water Resources Research* 37, 6 (2001), 1543–1550.
- [8] Bahr, J. M., and Rubin, J. Direct comparison of kinetic and local equilibrium formulations for solute transport affected by surface reactions. *Water Resources Research* 23, 3 (1987), 438–452.
- [9] Bajracharya, K., and Barry, D. A. Nonequilibrium solute transport parameters and their physical significance : numerical and experimental results. *Journal of Contaminant Hydrology* 24 (1997), 185–204.
- [10] Barth, G. R., Hill, M. C., Illangasekare, T. H., and Rajaram, H. Predictive modeling of flow and transport in a two-dimensional intermediatescale, heterogeneous medium. *Water Resources Research* 37, 10 (2001), 2503– 2512.
- [11] Barth, G. R., Illangasekare, T. H., Hill, M. C., and Rajaram, H. A new tracer-density criterion for heterogeneous porous media. *Water Resources Research* 37, 1 (2001), 21–31.
- [12] Baveye, P., Jacobson, A., Allaire, S., Tandarich, J., and Bryant, R. Whither goes soil science in the us and canada? Survey results and analysis. *Soil Science* in press (2006).
- [13] Bear, J. Dynamics of fluids in porous media. American Elsevier Publishing Company, 1972.

- [14] Bellin, A., Salandin, P., and Rinaldo, A. Simulation of dispersion in heterogeneous porous formations : statistics, first-order theories, convergence of computations. *Water Resources Research* 28, 9 (1992), 2211–2227.
- [15] Benson, D. A., , Meerschaert, M. M., Baeumer, B., and Scheffler, H.-P. Aquifer operator scaling and the effect on solute mixing and dispersion. *Water Resources Research* 42 (2006), doi:10.1029/2004WR003755.
- [16] Benson, D. A. The fractional advection-dispersion equation : development and application. PhD thesis, University of Nevada, Belgium, May 1998.
- [17] Benson, D. A., Tadjeran, C., Meerschaert, M. M., Farnham, I., and Pohl, G. Radial fractional-order dispersion through fractured rocks. *Water Resources Research* 40 (2004), doi:10.1029/2004WR003314.
- [18] Benson, D. A., Wheatcraft, S.W., and Meerschaert, M. M. Application of a fractional advection-dispersion equation. *Water Resources Research* 36, 6 (2000), 1403–1412.
- [19] Benson, D. A., Wheatcraft, S. W., and Meerschaert, M. M. The fractional-order governing equation of Lévy motion. *Water Resources Research* 36, 6 (2000), 1413–1423.
- [20] Berentsen, C. Upscaling of flow in porous media from a tracer perspective. PhD thesis, T. U. Delft, The Netherlands, 2003.
- [21] Berentsen, C. W. J., Verlaan, M. L., and van Kruijsdijk, C. P. J. W. Upscaling and reversibility of Taylor dispersion in heterogeneous porous media. *Physical Review E* 71 (2005), doi:10.1103/PhysRevE.71.046308.
- [22] Berkowitz, B., Klafter, J., Metzler, R., and Scher, H. Physical pictures of transport in heterogeneous media : advection-dispersion, random walk and fractional derivatives formulations. *Water Resources Research* 38, 10 (2002).
- [23] Berkowitz, B., Kosakowski, G., Margolin, G., and Scher, H. Application of continuous time random walk theory to tracer test measurements in fractured and heterogeneous porous media. *Groundwater* 39, 4 (2001), 593–604.
- [24] Berkowitz, B., and Scher, H. On characterization of anomalous dispersion in porous and fractured media. *Water Resources Research* 31, 6 (1995), 1461–1466.
- [25] Berkowitz, B., and Scher, H. The role of probabilistic approaches to transport theory in heterogeneous media. *Transport in Porous Media* 42 (2001), 241–263.
- [26] Berkowitz, B., Scher, H., and Silliman, S. E. Anomalous transport in laboratory-scale, heterogeneous porous media. *Water Resources Research* 36, 1(2000), 149–158.
- [27] Berkowitz, B., Scher, H., and Silliman, S. E. Correction to : Anomalous transport in laboratory-scale, heterogeneous porous media. *Water Resources Research* 36, 5 (2000), 1371.
- [28] Bogaert, P. Introduction a la geostatistique. Université catholique de Louvain, Louvain-la-Neuve, Belgium, 2003.
- [29] Bridge, J. S., and Leeder, M. R. A simulation model for alluvial stratigraphy. *Sedimentology* 26 (1979), 617–644.

- [30] Bromly, M., and Hinz, C. Non-fickian transport in homogeneous unsaturated repacked sand. *Water Resources Research* 40 (2004),doi:10.1029/2003WR002579.
- [31] Brusseau, M. L. Application of a multiprocess nonequilibrium sorption model to solute transport in a stratified porous medium. *Water Resources Research* 27, 4 (1991), 589–595.
- [32] Brusseau, M. L., Gerstl, Z., Augustijn, D., and Rao, P. S. C. Simulating solute transport in an aggregated soil with the dual-porosity model: measured and optimized parameter values. *Journal of Hydrology* 163 (1994), 187–193.
- [33] Brusseau, M. L., Hu, Q., and Srivastava, R. Using flow interruption to identify factors causing non ideal contaminant transport. *Journal of Contaminant Hydrology* 24 (1997), 205–219.
- [34] Caccia, D. C., Percival, D., Cannon, M. J., Raymond, G., and Bassingthwaite, J. B. Analyzing exact fractal time series: evaluating dispersional analysis and rescaled range methods. *Physica A* 246 (1997), 609–632.
- [35] Camacho, J. Purely global model for Taylor dispersion. *Physical Review E* 48, 1 (1993), 310–321.
- [36] Camacho, J. Thermodynamic functions for Taylor dispersion. *Physical Review E* 48, 3 (1993), 1844–1849.
- [37] Camacho, J. Thermodynamics of Taylor dispersion : Constitutive equations. *Physical Review E* 47, 2 (1993), 1049–1053.
- [38] Carle, S. F. T-Progs : Transition probability geostatistical software version 2.1. University of California, Davis, 1999.
- [39] Carle, S. F., and Fogg, G. E. Transition probability-based indicator geostatistics. *Mathematical Geology* 28, 4 (1996), 453–476.
- [40] Carle, S. F., and Fogg, G. E. Modeling spatial variability with one and multidimensional continuous-lag Markov chains. *Mathematical Geology* 29, 7 (1997), 891–918.
- [41] Chao, H.-C., Rajaram, H., and Illangasekare, T. Intermediate scale experiments and numerical simulations of transport under radial flow in twodimensional heterogeneous porous medium. *Water Resources Research* 36, 10 (2000), 2869–2878.
- [42] Christakos, G., Bogaert, P., and Serre, M. *Temporal GIS: Advanced Functions for Field-Based Applications*. Springer-Verlag, New York, 2002.
- [43] Cirpka, O. A. Spectral methods for flow and transport in heterogeneous formations. In *20th Course on Groundwater Management : Stochastic tools for groundwater modelling* (ETH-Zürich, March 10-14 2003).
- [44] Coats, K. H., and Smith, B. D. Dead-end pore volume and dispersion in porous media. *Society of Petroleum Engineering Journal* 4 (1964), 73–84.
- [45] Cortis, A., and Berkowitz, B. Computing anomalous contaminant transport in porous media : The CTRW Matlab toolbox. *Groundwater* 43, 6 (2005), 947–950.
- [46] Cortis, A., Gallo, C., Scher, H., and Berkowitz, B. Numerical simulation of non-Fickian transport in geological formations with multiple-scale heterogeneities. *Water Resources Research* 40 (2004), doi:10.1029/2003WR002750.

