Modeling Solute Transport in Porous Media

1.1   Introduction

The study of solute transport in porous media is important for many environmental, industrial and biological problems.   Contamination of groundwater, diffusion of tracer particles in cellular bodies, underground oil flow in the petroleum industry and blood flow through capillaries are a few relevant instances where a good understanding of transport in porous media is important. Most of natural and biological phenomena such as solute transport in porous media exhibit variability which can not be modeled by using deterministic approaches, therefore we need more sophisticated concepts and theories to capture the complexity of system behavior. We believe that the recent developments in stochastic calculus along with stochastic partial differential equations would provide a basis to model natural and biological systems in a comprehensive manner. Most of the systems contain variables that can be modeled by the laws of thermodynamics and mechanics, and relevant scientific knowledge can be used to develop inter-relationships among the variables. However, in many instances, the natural and biological systems modeled this way do not adequately represent the variability that is observed in the systems' natural settings. The idea of describing the variability as an integral part of systems dynamics is not new, and the methods such as Monte Carlo simulations have been used for decades. However there is evidence in natural phenomena to suggest that some of the observations can not be explained by using the models which give deterministic solutions, i.e. for the given sets of inputs and parameters we only see a single set of output values. The complexity in nature can not be understood through such deterministic descriptions in its entirety even though one can obtain qualitative understanding of complex phenomena by using them. We believe that new approaches should be developed to incorporate both the scientific laws and interdependence of system components in a

manner to include the "noise" within the system. The term "noise" needs further explaining.

We usually define "noise" of a system in relation to the observations of the variables within the system, and we assume that the noise of the variable considered is superimposed on a more cleaner signal, i.e. a smoother set of observations. This observed "noise" is an outcome of the errors in the observations, inherent variability of the system, and the scale of the system we try to model. If our model is a perfect one for the scale chosen, then the "noise" reflects the measurement errors and the scale effects. In developing models for the engineering systems, such as an electrical circuit, we can consider "noise" to be measurement errors because we can design the circuit fairly accurately so that the equations governing the system behavior are very much a true representation of it. But this is not generally the case in biological and natural systems as well as in the engineering systems involving, for example, the components made of natural materials. We also observe that "noise" occurs randomly, i.e. we can not model them using the deterministic approaches. If we observe the system fairly accurately, and still we see randomness in spatial or temporal domains, then the "noise" is inherent and caused by system dynamics. In these instances, we refer to "noise" as randomness induced by the system.

There is a good example given by Øksendal et al. (1998) of an experiment where a liquid is injected into a porous body and the resulting scattered distribution of the liquid is not that one expects according to the deterministic diffusion model. It turns out that the permeability of the porous medium, a rock material in this case, varies within the material in an irregular manner. These kinds of situations are abound in natural and other systems, and stochastic calculus provides a logical and mathematical framework to model these situations. Stochastic processes have a rich repository of objects which can be used to express the randomness inherent in the system and the evolution of the system over time. The stochastic models purely driven by the historical data, such as Markov's chains, capture the system's temporal dynamics through the information contained in the data that were used to develop the models. Because we use the probability distributions to describe appropriate sets of data, these models can predict extreme events and generate various different scenarios that have the potential of being realized in the real system. In a very general sense, we can say that the probabilistic structure based on the data is the engine that drives the model of the system to evolve in time. The deterministic models based on differential calculus contain differential equations to describe the mechanisms based on which the model is driven to evolve over time. If the differential equations developed are based

on the conservation laws, then the model can be used to understand the behavior of the system even under the situations where we do not have the data. On the other hand, the models based purely on the probabilistic frameworks can not reliably be extended to the regimes of behavior where the data are not available.

The attractiveness of the stochastic differential equations (SDE) and stochastic partial differential equations (SPDE) come from the fact that we can integrate the variability of the system along with the scientific knowledge pertaining to the system. In relation to the above-mentioned diffusion problem of the liquid within the rock material, the scientific knowledge is embodied in the formulation of the partial differential equation, and the variability of the permeability is modeled by using random processes making the solving of the problem with the appropriate boundary conditions is an exercise in stochastic dynamics. We use the term "stochastic dynamics" to refer to the temporal dynamics of random variables, which includes the body of knowledge consisting of stochastic processes, stochastic differential equations and the applications of such knowledge to real systems. Stochastic processes and differential equations are still a domain where mathematicians more than anybody else are comfortable in applying to natural and biological systems. One of the aims of this book is to explain some useful concepts in stochastic dynamics so that the scientists and engineers with a background in undergraduate differential calculus could appreciate the applicability and appropriateness of these recent developments in mathematics. We have attempted to explain the ideas in an intuitive manner wherever possible without compromising rigor.

We have used the solute transport problem in porous media saturated with water as a natural setting to discuss the approaches based on stochastic dynamics. The work is also motivated by the need to have more sophisticated mathematical and computational frameworks to model the variability one encounters in natural and industrial systems. The applications of stochastic calculus and differential equations in modeling natural systems are still in infancy; we do not have widely accepted mathematical and computational solutions to many partial differential equations which occur in these models. A lot of work remains to be done. Our intention is to develop ideas, models and computational solutions pertaining to a single problem: stochastic flow of contaminant transport in the saturated porous media such as that we find in underground aquifers. In attempting to solve this problem using stochastic concepts, we have experimented with different ideas, learnt new concepts and developed mathematical and computational frameworks in the process. We

discuss some of these concepts, arguments and mathematical and computational constructs in an intuitive manner in this book.

1.2   Solute Transport in Porous Media

Flow in porous media has been a subject of active research for the last four to five decades. Wiest et al. (1969) reviewed the mathematical developments used to characterize the flow within porous media prior to 1969. He and his co-authors concentrated on natural formations, such as ground water flow through the soil or in underground aquifers.

