[4]

Forecasting scale-dependent dispersion from spills in heterogeneous aquifers

Sergio E. Serrano

Department of Civil Engineering, University of Kentucky, Lexington, KY 40506-0281, USA

Abstract

Existing theories of flow and contaminant transport in aquifers are either based on Monte Carlo simulations or small perturbation solutions of the governing stochastic partial differential equations, which limit the applications to cases of small variances in the physical parameters. In this article scale-dependent models to predict mean contaminant concentration from point sources (well injection), and non-point sources (ground surface spills) in hetero- geneous aquifers are developed and tested. A general analytic technique, the Neumann expansion, is used in the solution of the equations. This method does not require the assump- tions of small perturbation, logarithmic transformations, or a specific probability law in the random quantities. In addition, aquifer parameters such as the mean pore velocity are functionally defined in terms of the underlying groundwater flow problem, and field- measurable aquifer hydrogeologic properties such as mean transmissivity, mean hydraulic gradient, mean porosity and aquifer thickness. Comparison with theoretical models, and verification with field tracer tests at the Borden aquifer indicated that the proposed models reproduced the enhanced longitudinal dispersion as a function of distance reported in the literature.

1. Introduction

Predicting the propagation of contaminants as a result of accidental spills requires the implementation of the solution of a differential equation governing solute dispersion in porous media. If the contaminant is injected directly in the saturated zone, the saturated media dispersion equation subject to a point source is needed. If the contaminant is applied at the ground surface, the unsaturated media dispersion equation is needed to describe the concentration in the soil, and the space–time contaminant distribution at the interface between the saturated and the saturated

zone near the water table. The contaminant distribution at the interface is then used as a non-point source for the saturated zone.

The point or the non-point source contaminant migration requires a fundamental solution (Green's function) of an appropriate dispersion equation. Traditionally the convection dispersion equation (CDE) with constant coefficients has been used for that purpose. However, recent theoretical and field studies have demonstrated that the movement of inert solutes in aquifers is governed by a dispersion equation whose dispersion coefficients are functions of the spatial coordinate or travel time, and that only under ideal circumstances, i.e. usually at the laboratory scale, the classical form of the CDE with constant coefficients is adequate for describing contaminant transport (Fried, 1975; Dagan, 1984). This scale dependency of the dispersion parameters raises a number of obstacles for the applied modeler who wishes to predict the time and space evolution of a contaminant concentration in a heterogeneous aquifer.

In the search for the definition of transport equations which adequately represent the evolving nature of the dispersion parameters at large scales, some researchers have conceived the variability of the dispersion parameters as deterministic evolving or periodic functions of space or time (Pickens and Grisak, 1981; Gupta and Bhatthacharya, 1986; Barry and Sposito, 1989; Yates, 1990). Recently Serrano (1992b, 1993) attempted to incorporate aquifer physical variables in the definition of the functional form of dispersion parameters. An equation of dispersion in one- and two-dimensional homogeneous and heterogeneous aquifers with scale-dependent parameters given as functions of natural recharge rate from rainfall, aquifer transmissivity, head hydraulic gradient, aquifer thickness and aquifer soil porosity were derived. It was found that aquifer recharge partially explains the scale dependency of aquifer parameters, even in homogeneous aquifers, and that its inclusion implies the solution of difficult equations with spatially variable coefficients.

Stochastic analyses have played an important role with a variety of studies that investigate the effect of field-scale heterogeneities on the dispersion phenomenon. Researchers have focused on representations of the hydraulic conductivity tensor as realizations of a random field, and its influence on the groundwater velocity variability and the dispersion parameters. For a summary and a critical review of stochastic methods to derive transport equations the reader is referred to Sposito and Jury (1986) and Cushman (1987). The major advantage of existing solution methods of stochastic transport equations is that they have permitted the development of some fundamental understanding of the phenomenon of mass transport in aquifers. The major disadvantage is that most of them have been built based on excessive restrictions and assumptions created for the purpose of making the mathematics of the problem tractable and the solution of the equations possible, and not necessarily to reflect physical conditions. Except for the Monte Carlo simulation approaches, which are empirical and expensive, most of the existing stochastic theories of dispersion are based on the small perturbation assumption, whereby the stochastic terms in the differential equation are assumed to be small and thus the truncation of the series may be justified. However the size of 'small' is usually a subjective statement of the modeler since no mathematical criteria restricting the acceptable bounds in the

variances is presented. It has become widely acceptable to force the 'smallness' in the random quantities by assuming the logarithm of the hydraulic conductivity, K, to be normally distributed. Considering $\log(K)$, rather than K, in the flow equations conveniently minimizes the variance in the random term, but eliminates valuable information about the parameter, and generates an unbounded function for regions of low K. Although some univariate log–normal distributions have been fitted to the hydraulic conductivity of some aquifers, the log–normality of this parameter is usually assumed to justify the small perturbation solution. Finally, the small perturbation solutions claim three-dimensionality in the domains, yet the hydrology of the aquifer and the existence of boundary conditions are eliminated from the analyses. These assumptions may mean that the equation being solved is no longer a proper representation of the physical problem whose solution is desired.