- [47] Curtis, G. P., Davis, J. A., and Naftz, D. L. Simulation of reactive transport of uranium(VI) in groundwater with variable chemical conditions. *Water Resources Research* 42 (2006), doi:10.1029/2005WR003979.
- [48] Cushman, J. H., and Ginn, T. R. Fractional advection-dispersion equation : a classical mass-balance with convolution-Fickian flux. *Water Resources Research* 36, 12 (2000).
- [49] Cvetkovic, V., and Haggerty, R. Transport with multiphase exchange in disordered media. *Physical Review E* 65 (2002), doi:10.1103/PhysRevE.65.051308.
- [50] Dagan, G. Models of groundwater flow in statistically homogeneous porous formations. *Water Resources Research* 15, 1 (1979), 47–63.
- [51] Dagan, G. Solute transport in heterogeneous formations. *Journal of Fluid Mechanics* 145 (1984), 151–177.
- [52] Dagan, G. Time-dependent macrodispersion for solute transport in anisotropic heterogeneous aquifer. *Water Resources Research* 24, 9 (1988), 1491–1500.
- [53] Dagan, G. *Flow and Transport in porous formations*. Springer, New-York, 1989.
- [54] Dagan, G., and Fiori, A. Time-dependent transport in heterogeneous formations of bimodal structure. 1. The model. *Water Resources Research* 39, 5 (2003), doi:10.1029/2002WR001396.
- [55] Dagan, G., Fiori, A., and Jankovic, I. Flow and transport in highly heterogeneous formations. 1. Conceptual framework and validity of first-order approximations. *Water Resources Research* 39, 9 (2003), doi:10.1029/2002WR001717.
- [56] Dagan, G., and Lesoff, S. C. Solute transport in heterogeneous formations of bimodal conductivity distribution. 1. Theory. *Water Resources Research* 37, 3 (2001), 465–472.
- [57] Dai, Z., Ritzi, R. W., and Dominic, D. F. Improving permeability semivariograms with transition probability models of hierarchical sedimentary architecture derived from outcrop analog studies. *Water Resources Research* 41 (2005), doi:10.1029/2004WR003515.
- [58] Dai, Z., Ritzi, R. W., Huand, C., Rubin, Y. N., and Dominic, D. F. Transport in heterogeneous sediments with multimodal conductivity and hierarchical organization across scales. *Journal of Hydrology* 294 (2004), 68–86.
- [59] Danquigny, C., Ackerer, P., and Carlier, J.-P. Laboratory tracer tests on 3d heterogeneous porous media. *Journal of Hydrology* 294 (2004), 196–212.
- [60] de Marsily, G., Delay, F., Teles, V., and Schafmeister, M. T. Some current methods to represent the heterogeneity of natural media in hydrogeology. *Hydrogeology Journal*, 6 (1998), 115–130.
- [61] Dentz, M., and Berkowitz, B. Transport behavior of a passive solute in continuous time random walks and multirate mass transfer. *Water Resources Research* 39, 5 (2003), doi:10.1029/2001WR001163.
- [62] Desbarats, A. J. Macrodispersion in sand-shale sequences. *Water Resources Research* 26, 1 (1990), 153–163.

- [63] Deutsch, C. V., and Journel, A. G. *GSLIB : Geostatistical software library and user's guide*, 2nd ed. Applied Geostatistics Series. Oxford University Press, New-York, 1998.
- [64] Deutsch, C. V., and Wang, L. Hierarchical object-based stochastic modeling of fluvial reservoirs. *Mathematical Geology* 28, 7 (1996), 857–880.
- [65] Domenico, P. A., and Robbins, G. A. A dispersion scale effect in model calibration and field tracer experiments. *Journal of Hydrology*, 70 (1984), 123– 132.
- [66] Domenico, P. A., and Schwartz, F. W. *Physical and Chemical hydrogeology*. J. Wiley and sons, 1998.
- [67] Eames, I., and Bush, J. W. M. Longitudinal dispersion by bodies fixed in a potential flow. *Proc. Royal Soc. London* 455 (1999), 3665–3686.
- [68] Elfeki, A. M. M., Uffink, G. J. M., and Barends, F. B. J. *Groundwater contaminant transport: impact of heterogeneous characterization*. Balkema, Rotterdam, 1997.
- [69] Feehley, C. E., Zheng, C., and Molz, F. J. A dual-domain mass transfer approach for modeling solute transport in heterogeneous aquifers : application to the Macrodispersion Experiment (MADE) site. *Water Resources Research* 36, 9 (2000), 2501–2515.
- [70] Fernandez-Garcia, D., Illangasekare, T. H., and Rajaram, H. Conservative and sorptive forced-gradient and uniform flow tracer tests in a threedimensional laboratory test aquifer. *Water Resources Research* 40 (2004), doi:10.1029/2004WR003112.
- [71] Fernandez-Garcia, D., Sanchez-Vila, X., and Illangasekare, T. H. Convergent-flow tracer tests in heterogeneous media : combined experimentalnumerical analysis for determination of equivalent transport parameters. *Journal of Contaminant Hydrology* 57 (2002), 129–145.
- [72] Fetter, C. W. *Contaminant Hydrology*, 2nd ed. Prentice Hall, Englewood Cliffs, New-Jersey, 1999.
- [73] Fiori, A., and Dagan, G. Time-dependent transport in heterogeneous formations of bimodal structure. 2. Results. *Water Resources Research* 39, 5 (2003), doi:10.1029/2002WR001398.
- [74] Fiori, A., Jankovic, I., and Dagan, G. Flow and transport in highly heterogeneous formations. 2. Semianalytical results for isotropic media. *Water Resources Research* 39, 9 (2003), doi:10.1029/2002WR001719.
- [75] Fiori, A., Jankovic, I., and Dagan, G. Flow and transport through twodimensional isotropic media of binary conductivity distribution. Part 1 : Numerical methodology and semi-analytical solutions. *Stochastic Environmental Research and Risk Assessment* 17 (2003), 370–383.
- [76] Freeze, R. A., and Cherry, J. A. *Groundwater*. Prentice Hall, 1979.
- [77] Fried, J. J. *Groundwater Pollution*. Elsevier, 1975.
- [78] Frappiat, C. C., and Holeyman, A. E. Upscaling of solute transport in mildly heterogeneous media: comparison of Fickian and non-Fickian approaches. In *Calibration and Reliability in Groundwater Modelling: From Uncertainty to Decision*

Making, vol. 304. International Association of Hydrological Science, 2006, pp. 167–173.

[79] Gelhar, L. W. Stochastic subsurface hydrology. Prentice Hall, Englewood Cliffs, New-Jersey, 1993.

[80] Gelhar, L. W., and Axness, C. L. Three-dimensional stochastic analysis of macrodispersion in aquifers. *Water Resources Research* 19, 1 (1983), 161–180.

[81] Gelhar, L. W., Gutjahr, A. L., and Naff, R. L. Stochastic analysis of macrodispersion in a stratified aquifer. *Water Resources Research* 15, 6 (1979), 1387–1397.

[82] Gelhar, L. W., Welty, C., and Rehfeldt, K. R. A critical review of data on field-scale dispersion in aquifers. *Water Resources Research* 28, 7 (1992), 1955–1974.

[83] Gerke, H. H., and van Genuchten, M. T. A dual-porosity model for simulating the preferential movement of water and solutes in structured porous media. *Water Resources Research* 29, 2 (1993), 305–319.

[84] Gomez-Hernandez, J. J., and Wen, X.-H. To be or not to be multi-Gaussian? A reflection on stochastic hydrogeology. *Advances in Water Resources* 21, 1 (1998), 47–61.

[85] Greenkorn, R. A. Flow phenomena in porous media. Marcel Dekker, 1983.

[86] Griffioen, J. Suitability of the first-order mass transfer concept for describing cyclic diffusive mass transfer in stagnant zones. *Journal of Contaminant Hydrology* 34 (1998), 155–165.

[87] Griffioen, J. W., Barry, D. A., and Parlange, J.-Y. Interpretation of two-region model parameter. *Water Resources Research* 34, 3 (1998), 373–384.

[88] Guswa, A. J., and Freyberg, D. L. Slow advection and diffusion through low permeability inclusions. *Journal of Contaminant Hydrology* 46 (2000), 205–232.

[89] Güven, O., and Molz, F. J. Deterministic and stochastic analyses of dispersion in an unbounded stratified porous medium. *Water Resources Research* 22, 11 (1986), 1565–1574.

[90] Güven, O., Molz, F. J., and Melville, J. G. An analysis of dispersion in a stratified aquifer. *Water Resources Research* 20, 10 (1984), 1337–1354.

[91] Haggerty, R., and Gorelick, S. M. Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity. *Water Resources Research* 31, 10 (1995), 2383–2400.

[92] Haggerty, R., McKenna, S., and Meigs, L. C. On the late-time behavior of tracer test breakthrough curves. *Water Resources Research* 36, 12 (2000), 3467–3479.

[93] Haggerty, R., and Reeves, P. C. *Stamnt-1 1.0, formulation and user's guide*. Tech. Rep. 520308, Sandia National Laboratories, 2002.

[94] Hantush, M. M., and Marino, M. A. Interlayer diffusive transfer and transport of contaminants in stratified formations. I. Theory. *Journal of Hydrologic Engineering* 3, 4 (1998), 232–240.