Study of fluid and heat flow within porous media is also of significant importance in many other fields of science and engineering, such as drying of biological materials and biomedical studies. But in these situations we can study the micro-structure of the material and understand the transfer processes in relation to the micro-structure even though modeling such transfer processes could be mathematically difficult. Simplified mathematical models can be used to understand and predict the behavior of transport phenomena in such situations and in many cases direct monitoring of the system variables such as pressure, temperature and fluid flow may be feasible. So the problem of prediction can be simplified with the assistance of the detailed knowledge of the system and real-time data.

However, the nature of porous formation in underground aquifers is normally unknown and monitoring the flow is prohibitively expensive. This forces scientists and engineers to rely heavily on mathematical and statistical methods in conjunction with computer experiments of models to understand and predict, for example, the behavior of contaminants in aquifers. In this monograph, we confine our discussion to porous media saturated with fluid (water), which is the case in real aquifers. There are, in fact, two related problems that are of interest. The first is the flow of the fluid itself, and the second the transport of a solute introduced into the flow at a specific point in space.

The fluid flow problem is usually one of stationary flow, i.e, the fluid velocity does not change with time as long as external influences such as pressure remain constant. The overall flow rate (fluid mass per unit time) through a porous medium is well described by Darcy's law, which states that the flow rate is proportional to the pressure gradient. This is analogous to Ohm's law in the more familiar context of the flow of electric current. The coefficient of proportionality is a constant describing a property of the porous material, as is

resistance for the case of an electrical conductor. The most obvious property of a porous material is that it partially occupies the volume that would otherwise be available to the fluid. This is quantified by defining the porosity ϕ of a particular porous medium, as the fraction of the overall volume that is occupied by the pores or voids, and hence filled by liquid for a saturated medium. Taking the porosity value separately, the coefficient in Darcy's equation is defined as the hydraulic conductivity of the medium.

The solute transport problem on the other hand, is a non-stationary problem: solute is introduced into the flow at a specific time and place, and the temporal development of its spatial distribution is followed. It is important in its own right, for example, to describe the propagation of a contaminant or nutrient introduced into an aquifer at some point. In addition, it can be used as an experimental tool to study the underlying flow of the carrier liquid, such as by observing the spread of a dye droplet, a technique also used to observe a freely flowing liquid. In free flow, the dye is carried along by the flow, but also gradually spreads due to diffusion on the molecular scale. This molecular scale or microdiffusion, takes place also in a static liquid because of the thermal motion of the fluid and dye molecules. It is well described mathematically by Fick's law, which postulates that the diffusive flow is proportional to the concentration gradient of the dye.

Past experience shows that when a tracer, which is a labeled portion of water which may be identified by its color, electrical conductivity or any other distinct feature, is introduced into a saturated flow in a porous medium, it gradually spreads into areas beyond the region it is expected to occupy according to micro diffusion combined with Darcy's law. As early as 1905 Slitcher studied the behavior of a tracer injected into a groundwater movement upstream of an observation well and observed that the tracer, in a uniform flow field, advanced gradually in a pear-like form which grew longer and wider with time. Even in a uniform flow field given by Darcy's law, an unexpectedly large distribution of tracer concentration showed the influence of the medium on the flow of the tracer. This result is remarkable, since the presence of the grains or pore walls that make up the medium might be expected to impede rather than enhance the distribution of tracer particles – as it does indeed happen when the carrier fluid is stationary. The enhanced distribution of tracer particles in the presence of fluid flow is termed hydrodynamic dispersion, and Bear (1969) described this phenomenon in detail.

Hydrodynamic dispersion is the macroscopic outcome of a large number of particles moving through the pores within the medium. If we consider the

movement of a single tracer particle in a saturated porous medium under a constant piezometric head gradient in the x direction, we can understand the phenomenon clearly (Figure 1.1). In the absence of a porous medium, the particle will travel in the direction of the decreasing pressure (x- direction) without turbulence but with negligibly small Brownian transverse movements. (Average velocity is assumed low and hence, the flow field is laminar.) Once the tube in Figure 1.1 is randomly packed with, for example, solid spheres with uniform diameter, the tracer particle is forced to move within the void space, colliding with solid spheres and traveling within the velocity boundary layers of the spheres.
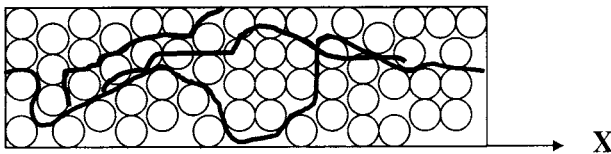

Figure 1.1   A possible traveling path of a tracer particle in a randomly packed bed of solid spheres.

As shown in Figure 1.1, a tracer particle travels in the general direction of x but exhibits local transverse movements, the magnitude and direction of which depend on a multitude of localized factors such as void volume, solid particle diameter and local fluid velocities. It can be expected that the time taken for a tracer particle to travel from one end of the bed to the other is greater than that taken if the solid particles are not present. If a conglomeration of tracer particles is introduced, one can expect to see longitudinal and transverse dispersion of concentration of particles with time. The hydrodynamic dispersion of a tracer in a natural porous formation occurs due to a number of factors. The variation of the geometry of the particle that constitute the porous formations play a major role in "splitting" a trace into finer "off-shoots", in addition, changes in concentration of a tracer due to chemical and physical processes, interactions between the liquid and the solid phases, external influences such as rainfall, and molecular diffusions due to tracer concentration. Diffusion may have significant effect on the hydrodynamic dispersion; however, we are only concerned with the effects of

the geometry to larger extent and effects of diffusion to lesser extent. For the current purpose, in essence, the hydrodynamic dispersion is the continuous subdivision of tracer mass into finer 'offshoots', due to the microstructure of the medium, when carried by the liquid flowing within the medium. Because the velocities involved are low, one can expect molecular diffusion to have a significant impact on the concentration distribution of the tracer over a long period of time. If the effects of chemical reactions within the porous medium can be neglected, dispersion of tracer particles due to local random velocity fields, and molecular diffusion due to concentration gradients, are the primary mechanisms that drive the hydrodynamic dispersion.