- [95] Hantush, M. M., and Marino, M. A. Interlayer diffusive transfer and transport of contaminants in stratified formations. II. Analytical solutions. *Journal of Hydrologic Engineering* 3, 4 (1998), 241–246.
- [96] Harbaugh, A. W., Banta, E. R., Hill, M. C., and McDonald, M. G. Modflow-2000, the U.S. Geological Survey modular ground-water model. User guide to modularization concepts and the ground-water flow process. Tech. Rep. 00-92, USGS, 2000.
- [97] Harvey, C., and Gorelick, S. M. Rate-limited mass transfer or macrodispersion: which dominates plume evolution at the Macrodispersion Experiment (MADE) site ? *Water Resources Research* 36, 3 (2000), 637–650.
- [98] Hassanizadeh, S. M. On the transient non-Fickian dispersion theory. *Transport in Porous Media* 23 (1996), 107–124.
- [99] Hill, M. C., Banta, E. R., Harbaugh, A. W., and Anderman, E. R. Modflow-2000, the U.S. Geological Survey modular ground-water model. User guide to the observation, sensitivity and parameter-estimation processes and three post-processing programs. Tech. Rep. 00-184, USGS, 2000.
- [100] Hsu, K.-C. The influence of the log-conductivity autocovariance structure on macrodispersion coefficients. *Journal of Contaminant Hydrology* 65 (2003), 65– 77.
- [101] Huang, K., van Genuchten, M. T., and Zhang, R. Exact solutions for one-dimensional transport with asymptotic scale-dependent dispersion. *Appl. Math. Modelling* 20 (1996), 298–308.
- [102] Hunt, B. Contaminant sources solutions with scale-dependent dispersivities. *Journal of Hydrologic Engineering* 3, 4 (1998), 268–275.
- [103] Hunt, B. Scale-dependent dispersion from a pit. *Journal of Hydrologic Engineering* 7, 2 (2002), doi:10.1061/(ASCE)1084-0699(2002)7:2(168).
- [104] Illangasekare, T. H., Ramsey, J. L., Jensen, K. H., and Butts, M. B. Experimental study of movement and distribution of dense organic contaminants in heterogeneous aquifers. *Journal of Contaminant Hydrology* 20 (1995), 1–25.
- [105] Jankovic, I., Fiori, A., and Dagan, G. Flow and transport in highly heterogeneous formations. 3. Numerical simulations and comparison with theoretical results. *Water Resources Research* 39, 9 (2003), doi:10.1029/2002WR001721.
- [106] Jankovic, I., Fiori, A., and Dagan, G. Flow and transport through twodimensional isotropic media of binary conductivity distribution. Part 2 : Numerical simulations and comparison with theoretical results. *Stochastic Environmental Research and Risk Assessment* 17 (2003), 384–393.
- [107] Jarvis, N. J., Jansson, P.-E., Dk, P. E., and Messing, I. Modelling water and solute transport in macroporous soil. I. Model description and sensitivity analysis. *Journal of Soil Science* 42 (1991), 59–70.
- [108] Javaux, M., and Vanclooster, M. Scale- and rate-dependent solute transport within an unsaturated sandy monolith. *Soil Science Society of America Journal* 67, 5 (2003), 1334–1343.

- [109] Jose, S. C., Rahman, A., and Cirpka, O. A. Large-scale sandbox experiment on longitudinal effective dispersion in heterogeneous porous media. *Water Resources Research* 40 (2004), doi:10.1029/2004WR003363.
- [110] Journel, A. G., and Isaaks, E. H. Conditional indicator simulation : Application to a Saskatchewan uranium deposit. *Mathematical Geology* 16, 7 (1984), 685–718.
- [111] Klotz, D., Seiler, K.-P., Moser, H., and Neumaier, F. Dispersivity and velocity relationship from laboratory and field experiments. *Journal of Hydrology* 45 (1980), 169–184.
- [112] Koltermann, C. E., and Gorelick, S. M. Paleoclimatic signature in terrestrial flood deposit. *Science* 256 (1992), 1775–1782.
- [113] Koltermann, C. E., and Gorelick, S. M. Heterogeneity in sedimentary deposits : a review of structure-imitating, process-imitating and descriptive approaches. *Water Resources Research* 32, 9 (1996), 2617–2658.
- [114] Kreft, A., and Zuber, A. On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions. *Chemical Engineering Science* 33 (1978), 1471–1480.
- [115] Labolle, E. M. RWHet : random walk particle model for simulating transport in heterogeneous permeable media version 2.0. University of California, Davis, 2000.
- [116] Lallemand-Barrès, A., and Peaudecerf, P. Recherche des relations entre la valeur de la dispersivité macroscopique d'un milieu aquifère, ses autres caractéristiques et les conditions de mesure. Etude bibliographique. *Bulletin du BRGM 2e s'erie - section III*, 4 (1992), 277–284.
- [117] Lambot, S., Slob, E. C., van den Bosch, I., Stockbroeckx, B., Scheers, B., and Vanclooster, M. Estimating soil electric properties from monostatic ground-penetrating radar signal inversion in the frequency domain. *Water Resources Research* 40 (2004), doi:10.1029/2003WR002095.
- [118] Landman, A.-J. unpublished. PhD thesis, TU Delft, The Netherlands, 2004.
- [119] Leij, F. J., and Dane, J. H. Solute transport in a two-layer medium investigated with time moments. *Soil Science Society of America Journal* 55 (1991), 1529–1535.
- [120] Lessoff, S. C., and Dagan, G. Solute transport in heterogeneous formations of bimodal conductivity distribution. 2. Applications. *Water Resources Research* 37, 3 (2001), 473–480.
- [121] Levy, M., and Berkowitz, B. Measurement and analysis of non-Fickian dispersion in heterogeneous porous media. *Journal of Contaminant Hydrology* 64 (2003), 203–226.
- [122] Lin, A. Y.-C., Debroux, J.-F., Cunningham, J. A., and Reinhard, M. Comparison of Rhodamine WT and bromide in the determination of hydraulic characteristics of constructed wetlands. *Ecological Engineering* 20 (2003), 75– 88.
- [123] Liu, G., Zheng, C., and Gorelick, S. M. Limits of applicability of the advection-dispersion model in aquifers containing connected high-conductivity channels. *Water Resources Research* 40 (2004), doi:10.1029/2003WR002735.
- [124] Logan, J. D. Solute transport in porous media with scale-dependent dispersion and periodic boundary conditions. *Journal of Hydrology*, 184 (1996), 261–276.

- [125] Lu, S., Molz, F. J., and Fix, G. J. Possible problems of scale dependency in applications of the three-dimensional fractional advection-dispersion equation to natural porous media. *Water Resources Research* 38, 9 (2002).
- [126] Lu, S., Molz, F. J., Fogg, G. E., and Castle, J. W. Combining stochastic facies and fractal models for representing natural heterogeneity. *Hydrogeology Journal*, 10 (2002), 475–482.
- [127] Margolin, G., and Berkowitz, B. Application of continuous time random walk to transport in porous media. *Journal of Physical Chemistry B* 104 (2000), 3942–3947.
- [128] Margolin, G., and Berkowitz, B. Correction to : Application of continuous time random walk to transport in porous media. *Journal of Physical Chemistry B* 104 (2000), 3942.
- [129] Margolin, G., and Berkowitz, B. Spatial behavior of anomalous transport. *Physical Review E* 65 (2002).
- [130] Margolin, G., and Berkowitz, B. Continuous time random walk revisited: first passage time and spatial distributions. *Physica A* 334 (2004), 46–66.
- [131] Marle, C., Simandoux, P., Pacsirszky, J., and Gaulier, C. Etude du d'éplacement de fluides miscibles en milieu poreux stratifié. *Rue de l'Institut Francais du Pétrole* 22, 2 (1967), 272–294.
- [132] Matheron, G., and De Marsily, G. Is transport in porous media always diffusive ? A counterexample. *Water Resources Research* 16, 5 (1980), 901–917.
- [133] Meerschaert, M. M., Benson, D. A., and Baeumer, B. Multidimensional advection and fractional dispersion. *Physical Review E* 59, 5 (1999), 5026–5028.
- [134] Meerschaert, M. M., Benson, D. A., and Baeumer, B. Operator Lévy motion and multiscaling anomalous diffusion. *Physical Review E* 63 (2001), 1112–1117.
- [135] Meerschaert, M. M., Benson, D. A., Scheffler, H.-P., and Baeumer, B. Stochastic solution of space-time fractional diffusion equations. *Physical Review E* 65, 4 (2002), 102–105.
- [136] Mercado, A. The spreading pattern of injected water in a permeability stratified aquifer. In *Artificial recharge and management of aquifers* (1967), IAHSAIHS, Ed., vol. 72, pp. 23–36.
- [137] Metzler, R., and Klafter, J. The random walk's guide to anomalous diffusion: a fractional dynamics approach. *Physics Reports* 339 (2000), 1–77.
- [138] Molz, F. J., G"uven, O., and Melville, J. G. An examination of scaledependent dispersion coefficient. *Groundwater* 21, 6 (1983), 715–725.
- [139] Montroll, E. W., and Weiss, G. H. Random walks on lattices. II. *Journal of Mathematical Physics* 6, 2 (1965), 167–181.
- [140] Murphy, E. M., Ginn, T. R., Chilakapati, A., Resch, T., Phillips, J., Wietsma, T., and Spadoni, C. M. The influence of physical heterogeneity on microbial degradation and distribution in porous media. *Water Resources Research* 33 (1997), 1087–1104.
- [141] Neuman, S. P., Winter, C. L., and Newman, C. M. Stochastic theory of field-scale Fickian dispersion in anisotropic porous media. *Water Resources Research* 23, 3 (1987), 453–466.

- [142] Nkedi-Kizza, P., Biggar, J. W., Selim, H. M., van Genuchten, M. T., Wierenga, P. J., Davidson, J. M., and Nielsen, D. R. On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol. *Water Resources Research* 20, 8 (1984), 1123–1130.
- [143] Pang, L., and Hunt, B. Solutions and verification of a scale-dependent dispersion model. *Journal of Contaminant Hydrology*, 53 (2001), 21–39.
- [144] Parker, J. C., and Valocchi, A. J. Constraints on the validity of equilibrium and first-order kinetic models in structured soils. *Water Resources Research* 22, 3 (1986), 399–407.
- [145] Peters, G. P., and Smith, D. W. Spatially and temporally varying dispersivity. In *GeoEng 2000 Conference Proceedings* (2000).
- [146] Pickens, J. F., and Grisak, G. E. Modeling of scale-dependent dispersion in hydrogeologic systems. *Water Resources Research* 17, 6 (1981), 1701–1711.
- [147] Pickens, J. F., and Grisak, G. E. Scale-dependent dispersion in a stratified granular aquifer. *Water Resources Research* 17, 4 (1981), 1191–1211.
- [148] Ptak, T., and Schmid, G. Dual-tracer transport experiments in a physically and chemically heterogeneous porous aquifer : effective transport parameters and spatial variability. *Journal of Hydrology* 183 (1996), 117–138.
- [149] Rao, P. S. C., Rolston, D. E., Jessup, R. E., and Davidson, J. M. Solute transport in aggregated porous media : theoretical and experimental evaluation. *Soil Science Society of America Journal* 44 (1980), 1139–1146.
- [150] Rentier, C. Méthode stochastique de d'élimination des zones de protection autour des captages d'eau. PhD thesis, Université de Liège, Belgium, November 2002.
- [151] Rovey, C. W., and Niemann, W. L. Do conservative solutes migrate at average pore-water velocity ? *Groundwater* 43, 1 (2005), 52–62.
- [152] Rubin, Y. Flow and transport in bimodal heterogeneous formations. *Water Resources Research* 31, 10 (1995), 2461–2468.
- [153] Rubin, Y., and Dagan, G. Stochastic analysis of the effects of boundaries on spatial variability in groundwater flows: 2. Impervious boundary. *Water Resources Research* 25, 4 (1989), 707–712.
- [154] Sabatini, D. A. Sorption and intraparticle diffusion of fluorescent dyes with consolidated aquifer media. *Groundwater* 38, 5 (2000), 651–656.
- [155] Sabatini, D. A., and Al Austin, T. Characteristics of Rhodamine WT and Fluorescein as adsorbing ground-water tracers. *Groundwater* 29, 3 (1991), 341– 349.
- [156] Sakaki, T., and Komatsu, M. Physical properties of silica sands for laboratory experiments. Colorado School of Mines, ESE division, internal report, April 2005.
- [157] Salandin, P., and Fiorotto, V. Solute transport in highly heterogeneous aquifers. *Water Resources Research* 34, 5 (1998), 949–961.
- [158] Salandin, P., Rinaldo, A., and Dagan, G. A note on transport in stratified formations by flow tilted with respect to the bedding. *Water Resources Research* 27, 11 (1991), 3009–3017.

- [159] Saupe, D., and Peitgen, H. The Science of Fractal Images. Springer-Verlag, 1988, p. 312 p.
- [160] Sauty, J. Mise au point et utilisation d'abaques pour l'interprétation des expériences de traçages dans les nappes d'eau souterraine. Bulletin du BRGM 2e série - section III, 4 (1978), 285–291.
- [161] Sauty, J. An analysis of hydrodispersive transfer in aquifers. Water Resources Research 16, 1 (1980), 145–158.
- [162] Scheidegger, A. E. Typical solutions of the differential equations of statistical theories of flow through porous media. Transactions, American Geophysical Union 39, 5 (1958), 929–932.
- [163] Scheidegger, A. E. The physics of flow through porous media. Mac Millan Company, 1960.
- [164] Scher, H., and Lax, M. Stochastic transport in a disordered solids. II Impurity conduction. Physical Review B 7 (1973), 4502–4519.
- [165] Schäfer, W., and Kinzelbach, W. K. H. Transport of reactive species in heterogeneous porous media. Journal of Hydrology 183 (1996), 151–168.
- [166] Schincariol, R. A., and Schwartz, F. An experimental investigation of variable density flow and mixing in homogeneous and heterogeneous media. Water Resources Research 26, 10 (1990), 2317–2329.
- [167] Schumer, R., Benso, D. A., Meerschaert, M. M., and Baeumer, B. Fractal mobile/immobile solute transport. Water Resources Research 39, 10 (2003), doi:10.1029/2003WR002141.
- [168] Schumer, R., Benson, D. A., Meerschaert, M. M., and Baeumer, B. Multiscaling fractional advection-dispersion equations and their solutions. Water Resources Research 39, 1 (2003).
- [169] Schumer, R., Benson, D. A., Meerschaert, M. M., and Wheatcraft, S. W. Eulerian derivation of the fractional advection-dispersion equation. Journal of Contaminant Hydrology, 48 (2001), 69–88.
- [170] Silliman, S. E., and Zheng, L. Comparison of observations from a laboratory model with stochastic theory: Initial analysis of hydraulic and tracer experiments. Transport in Porous Media 42, 1/2 (2001), 85–107.
- [171] Silliman, S. E. Laboratory study of chemical transport to wells within heterogeneous porous media. Water Resources Research 37, 7 (2001), 1883–1892.
- [172] Silliman, S. E., and Caswell, S. Observations of measured hydraulic conductivity in two artificial, confined aquifers with boundaries. Water Resources Research 34, 9 (1998), 2203–2213.
- [173] Silliman, S. E., Konikow, L., and Voss, C. Laboratory investigation of longitudinal dispersion in anisotropic porous media. Water Resources Research 23, 11 (1987), 2145–2151.
- [174] Silliman, S. E., and Simpson, E. S. Laboratory evidence of the scale effect in dispersion of solutes in porous media. Water Resources Research 23, 8 (1987), 1667–1673.

- [175] Sposito, G., and Weeks, S. W. Tracer advection by steady groundwater flow in a stratified aquifer. *Water Resources Research* 34, 5 (1998), 1051–1059.
- [176] Strack, O. D. L. A mathematical model for dispersion with a moving front in groundwater. *Water Resources Research* 28, 11 (1992), 2973–2980.
- [177] Sudicky, E. A., Gillham, R. W., and Frind, E. O. Experimental investigation of solute transport in stratified porous media. 1. The non-reactive case. *Water Resources Research* 21 (1985), 1035–1041.
- [178] Sutton, D. J., Kabala, Z. J., Francisco, A., and Vasudevan, D. Limitations and potential of commercially available Rhodamine WT as a groundwater tracer. *Water Resources Research* 37, 6 (2001), 1641–1656.
- [179] Taylor, G. I. Dispersion of soluble matter in solvent flowing slowly through a tube. *Proc. Royal Soc. London A* 219 (1953), 186–203.
- [180] Taylor, G. I. Conditions under which dispersion of a solute in a stream of solvent can be used to measure molecular diffusion. *Proc. Royal Soc. London A* 225 (1954), 473–477.
- [181] Teles, V., Delay, F., and de Marsily, G. Comparison of genesis and geostatistical methods for characterizing the heterogeneity of alluvial media : groundwater flow and transport simulations. *Journal of Hydrology* 294 (2004), 103–121.
- [182] Tompson, A. F. B. On a new functional form for the dispersive flux in porous media. *Water Resources Research* 24, 11 (1988), 1939–1947. [183] Tompson, A. F. B., and Gray, W. G. A 2nd-order approach for the modeling of dispersive transport in porous media. 1. Theoretical development. *Water Resources Research* 22, 5 (1986), 591–599.
- [184] Trefry, M. G., Ruan, F. P., and McLaughlin, D. Numerical simulations of preasymptotic transport in heterogeneous porous media : departures from the Gaussian limit. *Water Resources Research* 39, 3 (2003), doi:10.1029/2001WR001101.
- [185] Ursino, N., Gimmi, T., and Flühler, H. Combined effects of heterogeneity, anisotropy, and saturation on steady state flow and transport: a laboratory sand tank experiment. *Water Resources Research* 2 (37), 201–208.
- [186] Valocchi, A. J. Validity of the local equilibrium assumption for modeling sorbing solute transport through homogeneous soils. *Water Resources Research* 21, 6 (1985), 808–820.
- [187] van Genuchten, M. T., Tang, D. H., and Guennelon, R. Some exact solutions for solute transport through soils containing large cylindrical macropores. *Water Resources Research* 20, 3 (1984), 335–346.
- [188] van Genuchten, M. T., and Wagenet, R. J. Two-site/two-region models for pesticide transport and degradation : theoretical development and analytical solutions. *Soil Science Society of America Journal* 53, 5 (1989), 1303–1310.
- [189] van Genuchten, M. T., and Wierenga, P. J. Mass transfer studies in sorbing porous media. I. Analytical solutions. *Soil Science Society of America Journal* 40, 4 (1976), 473–480.