1.3   Models of Hydrodynamic Dispersion

The basic laws of motion for a fluid are well known in principle, and are usually referred to as the Navier-Stokes equations. It turns out that the Navier-Stokes equations are a set of coupled partial differential equations that are difficult to solve even for flow in cavities with relatively simple geometric boundaries. It is clearly impossible to solve them for the multitude of complex geometries that will occur in a detailed description of the pore structure of a realistic porous medium. This level of detail is also not of practical use; what is desired is a description at a level of detail somewhere intermediate between that of Darcy's law and the pore level flow. Different approaches to achieve this have been described in literature (e.g. Taylor, 1953; Daniel, 1952; Bear and Todd, 1960; Chandrasekhar, 1943). These approaches can broadly be classified into two categories: deterministic and statistical.

In the deterministic models the porous medium is modeled as a single capillary tube (Taylor, 1953), a bundle of capillary tubes (Daniel, 1952), and an array of cells and associated connecting channels (Bear and Todd, 1960). These models were mainly used to explain and quantify the longitudinal dispersion in terms of travel time of particles and were confined to simple analytical solutions (Bear, 1969). They have been applied to explain the data from laboratory scale soil column experiments.

Statistical models, on the other hand, use statistical theory extensively to derive ensemble averages and variances of spatial dispersion and travel time of tracer particles. It is important to note that these models invoke an ergodic hypothesis of interchanging time averages with ensemble averages after sufficiently long time, and the law of large numbers. By the law of large numbers, after a sufficiently long time, the time averaged parameters such as velocity and displacement of a single tracer particle may replace the averages

taken over the assembly of many particles moving under the same flow conditions. Bear (1969) questioned the validity of this assumption arguing that it was impossible for a tracer particle to reach any point in the flow domain without taking the molecular diffusion into account.

In statistical models, the problem of a cloud of tracer particles traveling in a porous medium is reduced to a problem of a typical single particle moving within an ensemble of randomly packed solids. Characteristic features of these models are: (a) assumed probability distributions for the properties of the ensemble; (b) assumptions on the micro dynamics of the flow, such as the relationships between the forces, the liquid properties and velocities during each small time step; (c) laminar flow; and (d) assumed probability distributions for events during small time step within the chosen ensemble. The last assumption usually requires correlation functions between velocities at different points or different times, or joint probability distributions of the local velocity components of the particle as functions of time and space, or a probability of an elementary particle displacement (Bear, 1969).

Another modeling approach that has been used widely is to consider the given porous medium as a continuum and apply mass and momentum balance over a Representative Elementary Volume (REV) (Bear et al., 1992). Once the assumption is made that the properties of the porous medium, such as porosity can be represented by average values over the REV, then the mass and momentum balances can be applied to a REV to derive the governing partial differential equations which describe the flow in the medium. Since the concept of the REV is central to this development, it is important to summarize a working model based on this approach.

1.4   Modeling Macroscopic Behavior

1.4.1 Representative Elementary Volume

The introduction of a REV is once more analogous to the approach followed in electromagnetic theory, where the complexities of the microscopic description of electromagnetic fields at a molecular level, is reduced to that of smoothly varying fields in an averaged macroscopic continuum description. The basic idea is to choose a representative volume that is microscopically large, but macroscopically small. By microscopically large, we mean that the volume is large enough that fluctuations of properties due to individual pores are averaged out. Macroscopically small means that the volume is small enough that laboratory scale variations in the properties of the medium is faithfully represented by taking the average over the REV as the value associated with a point at the center of the REV. For this approach to be successful, the micro- and macro-scales must be well enough separated to
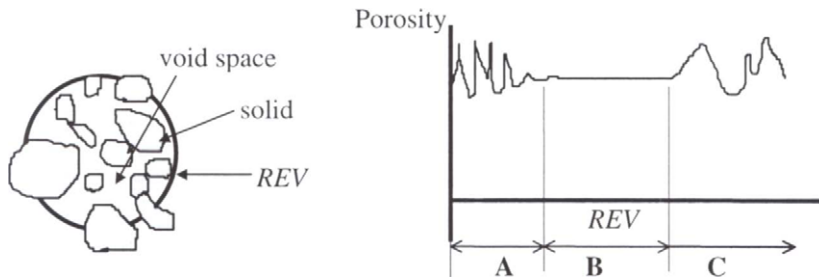

Figure 1.2 Variation of porosity with Representative Elementary Volume (REV).

allow an intermediate scale – that of the REV – at which the exact size and shape of the REV makes no difference.

Porosity is defined as the ratio between the void volume and the overall volume occupied by the solid particles within the REV. The variation of porosity with the size of REV is illustrated in Figure 1.2 (Bear et al., 1992). The fluctuation in porosity values in region A shows that the REV is not

sufficiently large to neglect the microscopic variations in porosity. If the porous medium is homogeneous, porosity is invariant once region B is reached, which can be considered as the operational region of REV for mass and momentum balance equations. For a heterogeneous porous medium, porosity variations still exist at a larger scale and are independent of the size of REV (Region C).

Once the size of REV in the region B is established for a given porous medium, macroscopic models can be developed for the transport of a tracer (solute). The variables, such as velocity and concentration, are considered to consist of a volume-averaged part and small perturbations, and these small perturbations play a significant role in model formulations (Gray, 1975; Gray et al., 1993; Hassanizadeh and Gray, 1979; Whitaker, 1967).