- [190] van Genuchten, M. T., and Wierenga, P. J. Mass transfer studies in sorbing porous media. II. Experimental evaluation with tritium ($^3\text{H}_2\text{O}$)., volume = 41, year = 1977. Soil Science Society of America Journal (1977), 272–278.
- [191] van Genuchten, M. T., Wierenga, P. J., and O'Connor, G. A. Mass transfer studies in sorbing porous media. III. Experimental evaluation with $^2,4,5\text{T}$.,. Soil Science Society of America Journal 41 (1977), 278–285.
- [192] Vanclooster, M., Javaux, M., and Vanderborght, J. Solute transport in soils. Encyclopedia of Hydrological Sciences. John Wiley and sons, 2005.
- [193] Wang, P. P., Zheng, C., and Gorelick, S. M. A general approach to advective-dispersive transport with multirate mass transfer. Advances in Water Resources 28 (2005), 33–42.
- [194] Weissmann, G. S., Carle, S. F., and Fogg, G. E. Three-dimensional hydrofacies modeling based on soil surveys and transition probability geostatistics. Water Resources Research 35, 6 (1999), 1761–1770.
- [195] Weissmann, G. S., and Fogg, G. E. Multi-scale alluvial fan heterogeneity modeled with transition probability geostatistics in a sequence stratigraphic framework. Journal of Hydrology 226 (1999), 48–65.
- [196] Welty, C., and Elsner, M. Construction of random fields in the laboratory for observations of fluid flow and mass transport. Journal of Hydrology 202 (1997), 192–211.
- [197] Wheatcraft, S. W., and Tyler, S. W. An explanation of scale-dependent dispersivity using concepts of fractal geometry. Water Resources Research 24, 4 (1988), 566–578.
- [198] Wood, B. D., Dawson, C. N., Szecsody, J. E., and Streile, G. P. Modeling contaminant transport and biodegradation in a layered porous media system. Water Resources Research 30, 6 (1994), 1833–1845.
- [199] Yates, S. R. An analytical solution for one-dimensional transport in heterogeneous porous media. Water Resources Research 26, 10 (1990), 2331–2338.
- [200] Yu, C., Warrick, A. W., and Conklin, M. H. A moment method for analysing breakthrough curves of step inputs. Water Resources Research 35, 11 (1999), 3567–3572.

References – Upscaling of transport Parameters under the Non Fickian approach

- Abramowitz, M., and I. Stegun (1970), *Handbook of Mathematical Functions*, Dover, Mineola, N. Y.
- Adams, E. E., and L.W. Gelhar (1992), Field study of dispersion in a heterogeneous aquifer: 2. Spatial moment analysis, *Water Resour. Res.*, 28(12), 3293–3308.
- Aronofsky, J. S., and J. P. Heller (1957), A diffusion model to explain mixing of flowing miscible fluids in porous media, *Trans. Am. Inst. Min. Metall. Pet. Eng.*, 210, 345–349.
- Attinger, S., M. Dentz, H. Kinzelbach, and W. Kinzelbach (1999), Temporal behavior of a solute cloud in a chemically heterogeneous porous medium, *J. Fluid Mech.*, 386, 77–104.
- Attinger, S., M. Dentz, and W. Kinzelbach (2004), Exact transverse macro dispersion coefficients for transport in heterogeneous porous media, *Stochastic Environ. Res. Risk Assess.*, 18(1), 9–15.
- Auriault, J. L., and P. M. Adler (1995), Taylor dispersion in porous media—Analysis by multiple scale expansions, *Adv. Water Resour.*, 18, 217–226.
- Baeumer, B., D. A. Benson, M. M. Meerschaert, and S. W. Wheatcraft (2001), Subordinated advection-dispersion equation for contaminant transport, *Water Resour. Res.*, 37(6), 1543–1550.
- Batchelor, G. K. (1949), Diffusion in a field of homogeneous turbulence. I. Eulerian analysis, *Austral. J. Sci. Res.*, 2, 437–450.
- Bear, J. (1972), *Dynamics of Fluids in Porous Media*, Elsevier, New York.
- Benson, D. A., S. W. Wheatcraft, and M. M. Meerschaert (2000), The fractional-order governing equation of Lévy motion, *Water Resour. Res.*, 36(6), 1413–1423.
- Berkowitz, B., and Y. Bachmat (1987), A scale-dependent equation for solute transport in porous media, *Transp. Porous Media*, 3, 199–205.
- Berkowitz, B., and H. Scher (1997), Anomalous transport in random fracture networks, *Phys. Rev. Lett.*, 79(20), 4038–4041.
- Berkowitz, B., and H. Scher (1998), Theory of anomalous chemical transport in fracture networks, *Phys. Rev. E*, 57(5), 5858–5869.
- Berkowitz, B., H. Scher, and S. E. Silliman (2000), Anomalous transport in laboratory-scale, heterogeneous porous media, *Water Resour. Res.*, 36(1), 149–158.
- Berkowitz, B., J. Klafter, R. Metzler, and H. Scher (2002), Physical pictures of transport in heterogeneous media: Advection-dispersion, random walk and fractional derivative formulations, *Water Resour. Res.*, 38(10), 1191, doi:10.1029/2001WR001030.
- Bhattacharya, R., and V. K. Gupta (1990), *Dynamics of Fluids in Hierarchical Porous Media*, chap. IV, pp. 61–95, Elsevier, New York.

Bijeljic, B., and M. J. Blunt (2006), Pore-scale modeling and continuous time random walk analysis of dispersion in porous media, *Water Resour. Res.*, 42, W01202, doi:10.1029/2005WR004578.

Bijeljic, B., A. H. Muggeridge, and M. J. Blunt (2004), Pore-scale modeling of longitudinal dispersion, *Water Resour. Res.*, 40, W11501, doi:10.1029/2004WR003567.

Bos, F. C., and D. M. Burland (1987), Hole transport in polyvinylcarbazole—The vital importance of excitation-light intensity, *Phys. Rev. Lett.*, 58(2), 152–155.

Bouchaud, J. P., and A. Georges (1990), Anomalous diffusion in disordered media: Statistical mechanisms, models and physical applications, *Phys. Rep.*, 195(4–5), 127–293.

Bourgeat, A., M. Quintard, and S. Whitaker (1988), Éléments de comparaison entre la méthode d'homogénéisation et la méthode de prise de moyenne avec fermeture, *C. R. Acad. Sci., Ser. II*, 306, 463–466.

Brenner, H. (1980), Dispersion resulting from flow through spatially periodic porous media, *Proc. R. Soc. London, Ser. A*, 297(1430), 81–133.

Bromly, M., and C. Hinz (2004), Non-Fickian transport in homogeneous unsaturated repacked sand, *Water Resour. Res.*, 40, W07402, doi:10.1029/2003WR002579.

Carrera, J., X. Sánchez-Vila, I. Benet, A. Medina, G. Galarza, and J. Guimerà (1998), On matrix diffusion: Formulations, solution methods, and qualitative effects, *Hydrogeol. J.*, 6, 178–190.

Christakos, G. (2004), A sociological approach to the state of stochastic hydrogeology, *Stochastic Environ. Res. Risk Assess.*, 18(4), 274–277.

Clinchy, M., and H. Kinzelbach (2001), Stratified disordered media: Exact solutions for transport parameters and their self-averaging properties, *J. Phys. A Math. Gen.*, 34, 7141–7152.

Cortis, A., and B. Berkowitz (2004), Anomalous transport in “classical” soil and sand columns, *Soil Sci. Soc. Am. J.*, 68, 1539–1548.

Cortis, A., and B. Berkowitz (2005), Computing ‘anomalous’ contaminant transport in porous media: The CTRW MATLAB toolbox, *Ground Water*, 43(6), 947–950.

Cortis, A., Y. Chen, H. Scher, and B. Berkowitz (2004a), Quantitative characterization of pore-scale disorder effects on transport in “homogeneous” granular media, *Phys. Rev. E*, 70(10), 041108, doi:10.1103/PhysRevE.70.041108.

Cortis, A., C. Gallo, H. Scher, and B. Berkowitz (2004b), Numerical simulation of non-Fickian transport in geological formations with multiple-scale heterogeneities, *Water Resour. Res.*, 40, W04209, doi:10.1029/2003WR002750.

Cunningham, J. A., C. J. Werth, M. Reinhard, and P. V. Roberts (1997), Effects of grain-scale mass transfer on the transport of volatile organics through sediments: 1. Model development, *Water Resour. Res.*, 33(12), 2713–2726.

Cushman, J. (1984), On unifying the concepts of scale, instrumentation, and stochasticity in the development of multiphase transport theory, *Water Resour. Res.*, 20(11), 1668–1676.

Cushman, J. (1991), On diffusion in fractal media, *Water Resour. Res.*, 27(4), 643–644.