1.4.3 Review of a Continuum Transport Model

To make the discussion of the transport problem more concrete, we turn our attention to an example with a simple geometry. Consider a cylindrical column of internal radius R with the Cartesian coordinate system as shown in Figure 1.3. The column is filled with a solid granular material and it is assumed that the typical grain diameter $(l_d) << R$. Assuming that the porous matrix is saturated with a liquid of density, ρ, the local flow velocity of the liquid with respect to the stationary porous structure and the local concentration of a neutral solute in the fluid are denoted by $v(x,y,z,t)$ and $c(x,y,z,t)$, respectively. The REV or averaging volume (δV) for this system is a cross sectional volume of the column of some width, $\Delta\varsigma$. It is assumed that δV is sufficiently large so that statistical averages are insensitive to small variations in δV (Rashidi et al., 1996).
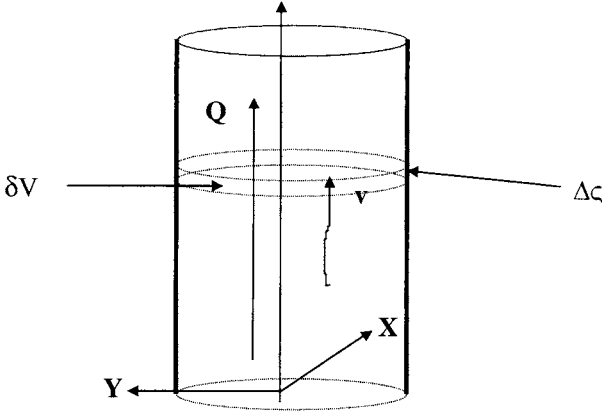
Figure 1.3   Geometry for the cylindrical column flow model.

The volume average of a pore scale quantity, ψ, associated with the liquid phase is defined by (The notation for the model is adopted from Rashidi et al. (1996).)

$$\left\langle \, \psi(z,t) \, \right\rangle = \frac{1}{\pi R^2 \Delta\zeta} \int_{-\Delta\zeta/2}^{\Delta\zeta/2} \int_A \psi(x,y,z+\zeta,t) \; \gamma\,(x,y,z+\zeta) \; dA \; d\zeta \qquad (1.1)$$

where A represents the cross-sectional area of the column and γ is an indicator function which equals 1 if the point (x,y,z+ς) lies in the void space, and zero otherwise. The cross sectional porosity, $\varphi(z)$, is obtained by setting ψ=1 in equation (1.1).

The volumetric flux, q_z is defined as the volume of fluid passing a point z per unit time. Since the microscopic momentum flux (momentum per unit area) carried by the fluid at any point (x,y,z) is given by $\rho\underline{v}$ the macroscopic momentum flux for an incompressible fluid is given by

$$\left\langle \, \rho\underline{v} \, \right\rangle \; = \; \rho\underline{q} = \rho q_z \underline{k} \qquad (1.2)$$

where $\underline{k}$ is a unit vector along the z- axis. The total volumetric flux through the cross section is given by

$$Q = q_z(\pi R^2),$$
(1.3)

and the mean velocity can be defined by,

$$\bar{v} = q_z \underline{k} / \varphi \ .$$
(1.4)

The instantaneous, local solute flux consists of a contribution (cv) representing solute carried along by the liquid flow (advection), and a diffusion contribution proportional to the concentration gradient. Because the solute flux is non-stationary, conservation of solute mass is expressed by the time-dependent equation of continuity.

Using averaging theorems, this can be reduced to the following one-dimensional macroscopic mass balance equation for the solute (Thompson et al., 1986):

$$\frac{\partial(\varphi \bar{c})}{\partial t} + \overbrace{\frac{\partial(\varphi \overline{v_z}\bar{c})}{\partial z}}^{A} + \overbrace{\frac{\partial(\varphi J_z)}{\partial z}}^{B} - \overbrace{\frac{\partial}{\partial z}\left(\varphi D_m(\frac{\partial \bar{c}}{\partial z} + \tau_z)\right)}^{C} = 0 \ .$$
(1.5)

The various terms in this equation can be interpreted as a rate of change of the intrinsic volume average concentration, balanced by the spatial gradients of the terms, A, B, and C respectively.

Term A represents the average volumetric flux of the solute transported by the average flow of fluid in the z-direction at a given point in the porous matrix, (x,y,z). But the total solute flux at a given point is the sum of the average flux and the fluctuating component due to the velocity fluctuation above the mean velocity, $\overline{v_z}$. We introduce the perturbation terms of velocity (v_z') and concentration (c'), each of which represents the difference between the microscopic quantity evaluated at (x, y, z+ς) (within a REV), and the corresponding intrinsic average evaluated at z.   In terms of these, the fluctuating component of the flux is given by:

$$J_z(z,t) = \overline{v_z' \, \bar{c}'} \ .$$
(1.6)

The terms A and B are called the mean advective flux and the mean dispersive flux, respectively. Making the following assumption for the dispersive flux, based on plausibility arguments, often circumvents the need for the detailed knowledge of the fluctuation terms:

$$J_z(z,t) \approx -\alpha_L \bar{v}_z \frac{\partial \bar{c}}{\partial z}. \tag{1.7}$$

Why would the dispersive flux be proportional to a concentration gradient? The velocity fluctuations that underlie this term, must by definition sum to zero over an REV. They therefore have the effect of exchanging fluid elements from different spatial locations rather than a net flow of liquid. Nevertheless, if the concentration is different at these locations, this will have the effect of a net transport of solute mass, while if the concentration gradient is zero, no net solute mass will be transported. Any existing concentration gradient will tend to be decreased by such a mixing mechanism, which accounts for the negative sign in equation (1.7). The proportionality to the average velocity assumed in that equation is plausible since the fluctuations under discussion do not have an independent origin but arise from deflection of fluid elements away from the averaged flow by the pore walls. Therefore, these fluctuations will be zero in the absence of flow and progressively increase as the flow increases. Both of these dependencies might conceivably be more complex, but the assumption of simple proportionality in equation (1.7) seems a reasonable working assumption.

The proportionality constant in the equation, α_L , is defined as the dispersivity of the porous medium. Dimensional considerations show that it has the dimensions of a length, and an obvious hypothesis is to connect it with the granularity scale of the medium, i.e. with a typical particle diameter. Although of a different physical origin, the form of equation (1.7) is reminiscent of Fick's law and the similarity is often emphasized by defining the product $D = \alpha_L \bar{v}_z$ as the dispersion coefficient in analogy to the diffusion coefficient, D_m.

The term C in equation (1.5) is the modified Fick's law for micro diffusion of the solute. A modification is needed, because even in the absence of any averaged flow of the liquid, molecular diffusion will be affected by the presence of the porous medium. In particular, an increased path length is needed by a diffusing particle, to reach the same displacement relative to its starting position as in free flow conditions. This increased path length is a measure of the degree of tortuous paths present within the porous medium. The term τ_z that arises from the mathematical averaging is in fact the total surface area perpendicular to the flow presented by the grains of the porous medium within the REV, and weighted by the concentration at each point. It can be seen as a measure of the total barrier to diffusion caused by the tortuosity of the medium.

While the tortuosity is essentially a geometric concept, its effect appears in equation (1.5) as a modification of the diffusion term and hence τ_z is referred to as the diffusive tortuosity. It is reduced to a dimensionless parameter β that characterizes the structure of the medium by writing

$$\tau_z(z,t) \approx -\beta \frac{\partial \overline{c}}{\partial z}. \tag{1.8}$$

The assumption that this is also proportional to the concentration gradient, may be justified by considering that the existence of a barrier only has an effect if there is a non-zero concentration gradient at a particular position x. Substituting equations (1.7) and (1.8) into (1.5), yields

$$\frac{\partial}{\partial t}\left(\varphi \overline{c}\right) + \frac{\partial}{\partial z}\left(\varphi \overline{v_z}\overline{c}\right) - \frac{\partial}{\partial z}\left[\left[\varphi D + \varphi D_m(1-\beta)\right]\frac{\partial \overline{c}}{\partial z}\right] = 0. \tag{1.9}$$

From this expression it becomes clear that the entire range of plausible effects on diffusion by the tortuosity of the medium, ranging from negligible effect when the medium allows fluid elements to proceed along free flow fluid lines, to complete blocking of diffusion when fluid elements are forced by the pore geometry into infinite path lengths to cover a finite displacement, can be represented by letting β range over the values 0 to 1 respectively.

The sum $D_H = D + D_m(1-\beta)$ is called the coefficient of hydrodynamic dispersion. In many cases, $D \gg D_m$ such that $D_H \approx D$ (Rashidi et al., 1996).
Equation (1.9) is the commonly-used working model for solute transport in porous media and is usually called the advection-dispersion equation. Note that it is dependent on the Fickian assumptions expressed by equations (1.7) and (1.8).

A mental picture of the interplay between dispersion and micro diffusion can perhaps be facilitated by the following analog. Consider a spoonful of sugar at the bottom of a teacup. As the sugar dissolves, it will spread slowly through the cup as a result of micro diffusion. If the tea is stirred, this action introduces advection, moving sugar to other parts of the liquid; and in so doing, larger gradients in the concentration are produced and diffusion is enhanced, leading to a very quick spreading of the sugar. In a porous medium, the deflection of the flow by pore walls plays the role of the stirring, but unlike the case of the teacup the pore walls also slows down the diffusion. The net effect is nevertheless an enhancement of the spreading beyond that produced by diffusion alone.

We have seen that the division of solute flux into advective and dispersive components is a result of the mathematical division of velocity and concentration into the mean and perturbation terms. Then the perturbations are linearized through Fickian assumptions making the model deterministic so that we can understand the behavior of solute dispersion. However, this liberalization changes the inherent random character of the problem into a deterministic one. In addition we observe that:

- the coefficient of hydrodynamic dispersion depends upon the velocity fluctuations induced by the pore structure; therefore, it can be expected to be scale dependent;
- Fickian type assumptions are made for dispersive flux as well as for diffusive tortuosity. These assumptions are based on plausibility arguments, not justified on the basis of detailed microscopic theory as in the case of micro-diffusion;
- there are only two physical phenomena involved in the solute transport in a porous medium: the solute is carried by the flowing fluid (advection) and, if the velocities are very small, micro-diffusion can occur as described by the Fick's law; and,
- the working model described above can only be applied to homogeneous porous media where a representative elementary volume can be defined.

1.5   Measurements of Dispersivity

Rashidi et al. (1996) experimentally investigated the solute transport in a bed of packed polymethylmethacryle (PMMA) plastic spherical beads of 0.31 cm diameter contained in a cylindrical column having 4.5 cm diameter. Their experiments are designed to test the validity the Fickian assumptions as well as several other measurement and estimation techniques commonly used in applying the advection-dispersion equation, by performing direct measurement of the pore-scale velocity and concentration fields.

In their experiment, the beads and the fluid were chosen to be transparent and have the same refractive index to allow direct optical probing at any point within the porous system. Fluid velocity was measured by introducing fluorescent micro-spheres of 6.5 μm diameter into the flow, and measuring their velocity by observing their movement across a series of illumination planes. Using laser optics, the illumination planes were prepared to a resolution orders of magnitude smaller than the grain and pore diameters, allowing non-invasive velocimetry at essentially point-like resolution within the pores. In a similar way, concentrations were measured non-invasively at the same point grid by introducing a fluorescent dye as the solute tracer. Their results are reproduced in Table 1.1.