- Cushman, J., and T. Ginn (1993), Non-local dispersion in media with continuously evolving scales, *Transp. Porous Media*, 13, 123–138.
- Cushman, J. H., and T. R. Ginn (2000), Fractional advective dispersion equations: A classical mass balance with convolution-Fickian flux, *Water Resour. Res.*, 36, 3763–3766.
- Cushman, J. H., and M. Moroni (2001), Statistical mechanics with three-dimensional particle tracking velocimetry experiments in the study of anomalous dispersion. I. Theory, *Phys. Fluids*, 13, 75–80.
- Cushman, J. H., X. Hu, and T. R. Ginn (1994), Nonequilibrium statistical mechanics of preasymptotic dispersion, *J. Stat. Phys.*, 75(5/6), 859–878.
- Cushman, J. H., B. X. Hu, and F.-W. Deng (1995), Nonlocal reactive transport with physical and chemical heterogeneity: Localization errors, *Water Resour. Res.*, 31(9), 2219–2237.
- Cushman, J. H., L. S. Bennethum, and B. X. Hu (2002), A primer on up-scaling tools for porous media, *Adv. Water Resour.*, 25, 1043–1067.
- Dagan, G. (1984), Solute transport in heterogenous porous formations, *J. Fluid Mech.*, 145, 151–177.
- Dagan, G. (1987), Theory of solute transport by groundwater, *Annu. Rev. Fluid Mech.*, 19, 183–215.
- Dagan, G. (1988), Time-dependent macrodispersion for solute transport in anisotropic heterogeneous aquifers, *Water Resour. Res.*, 24(9), 1491–1500.
- Dagan, G. (1989), *Flow and Transport in Porous Formations*, Springer, New York.
- Dagan, G. (1990), Transport in heterogeneous porous formations: Spatial moments, ergodicity, and effective dispersion, *Water Resour. Res.*, 26(10), 1287–1290.
- Dagan, G. (1991), Dispersion of a passive scalar in non-ergodic transport, *J. Fluid Mech.*, 233, 197–210.
- Dagan, G. (1994a), The significance of heterogeneity of evolving scales to transport in porous formations, *Water Resour. Res.*, 30(12), 3327–3336.
- Dagan, G. (1994b), An exact nonlinear correction to transverse macrodispersivity for transport in heterogenous formations, *Water Resour. Res.*, 30(10), 2699–2705.
- Dagan, G. (2004), On application of stochastic modeling of groundwater flow and transport, *Stochastic Environ. Res. Risk Assess.*, 18(4), 266–267.
- Dagan, G., and E. Bresler (1979), Solute dispersion in unsaturated soil at field scale, I, Theory, *Soil Sci. Soc. Am. J.*, 43, 461–466.
- Dagan, G., and S. P. Neuman (Eds.) (1997), *Subsurface Flow and Transport: A Stochastic Approach*, Cambridge Univ. Press, New York.
- de Hoog, F. R., J. H. Knight, and A. N. Stokes (1982), An improved method for numerical inversion of Laplace transforms, *SIAM J. Sci. Stat. Comput.*, 3, 357–366.
- Deng, F.-W., J. H. Cushman, and J. W. Delleur (1993), A fast Fourier transform stochastic analysis of the contaminant transport problem, *Water Resour. Res.*, 29(9), 3241–3247.

- Dentz, M., and B. Berkowitz (2003), Transport behavior of a passive solute in continuous time random walks and multirate mass transfer, *Water Resour. Res.*, 39(5), 1111, doi:10.1029/2001WR001163.
- Dentz, M., and B. Berkowitz (2005), Exact effective transport dynamics in a one-dimensional random environment, *Phys. Rev. E*, 72(3), 031110, doi:10.1103/PhysRevE.72.031110.
- Dentz, M., and J. Carrera (2003), Effective dispersion in temporally fluctuating flow through a heterogeneous medium, *Phys. Rev. E*, 68(3), 036310, doi:10.1103/PhysRevE.68.036310.
- Dentz, M., H. Kinzelbach, S. Attinger, and W. Kinzelbach (2000), Temporal behavior of a solute cloud in a heterogeneous porous medium: 1. Point-like injection, *Water Resour. Res.*, 36(12), 3591–3604.
- Dentz, M., H. Kinzelbach, S. Attinger, and W. Kinzelbach (2003), Numerical studies of the transport behavior of a passive solute in a two-dimensional incompressible random flow field, *Phys. Rev. E*, 67(4), 046306, doi:10.1103/PhysRevE.67.046306.
- Dentz, M., A. Cortis, H. Scher, and B. Berkowitz (2004), Time behavior of solute transport in heterogeneous media: Transition from anomalous to normal transport, *Adv. Water Resour.*, 27, 155–173, doi:10.1016/j.advwatres.2003.11.002.
- Di Donato, G., E.-O. Obi, and M. J. Blunt (2003), Anomalous transport in heterogeneous media demonstrated by streamlinebased simulation, *Geophys. Res. Lett.*, 30(12), 1608, doi:10.1029/2003GL017196.
- Di Federico, V., and Y.-K. Zhang (1999), Solute transport in heterogeneous porous media with long-range correlations, *Water Resour. Res.*, 35(10), 3185–3191.
- Domenico, P. A., and Robbins, G. A. A dispersion scale effect in model calibration and field tracer experiments. *Journal of Hydrology*, 70 (1984), 123–132.
- Dorfman, K. D., and H. Brenner (2002), Generalized Taylor-Aris dispersion in discrete spatially periodic networks: Microfluidic applications, *Phys. Rev. E*, 65(2), 021103, doi:10.1103/Phys-RevE.65.021103.
- 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.
- Eggleston, J., and S. Rojstaczer (1998), Identification of large-scale hydraulic conductivity trends and the influence of trends on contaminant transport, *Water Resour. Res.*, 34(9), 2155–2168.
- Einstein, A. (1905), Über die von der molekulartheoretischen Theorie der Wärme geforderte Bewegung von in ruhenden Flüssigkeiten suspendierten Teilchen, *Ann. Phys. Leipzig*, 17, 549–560.
- Feehley, C. E., C. Zheng, and F. J. Molz (2000), A dual-domain mass transfer approach for modeling solute transport in heterogeneous aquifers: Application to the macrodispersion experiment (MADE) site, *Water Resour. Res.*, 36(9), 2501–2515.
- Freeze, R. A. (2004), The role of stochastic hydrogeological modelling in real-world engineering applications, *Stochastic Environ. Res. Risk Assess.*, 18(4), 286–289.

- Gelhar, L. W. (1993), *Stochastic Subsurface Hydrology*, Prentice-Hall, Upper Saddle River, N. J.
- Gelhar, L. W. (1997), Perspectives on field-scale application of stochastic subsurface hydrology, in *Subsurface Flow and Transport: A Stochastic Approach*, edited by G. Dagan and S. P. Neuman, pp. 157–176, Cambridge Univ. Press, New York.
- Gelhar, L. W., and C. L. Axness (1983), Three-dimensional stochastic analysis of macrodispersion in aquifers, *Water Resour. Res.*, 19(1), 161–180.
- Gelhar, L. W., C. Welty, and K. R. Rehfeldt (1992), A critical review of data on field-scale dispersion in aquifers, *Water Resour. Res.*, 28(7), 1955–1974.
- Ghodrati, M., and W. A. Jury (1992), A field study of the effects of water application method and surface preparation method on preferential flow of pesticides in unsaturated soil, *J. Contam. Hydrol.*, 11, 101–125.
- Ginn, T. R. (2004), On the application of stochastic approaches in hydrogeology, *Stochastic Environ. Res. Risk Assess.*, 18(4), 282–284.
- Glueckauf, E. (1955), Theory of chromatography, part 10—Formulae for diffusion into spheres and their application to chromatography, *Trans. Faraday Soc.*, 51, 1540–1551.
- Guadagnini, A., and S. Neuman (2001), Recursive conditional moment equations for advective transport in randomly heterogeneous velocity fields, *Transp. Porous Media*, 42, 37–67.
- Güven, O., Molz, F. J., and Melville, J. G. An analysis of dispersion in a stratified aquifer. *Water Resources Research* 20, 10 (1984), 1337–1354.
- Güven, O., and Molz, F. J. Deterministic and stochastic analyses of dispersion in an unbounded stratified porous medium. *Water Resources Research* 22, 11 (1986), 1565–1574.
- Haggerty, R., and S. M. Gorelick (1995), Multiple-rate mass transfer for modeling diffusion and surface reactions in media with pore-scale heterogeneity, *Water Resour. Res.*, 31(10), 2383–2400.
- Haggerty, R., S. A. McKenna, and L. C. Meigs (2000), On the late time behavior of tracer test breakthrough curves, *Water Resour. Res.*, 36(12), 3467–3479.
- Harvey, C. F., and S. M. Gorelick (1995), Temporal moment-generating equations: Modeling transport and mass transfer in heterogeneous aquifers, *Water Resour. Res.*, 31(8), 1895–1911.
- Hatano, Y., and N. Hatano (1998), Dispersive transport of ions in column experiments: An explanation of long-tailed profiles, *Water Resour. Res.*, 34(5), 1027–1033.
- Hoffman, F., D. Ronen, and Z. Pearl (1996), Evaluation of flow characteristics of a sand column using magnetic resonance imaging, *J. Contam. Hydrol.*, 22, 95–107.
- Hornung, G., B. Berkowitz, and N. Barkai (2005), Morphogen gradient formation in a complex environment: An anomalous diffusion model, *Phys. Rev. E*, 72(4), 041916, doi:10.1103/PhysRevE.72.041916.