From their measured velocities, the fluctuations and hence the dispersive flux as defined in equation   (1.6) could be directly calculated by averaging. From the observed concentrations, the gradient of the average was similarly found, and the ratio of these is a direct measurement of the dispersion coefficient and hence the dispersivity.

Table 1.1   Summary of measured or estimated dispersivities and dispersion coefficients (Rashidi et al., 1996).

Method	Dispersivity α_L (cm)	Dispersion Coefficient D (cm^2/min)	Assumptions and comments
Direct experiment	0.12	0.018	Rashidi et al. (1996); Constant velocity experiments to get α_L; D found directly.
Length-scale arguments	0.15	0.023	$Pe = \bar{v}_z l_d / D_m \approx 75$
$\alpha_L \approx 0.5\ l_d$	0.54	0.081	
$\alpha_L \approx 1.8\ l_d$	0.30	0.045	
$\alpha_L \approx l_d$			Bear (1972) pp 609
Breakthrough slope methods	0.20	0.031	Constant velocity; constant porosity; square Initial Conditions (IC); averages over 28 locations
Numerical curve fits:			Constant velocity
Square IC	0.20	0.030	Constant porosity; square IC
Slope IC	0.12	0.018	Constant velocity; porosity

As mentioned in the previous section, the dispersivity is essentially a length scale and as the primary length scale that characterizes the structure of a porous medium is the diameter of its pores or the particles that makes it up, it is reasonable to expect a relation between these. This line of argument has been elaborated by Bear (1972). He proposed a direct proportionality of the dispersivity to the grain diameter, but with different values for the proportionality constant according to the value of the Peclet number. The Peclet number is a dimensionless ratio that expresses the relative importance of advection, and diffusion or dispersion, for particular flow conditions. It is given by $Pe = \bar{v}_z l_d / D_m \approx 75$ for the experiment. This value is intermediate between zones distinguished by Bear, and Rashidi et al. compares the values yielded for the dispersivity by both zones as well as an average.

In the breakthrough slope methods, solute concentration is measured as a function of time at a fixed position when a solute front advances past the point. Comparing the measured curve with analytic solutions of the dispersion-advection equation for an idealized step function initial concentration, a value for the dispersion coefficient is extracted. This is less detailed than the complete measurement of concentration and velocity fields

in the direct method, but is similar to field measurements in macroscopic and aquifer experiments.

Finally, D is similarly estimated by comparison with numerically calculated solutions of the dispersion-advection equation (the curve-fitting solutions). Two cases are considered: a square step initial condition, and one where the initial concentration already contains some dispersion by assuming a sloped step. The latter provides for insufficient experimental control to produce the idealized mathematical initial condition. Values of dispersivity and dispersion coefficient obtained from different approaches for the same porous medium vary considerably as shown in Table 1.1.

Given the advanced laser beam measurement techniques employed in the method (Rashidi et al., 1996) it is reasonable to assume that the values reported by the direct method are 'true' values. Then the length scale arguments tend to overestimate the dispersivity, although giving reasonable agreement at the lower end of the range of estimates. A plausible explanation would be that the proportionality coefficients proposed by Bear, were found for natural media like sand containing irregularly shaped grains, and would be expected to overestimate dispersion caused by the smooth spheres in the experiment. Hence length scale arguments are good for first estimates but may need further refinement by measuring actual dispersion.

Applying the standard methods based on breakthrough curves, both analytical and numeric, also tended to overestimate the dispersion. In part, this may be due to the assumption of a physically unrealistic initial condition, as good agreement could be obtained in the last row in Table 1.1 by fitting a slope for the assumed initial condition step. However, Rashidi et al. also calculated the dispersive flux over the whole of the measurement volume, as a function of time, from the numerical solution. When this is compared to the true dispersive flux calculated by applying equation   (1.6) to the measured velocities, the dispersive flux calculated from the advection-dispersion equation overestimates the true value by a factor 3 for $D=0.03$ cm^2/min as obtained from the breakthrough curve analysis. Both reducing D to the true value of 0.018 cm^2/min, and introducing a sloped step initial condition, reduced the discrepancy to a factor 2. Rashidi et al. reported additional attempts to further reduce the discrepancy by allowing for spatial variability in the porosity or dispersivity, but without success. This strongly suggests that the Fickian assumption for the dispersive flux, and/or for the tortuosity, is not fully satisfied in the experiment.

Another point demonstrated by Table 1.1, is the dominance of dispersion over diffusion in the experiment. Typical diffusion coefficients in aqueous solutions vary from 0.00026 cm^2/min for a small non-ionic molecule such as sucrose, to 0.002 cm^2/min for a strong electrolyte like HCl (see Weast (1972)). The much higher dispersion coefficients in Table 1.1 shows that dispersion far outweighs micro diffusion in this experiment. A high dispersion coefficient is a result of relatively high velocity perturbations, i.e. increased randomness in the velocity field. We conclude that the random component in the velocity field plays a significant role in determining the concentration field, even in a homogeneous porous medium tested under laboratory conditions.

Moroni and Cushman (2001) conducted three-dimensional particle tracking velocimetry (3D-PTV) experiments for a homogenous porous medium of Pyrex 1.9-cm spheres and glycerol. Air bubbles diffused into the system was used as tracer particles and they were drained along with glycerol. Three-dimensional trajectories of the tracer particles were constructed and analyzed based on the data from the experiments. They found that the longitudinal velocity distributions were neither Gaussian nor lognormal, but the transverse velocity distributions were Gaussian. Dispersion coefficients in the transverse directions approaches to zero with increasing time but some trajectories showed sharp increases in dispersion coefficient at the beginning and others did not show significant increases. Normalized longitudinal velocity covariances for different flow rates had similar exponentially decaying behavior with respect to time. Longitudinal dispersion coefficient tends to be constant at a given flow rate after a relatively small time indicating that the flow in longitudinal direction can be considered Fickian. However, this can not be said about the other two directions which makes the application of the Fickian assumptions as a general rule even in a homogeneous medium questionable.