- Hu, B. X., F.-W. Deng, and J. H. Cushman (1995), Nonlocal reactive transport with physical and chemical heterogeneity: Linear nonequilibrium sorption with random k_d , *Water Resour. Res.*, 31(9), 2239–2252.
- Jaekel, U., and H. Vereecken (1997), Renormalization group analysis of macrodispersion in a directed random flow, *Water Resour. Res.*, 33(10), 2287–2299.
- Jiménez-Hornero, F. J., J. V. Giráldez, A. Laguna, and Y. Pachepsky (2005), Continuous time random walks for analyzing the transport of a passive tracer in a single fissure, *Water Resour. Res.*, 41, W04009, doi:10.1029/2004WR003852.
- Jury, W. A. (1982), Simulation of solute transport using a transfer function model, *Water Resour. Res.*, 18(2), 363–368.
- Jury, W. A., G. Sposito, and R. E. White (1986), A transfer function model of solute movement through soil: 1. Fundamental concepts, *Water Resour. Res.*, 22(2), 243–247.
- Kenkre, V. M., E. W. Montroll, and M. F. Shlesinger (1973), Generalized master equations for continuous-time random walks, *J. Stat. Phys.*, 9(1), 45–50.
- Kirchner, J. W., X. Feng, and C. Neal (2000), Fractal stream chemistry and its implications for contaminant transport in catchments, *Nature*, 403, 524–527.
- Kitanidis, P. K. (1988), Prediction by the method of moments of transport in heterogeneous formations, *J. Hydrol.*, 102, 453–473.
- Klafter, J., and R. Silbey (1980a), On electronic energy transfer in disordered systems, *J. Phys. Chem.*, 72(2), 843–848.
- Klafter, J., and R. Silbey (1980b), Derivation of continuous-time random walk equations, *Phys. Rev. Lett.*, 44(2), 55–58.
- Klafter, J., A. Blumen, and M. F. Shlesinger (1987), Stochastic pathway to anomalous diffusion, *Phys. Rev. A*, 35(7), 3081–3085.
- Klotz, D., Seiler, K.-P., Moser, H., and Neumaier, F. Dispersivity and velocity relationship from laboratory and field experiments. *Journal of Hydrology* 45 (1980), 169–184.
- Koch, D. L., and J. F. Brady (1987), A non-local description of advection-diffusion with application to dispersion in porous media, *J. Fluid Mech.*, 180, 387–403.
- Koch, D. L., and J. F. Brady (1988), Anomalous diffusion in heterogeneous porous media, *Phys. Fluids A*, 31, 965–1031.
- Koch, D. L., and E. S. G. Shaqfeh (1992), Averaged equation and diagrammatic approximations to the average concentration of a tracer dispersed by a Gaussian random velocity field, *Phys. Fluids A*, 4, 887–894.
- Kosakowski, G. (2004), Anomalous transport of colloids and solutes in a shear zone, *J. Contam. Hydrol.*, 72, 23–46, doi:10.1016/j.jconhyd.2003.10.005.
- Kosakowski, G., B. Berkowitz, and H. Scher (2001), Analysis of field observations of tracer transport in a fractured till, *J. Contam. Hydrol.*, 47, 29–51.
- Kraichnan, R. H. (1959), The structure of isotropic turbulence at very high Reynolds numbers, *J. Fluid Mech.*, 5, 497–543.

- Kreft, A., and A. Zuber (1978), On the physical meaning of the dispersion equation and its solutions for different initial and boundary conditions, *Chem. Eng. Sci.*, 33, 1471–1480.
- Krylov, V. I., and N. S. Skoblya (1977), *A Handbook of Methods of Approximate Fourier Transformation and Inversion of the Laplace Transform*, MIR, Moscow.
- Labolle, E. M., and G. E. Fogg (2001), Role of molecular diffusion in contaminant migration and recovery in an alluvial aquifer system, *Transp. Porous Media*, 42, 155–179.
- Lallemand-Barres, P., and P. Peaudecerf (1978), Recherche des relations entre la valeur de la dispersivité macroscopique d'un aquifère, ses autres caractéristiques et les conditions de mesure, *Bull. Bur. Rech. Geol. Min. Fr., Sect. 3, 4*, 277–284.
- Levy, M., and B. Berkowitz (2003), Measurement and analysis of non-Fickian dispersion in heterogeneous porous media, *J. Contam. Hydrol.*, 64, 203–226.
- Lowe, C. P., and D. Frenkel (1996), Do hydrodynamic dispersion coefficients exist?, *Phys. Rev. Lett.*, 77(22), 4552–4555.
- Lu, S. L., F. J. Molz, G. E. Fogg, and J. W. Castle (2002), Combining stochastic facies and fractal models for representing natural heterogeneity, *Hydrogeol. J.*, 10, 475–482.
- Lunati, I., S. Attinger, and W. Kinzelbach (2002), Macrodispersivity for transport in arbitrary nonuniform flow fields: Asymptotic and preasymptotic results, *Water Resour. Res.*, 38(10), 1187, doi:10.1029/2001WR001203.
- Margolin, G., and B. Berkowitz (2002), Spatial behavior of anomalous transport, *Phys. Rev. E*, 65(3), 031101, doi:10.1103/PhysRevE.65.031101.
- Margolin, G., M. Dentz, and B. Berkowitz (2003), Continuous time random walk and multirate mass transfer modeling of sorption, *Chem. Phys.*, 295, 71–80.
- Matheron, M., and G. de Marsily (1980), Is transport in porous media always diffusive?, *Water Resour. Res.*, 16, 901–917.
- Metzler, R. (2000), Generalized Chapman-Kolmogorov equation: A unifying approach to the description of anomalous transport in external fields, *Phys. Rev. E*, 62(5), 6233–6245.
- Metzler, R., and J. Klafter (2000), The random walk's guide to anomalous diffusion: A fractional dynamics approach, *Phys. Rep.*, 339(1), 1–77.
- Metzler, R., and J. Klafter (2004), The restaurant at the end of the random walk: Recent developments in fractional dynamics of anomalous transport processes, *J. Phys. A*, 37, R161–R208.
- Metzler, R., J. Klafter, and I. M. Sokolov (1998), Anomalous transport in external fields: Continuous time random walks and fractional diffusion equations extended, *Phys. Rev. E*, 58(2), 1621–1633.
- Molz, F. (2004), A rational role for stochastic concepts in subsurface hydrology: A personal perspective, *Stochastic Environ. Res. Risk Assess.*, 18(4), 278–279.
- Montroll, E. W., and H. Scher (1973), Random walks on lattices. IV. Continuous time random walks and influence of absorbing boundaries, *J. Stat. Phys.*, 9(2), 101–135.

- Montroll, E. W., and G. H. Weiss (1965), Random walks on lattices. II, *J. Math. Phys.*, 6(2), 167–181.
- Mori, H. (1965), Transport collective motion and Brownian motion, *Prog. Theor. Phys.*, 33(3), 423–455.
- Naff, R. L. (1990), On the nature of the dispersive flux in saturated heterogenous porous media, *Water Resour. Res.*, 26(5), 1013–1026.
- National Research Council (1996), *Rock Fractures and Fluid Flow: Contemporary Understanding and Applications*, Natl. Acad. Press, Washington D. C.
- Neretnieks, I. (1980), Diffusion in the rock matrix: An important factor in radionuclide transport?, *J. Geophys. Res.*, 85(B8), 4379–4397.
- Neuman, S., and Y. Zhang (1990), A quasi-linear theory of non-Fickian and Fickian subsurface dispersion: 1. Theoretical analysis with application to isotropic media, *Water Resour. Res.*, 26(5), 887–902.
- Neuman, S. P. (1993), Eulerian-Lagrangian theory of transport in space-time nonstationary velocity fields: Exact nonlocal formalism by conditional moments and weak approximation, *Water Resour. Res.*, 29(3), 633–645.
- Neuman, S. P. (2004), Stochastic groundwater models in practice, *Stochastic Environ. Res. Risk Assess.*, 18(4), 268–270.
- Neuman, S. P., C. L. Winter, and C. M. Newman (1987), Stochastic theory of field-scale Fickian dispersion in anisotropic porous media, *Water Resour. Res.*, 23(3), 453–466.
- Nielsen, D. R., and J. W. Biggar (1962), Miscible displacement in soils: III. Theoretical considerations, *Soil Sci. Soc. Am. Proc.*, 26, 216–221.
- Nkedi-Kizza, P., J. W. Biggar, H. M. Selim, M. T. van Genuchten, P. J. Wierenga, J. M. Davidson, and D. R. Nielsen (1984), On the equivalence of two conceptual models for describing ion exchange during transport through an aggregated oxisol, *Water Resour. Res.*, 20(8), 1123–1130.
- Noolandi, J. (1977), Multiple-trapping model of anomalous transittime dispersion in a-Se, *Phys. Rev. B*, 16, 4466–4473.
- O'Brien, G. S., C. J. Bean, and F. McDermott (2003a), Numerical investigations of passive and reactive flow through generic single fractures with heterogeneous permeability, *Earth Planet. Sci. Lett.*, 213(3–4), 271–284.
- O'Brien, G. S., C. J. Bean, and F. McDermott (2003b), A numerical study of passive transport through fault zones, *Earth Planet. Sci. Lett.*, 214(3–4), 633–643.
- Oppenheim, I., K. E. Shuler, and G. H. Weiss (1977), *Stochastic Processes in Chemical Physics: The Master Equation*, MIT Press, Cambridge, Mass.
- Oswald, S., W. Kinzelbach, A. Greiner, and G. Brix (1997), Observation of flow and transport processes in artificial porous media via magnetic resonance imaging in three dimensions, *Geoderma*, 80, 417–429.
- Pfister, G., and H. Scher (1978), Non-Gaussian transient transport in disordered solids, *Adv. Phys.*, 27, 747–798.

- Quintard, M., and S. Whitaker (1994), Transport in ordered and disordered porous media I: The cellular average and the use of weighting functions, *Transp. Porous Media*, 14, 163–177.
- Rajaram, H., and L. W. Gelhar (1993), Plume-scale dependent dispersion in heterogeneous aquifers: 2. Eulerian analysis and three-dimensional aquifers, *Water Resour. Res.*, 29(9), 3261–3276.
- Rajaram, H., and L. W. Gelhar (1995), Plume-scale dependent dispersion in aquifers with a wide range of scales of heterogeneity, *Water Resour. Res.*, 31(10), 2469–2482.
- Rao, P. S. C., R. E. Jessup, D. E. Rolston, J. M. Davidson, and D. P. Kilcrease (1980), Experimental and mathematical description of nonadsorbed solute transfer by diffusion in spherical aggregates, *Soil Sci. Soc. Am. J.*, 44(4), 684–688.
- Roberts, P. H. (1961), Analytical theory of turbulent diffusion, *J. Fluid Mech.*, 11, 257–283.
- Roth, K., and W. A. Jury (1993), Linear transport models for adsorbing solutes, *Water Resour. Res.*, 29(4), 1195–1203.
- Rubin, Y. (2003), *Applied Stochastic Hydrogeology*, Oxford Univ. Press, New York.
- Rubin, Y. (2004), Stochastic hydrogeology: Challenges and misconceptions, *Stochastic Environ. Res. Risk Assess.*, 18(4), 280–281.
- Rubinstein, J., and R. Mauri (1983), Dispersion and convection in periodic porous media, *SIAM J. Appl. Math.*, 46(6), 1018–1023.
- Sardin, M., D. Schweich, F. J. Leij, and M. T. van Genuchten (1991), Modeling the nonequilibrium transport of linearly interacting solutes in porous media: A review, *Water Resour. Res.*, 27(9), 2287–2307.
- Scheidegger, A. E. (1959), An evaluation of the accuracy of the diffusivity equation for describing miscible displacement in porous media, *Proc. Theory Fluid Flow Porous Media Conf.*, 2nd, 101–116.
- Scher, H., and M. Lax (1973a), Stochastic transport in a disordered solid. I. Theory, *Phys. Rev. B*, 7, 4491–4502.
- Scher, H., and M. Lax (1973b), Stochastic transport in a disordered solid. II. Impurity conduction, *Phys. Rev. B*, 7, 4502–4519.
- Scher, H., and E. W. Montroll (1975), Anomalous transit time dispersion in amorphous solids, *Phys. Rev. B*, 12, 2455–2477.
- Scher, H., G. Margolin, and B. Berkowitz (2002a), Towards a unified framework for anomalous transport in heterogeneous media, *Chem. Phys.*, 284, 349–359.
- Scher, H., G. Margolin, R. Metzler, J. Klafter, and B. Berkowitz (2002b), The dynamical foundation of fractal stream chemistry: The origin of extremely long retention times, *Geophys. Res. Lett.*, 29(5), 1061, doi:10.1029/2001GL014123.
- Schmidlin, F. W. (1977), Theory of trap-controlled transient photoconduction, *Phys. Rev. B*, 6, 2362–2385.
- Schumer, R., D. A. Benson, and M. M. Meerschaert (2003), Fractal mobile/immobile solute transport, *Water Resour. Res.*, 39(10), 1296, doi:10.1029/2003WR002141.

- Shlesinger, M. F. (1974), Asymptotic solutions of continuous-time random walks, *J. Stat. Phys.*, 10(5), 421–434.
- Shlesinger, M. F. (1988), Fractal time in condensed matter, *Annu Rev. Phys. Chem.*, 39, 269–290.
- Shlesinger, M. F. (1996), Random Processes, *Encyclopedia of Applied Physics*, vol. 16, John Wiley, Hoboken, N. J.
- Shlesinger, M. F., G. M. Zaslavsky, and J. Klafter (1993), Strange kinetics, *Nature*, 363, 31–37.
- Shvidler, M. J. (1993), Correlation model of transport in random fields, *Water Resour. Res.*, 29, 3189–3199.
- Sidle, C., B. Nilson, M. Hansen, and J. Fredericia (1998), Spatially varying hydraulic and solute transport characteristics of a fractured till determined by field tracer tests, Funen, Denmark, *Water Resour. Res.*, 34(10), 2515–2527.
- Silliman, S. E., and E. S. Simpson (1987), Laboratory evidence of the scale effect in dispersion of solutes in porous media, *Water Resour. Res.*, 23(8), 1667–1673.
- Sposito, G., R. E. White, P. R. Darrah, and W. A. Jury (1986), A transfer function model of solute transport through soil: 3. The convection dispersion equation, *Water Resour. Res.*, 22(2), 255–262.
- Stark, C. P., and M. Stieglitz (2000), The sting in a fractal tail, *Nature*, 403, 493–495.
- Sudicky, E. (2004), On certain stochastic hydrology issues, *Stochastic Environ. Res. Risk Assess.*, 18(4), 285.
- Tiedje, T. (1984), Information about band-tail states from time-offlight experiments, in *Semiconductors and Semimetals, Part C*, vol. 21, pp. 207–238, Elsevier, New York.
- Villermaux, J. (1974), Deformation of chromatographic peaks under the influence of mass transfer phenomena, *J. Chromatogr. Sci.*, 12, 822–831.
- Villermaux, J. (1987), Chemical engineering approach to dynamic modelling of linear chromatography, *J. Chromatogr.*, 406, 11–26.
- Weisbrod, N., M. R. Niemet, and J. Selker (2003), Light transmission technique for the evaluation of colloidal transport and dynamics in porous media, *Environ. Sci. Technol.*, 37(16), 3694–3700.
- Weissmann, G. S., S. F. Carle, and G. E. Fogg (1999), Threedimensional hydrofacies modeling based on soil surveys and transition probability geostatistics, *Water Resour. Res.*, 35(6), 1761–1770.
- Whitaker, S. (1999), *The Method of Volume Averaging*, Springer, New York.
- Winter, C. L. (2004), Stochastic hydrology: Practical alternatives exist, *Stochastic Environ. Res. Risk Assess.*, 18(4), 271–273.
- Zhang, D. (2002), *Stochastic Methods for Flow in Porous Media: Coping With Uncertainties*, Elsevier, New York.

Zhang, D., and S. Neuman (1995), Eulerian-Lagrangian analysis of transport conditioned on hydraulic data: 1. Analytical-numerical approach, *Water Resour. Res.*, 31(1), 39–52.

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

Zhang, X., J. W. Crawford, L. K. Deeks, M. I. Stutter, A. G. Bengough, and I. M. Young (2005), A mass balance based numerical method for the fractional advection-dispersion equation: Theory and application, *Water Resour. Res.*, 41, W07029, doi:10.1029/2004WR003818.

Zhang, Y., and D. Zhang (1996), Nonergodic solute transport in three-dimensional heterogeneous isotropic aquifers, *Water Resour. Res.*, 32, 2955–2963.

Zhang, Y.-K., and D. Zhang (2004), Forum: The state of stochastic hydrology, *Stochastic Environ. Res. Risk Assess.*, 18(4), 265.

Zwanzig, R. (1960), Ensemble method in the theory of irreversibility, *J. Chem. Phys.*, 33(5), 1338–1341.

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