1.6   Flow in Aquifers

1.6.1 Transport in Heterogeneous Natural Formations

Field experiments show that spatial heterogeneity is the most significant factor affecting dispersion of solute in natural formations such as aquifers (Anderson, 1979; Gelhar et al., 1985; Freyberg, 1986). Dagan (1988) referred to the experimental results depicting large scale spatial distribution of hydraulic conductivity at the Borden site. Large scale irregular variations in hydraulic properties, such as hydraulic conductivity and porosity, lead to a high degree of uncertainty of parameters in transport equations based on the continuum approach, whose application to solute transport in natural formations is questionable (Dagan, 1988). Dagan (1988) concluded that the concentration of a solute can be considered as a random variable, which can be described by its statistical moments; the ergodic hypothesis can not be applied except in a limited sense in describing some gross features such as the motion of the center of gravity and the second order spatial moment of the solute body; it is extremely difficult to predict accurately the point value of concentration in an irregularly distributed body of solute within the natural formations; the expected value of concentration does not necessarily satisfy a advection-dispersion type equation, such as equation 1.9, based on the continuum approach; and even if the latter is satisfied, the dispersion coefficient increases with the travel time reaching an asymptotic value. In other words, the flow is non-Fickian[1] during the preasymptotic period.

Dagan (1988, 1990) developed a mathematical formulation to predict the spatial moments of concentration plumes in aquifers introducing perturbation terms to describe random variations of variables such as concentration and velocity. It is usually assumed that a solute is transported by advection described by the Darcian steady velocity and by pore scale diffusion. The governing equation is the 3-dimensional generalization of equation (1.9) and is given by,

$$\frac{\partial C}{\partial t} + V_j \frac{\partial C}{\partial x_j} = \frac{\partial}{\partial x_j}\left(D_{d,jl}\frac{\partial C}{\partial x_l}\right) \quad j,l = 1,\,2,\,3 \tag{1.10}$$

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[1] When the flow can be described by a advection-dispersion type equation, the transport is said to be Fickian.

Here $C = \varphi\,\bar{c}$ is the concentration per unit volume of aquifer, $x = (x_1, x_2, x_3)$ is the coordinate vector, and V is the Eulerian velocity vector according to Darcy's law:

$$V = -\frac{K}{\varphi}\nabla\phi .$$ (1.11)

In Darcy's equation, K is the hydraulic conductivity; φ is the effective porosity and ϕ is the piezometric head. Since Darcy's equation gives V as a constant, it was factored out of the differentiation in the second term of equation (1.10). In order to provide for anisotropy in the dispersion, $D_{d,jl}$ in that equation is taken as a tensor rather than a scalar, and represents the effect of pore scale dispersion (Dagan, 1988). The standard summation convention for repeated indices was used.

Dispersive flux due to pore scale velocity variations is lumped into the right hand term in equation (1.10) through a diffusion tensor and the mean velocity given by Darcy's law is used in the advection term. Dagan (1988) assumed constant components for the pore scale dispersive tensor, $D_{d,jl}$, and introduced macro scale variations as perturbation terms to the velocity and concentration. After a non-trivial mathematical analysis he arrived at the expected values of the spatial second moments of a solute plume within a stationary heterogeneous porous structure.

Cushman (1987) stated that the transport process in natural formations can not be modeled by the advective-dispersive equation because of stochastic (random) fluctuations in flow velocity due to natural heterogeneity in the pore structure and failure of Fick's type diffusion equation to describe the pore scale dispersion.

A particular problem in the application of the advection-dispersion equation and attributed by many authors to the natural heterogeneity is the so-called scale dependence of the dispersivity. For example, Pickens and Grisak (1981) found from laboratory measurements of a 30-cm column of a certain aquifer, the longitudinal dispersivity to be $\alpha = 0.035$ cm. In single well field tests on the same aquifer, a value of $\alpha = 3$ cm was obtained for a flow length of 3.1 m and $\alpha = 9$ cm when the solute plume traveled 5 m. In two-well tests with wells located 8 m apart, the value $\alpha = 50$ cm was obtained.

Such variability of a "constant" is very disturbing in a model of which a major merit is intended to be the reduction of a complex phenomenon to simple

materials constants. At best, it indicates the presence of a key variable that was not recognized in the first formulation of the model. If this variable can be identified, the situation might be rescued. One attempt to do this, was to express α as proportional to the flow length. The results of Lallemand-Barres et al. (1978) fits such a relation to the measured values for a number of natural aquifer materials; despite considerable scatter, a reasonable fit over a scale range of 10^3 was obtained. However, when the range was extended to about 10^5 by Gelhar (1986), no simple relationship appears tenable any more.

Many authors concur that the root of the problem is that natural aquifers are not homogeneous. The measured values of hydraulic conductivity for different geological materials are found to vary by up to 9 orders of magnitude; porosity differs by more than 2 orders of magnitude. One can hardly expect the value of such a sensitive quantity to remain constant over the extent of a natural aquifer even if composed of a single mineral. This is borne out by actual measurements reported by Gelhar (1986) and by Sudicky (1986) showing spatial variations over one order of magnitude.

Scale dependence of the dispersion process has been examined in the light of spatial distribution of hydraulic conductivity in many studies (Serrano, 1988). However, Serrano (1988) has cited other researchers' work, which mentioned the inconsistencies of the approaches to solve the transport equation in their review article.   They have concluded that the advective-dispersive model neither explained the scale effect of the dispersion process nor elucidated the transient behavior of solute concentration. In addition, Serrano (1988) summarized the main difficulties with the existing solutions. The assumption that the perturbations are small random variations in the perturbation expansion solutions (Gelhar and Axness, 1983; Dagan, 1984) is not valid in a differential equation unless the variables have small variance.   One could argue that if the variances of the processes involved are indeed small as required by the perturbation solutions, then a completely deterministic model could be used as a sufficient tool for prediction purposes. Cushman (1987) made similar conclusions after an in-depth analysis of the perturbation solutions provided by Gelhar and Axness (1983).

The assumption that hydraulic conductivity is the only source of uncertainty in many existing solutions has to be challenged.   Dispersion in natural formations can not only be explained by the variability of hydraulic conductivity; and if this is feasible the large-scale hydraulic conductivity can safely be described by well defined deterministic functions. Some of the solutions are only valid in the steady state of the concentration field.

The assumed ergodicity in the hydraulic conductivity field in some solutions does not necessarily imply that the concentration field is ergodic. The temporal and spatial variations of the parameters affecting the aquifer heterogeneity significantly make the analytical solutions of dispersion equations almost impossible.   However, recent attempts to solve the advective-dispersion equation for heterogeneous aquifers are noteworthy (Serrano, 1996). Serrano (1996) solved the three-dimensional solute continuity equation in a large domain neglecting the micro diffusion and using a decomposition method. However, the probability law of the velocity fields needs to be provided to solve the solute transport equation for a particular aquifer.

1.7   Computational Modeling of Transport in Porous Media

As we have seen in the previous discussion on the solute transport in heterogeneous media, the problem of predicting the solute concentration of a plume is complicated by many factors. Usually the nature of the porous formation is not known in detail but in some aquifers we can know the approximate composition of the medium, its particle sizes and their distribution. But in many cases, values of parameters such as hydraulic conductivity and porosity can only be measured at a limited number of points in the field. Spatial variability of hydraulic conductivity, for example, can not be known experimentally to our satisfaction.

If our mathematical models incorporating the possible variabilities cannot be solved without significant simplifications and assumptions, and the experiments on real aquifers is prohibitively expensive, where do we turn to understand more about the phenomenon? Computer models built on basic conservation equations incorporating variabilities modeled by known processes would provide us with a tool for experimentation. The whole purpose of the exercise is to develop a tool by looking at the fundamentals of the solute transport process and develop them into mathematical equations and logical relationships with a high degree of flexibility, to incorporate the stochasticity in parameters such as hydraulic conductivity and porosity. Once we have such a tool, we can conduct computational experiments and investigate how the solute behaves within a porous medium. As we have seen before, velocity of a solute particle in a porous body is a random variable and the variability is very much influenced by the pore structure of the body.

Equation (1.7) models the fluctuating component of the solute flux in a representative elementary volume using a Fickian-type spatial gradient of the mean concentration. The dispersion coefficient is defined as the coefficient relating the gradient of the mean concentration to the fluctuating component of the flux. The dispersion coefficient itself is expressed as a multiplication of the diffusivity and the mean velocity, and the diffusivity is found to be scale dependent. This could be expected. The Fickian relationship itself is an attempt to linearize a random process with respect to quantities such as particle sizes. As shown by Rashidi et al. (1996), even though this works fairly well to predict concentration, discrepancies in the dispersive flux arise even when the porous bed is very homogeneous. So when particle sizes are not uniform, the fluctuating component of the flux may become highly random and modeling that component using a Fickian model is not desirable. We are left with the option of modeling velocity as a random variable, and the degree of randomness depends on the pore structure.

The above discussion leads us to model the transport phenomenon in natural formations by treating the variables and the parameters involved in the processes as stochastic variables each having its own probability law, and when they satisfy the conservation laws, subsequent differential equations have to be solved by using stochastic differential calculus and appropriate numerical methods.

It is appropriate here to point out the difference between a deterministic differential equation solved for random boundary or initial conditions, and a stochastic differential equation. If for example in a time domain differential equation, the initial conditions are inaccurately known, it is in principle possible to solve the differential equation for a large number of different initial conditions, and use the probability distribution of such initial conditions to find the probability distribution of the solutions. Equivalently, one may specify the initial condition as an average value, modified by a random perturbation, and find the effect of the perturbation by operating on it with the deterministic differential operator. The statistically based studies of aquifer flow discussed above are mainly of this type. However, it is quite a different matter when the differential operator is itself stochastic, e.g. containing coefficients that undergo random variations during the interval between the initial condition and the time for which the solution is found. This much more difficult case is the domain of stochastic differential equations.

The problem of flow in a heterogeneous porous medium, is of the latter type. For example, in Darcy's equation, if there are random variations in the

hydraulic conductivity over the spatial extent of the aquifer, a fluid element encounters continually changing values of the driving coefficient that determines its displacement as it follows a path through the porous medium. This is true of macro scale variations in the hydraulic conductivity, or the porosity, or both.

Moreover, this conceptual framework is just as applicable at the micro scale – pore level – length scale. If we consider the *gedanken-experiment* of observing the movement of a fluid element in a transparent porous medium, it will describe a path similar to Brownian motion. Brownian motion, indeed, represents the simplest possible stochastic differential equation.

This raises one of the main ideas to be explored in this book: that just as "real" Brownian motion is intimately connected with molecular scale diffusion, pore-scale Brownian motion may be used as a model of dispersion in a porous medium. In this way we will show that Fickian assumptions may be avoided and a more fundamental description addressing, for example, the scale dependence problem can be attempted. We are incorporating Brownian motion, a mathematical object or process representing variability in the system and the conservation laws in the stochastic dynamical description of the problem.

Before this idea can be implemented, it is first necessary to outline aspects of the theory of stochastic differential equations and some essential elements of stochastic processes that will be used. A comprehensive review of stochastic differential equations and related mathematical development are given by Kloeden and Platen (1992), Øksendal (1998) and their definitions and notation are extensively used. Reader may also refer to Klebaner (1998) to learn stochastic calculus with applications in finance.