Several problems in flow and contaminant subsurface hydrology, such as the scale dependency of the dispersion parameters, remain to be observed in the light of a systematic theory which includes the possibility of using normal, and sometimes large, variances in the random parameters, or at least with a rigorous mathematical framework that allows the construction of convergence theorems objectively restricting the sizes of the variances in the uncertain parameters.

In the present article I attempt to re-formulate the problem of dispersion in heterogeneous aquifers without the assumptions of small perturbation, logarithmic transformations, or specific probability laws in the random quantities. The fundamental solution and non-point source solution are derived. In the second section statistical measures of the pore velocity are derived in terms of the corresponding statistical measures of the transmissivity and determinant field measurable bulk hydrogeologic properties. Subsequently, in the third section, a large scale dispersion equation is derived based on the solute mass conservation and the random nature of the pore velocity. The Fickian approximation is avoided except as an initial term for the small scale problem, an assumption generally accepted. A solution of the dispersion equation in terms of the mean concentration distribution and expressions for the equivalent time-dependent dispersion parameters are given. In the fourth section we extend the scale-dependent fundamental solution of a point source problem in a saturated media to the practical case of a distributed source coming from the unsaturated zone. Finally, in the fifth section a comparison with the classical theory, the Dagan's model and field tracer tests in the Borden aquifer are described.

In order to observe the natural large variability effect of the transmissivity, the 'raw' transmissivity, rather than its logarithm, is considered in the flow equation. For the same reasons, The Neumann expansion method (Serrano, 1988a,b), rather than a small perturbation scheme, is used for the solutions of the flow and the dispersion equation. A specific measure to assure convergence of the series solution is given. This measure is based on a theorem with proof (Serrano, 1992a). Assumptions on the underlying probability distribution of the transmissivity have been avoided and instead information on the mean and spatial correlation structure is used (stationarity assumed out of necessity). From the applied point of view, this is the only reasonable information obtained from field data banks. In this study, only two scales of dispersion are adopted: A small scale of the order of less than ten meters,

where the classical convection dispersion equation and the Fickian approximation are assumed valid, and a large scale of the order of tens of meters, where the dispersion mechanism is controlled by the aquifer heterogeneity.

2. The velocity field in a heterogeneous aquifer

In this section we investigate the form of the groundwater velocity in a heterogeneous, long as compared with its thickness, hypothetical unconfined aquifer exhibiting mild slopes and with the usual assumptions of planar dimensions much larger than its thickness, formation properties of interest averaged over the depth and regarded as functions of the horizontal dimensions only, and Dupuit assumptions of shallow flow (Dagan, 1986). The governing flow equation is (Bear, 1979)

$$\frac{\partial}{\partial x}\left[T(x,\ y)\frac{\partial h}{\partial x}\right] + \frac{\partial}{\partial y}\left[T(x,\ y)\frac{\partial h}{\partial y}\right] = 0, \ \ 0 < x < \infty, \ \ -\infty < y < \infty \quad (1)$$

where $h(x,\ y)$ is the hydraulic head (m) above a specified datum; $T(x,\ y)$ is the aquifer transmissivity (m^2 month^{-1}); and $x,\ y$ are the spatial cartesian coordinates (m).

Consider an aquifer with a regional hydraulic gradient along x and negligible along y. This condition generates a mean groundwater velocity along x and negligible mean velocity along y. Since only random, zero mean, velocity fluctuations exist along y, a significantly greater variability in the longitudinal pore velocity than in the transverse pore velocity is expected. As a result the field-scale longitudinal dispersion coefficients will be greater than those in the transverse direction. This is the reason why some field studies report a strong scale dependency in the longitudinal dispersion coefficient, while a relatively small increase in the transverse one. In this study, we will assume that the effect of the random variability in the transverse pore velocity on the random variability of the longitudinal pore velocity is negligible. Under preparation is an analysis of the full three-dimensional random velocity field.

We further represent the transmissivity as $T = \bar{T} + T'$, where $\bar{T} = E\{T\}$, $E\{\ \}$ is the expectation operator, the random field T' has the properties $E\{T'\} = 0$, $E\{T'(x_1,\ y_1)T'(x_2,\ y_2)\} = \sigma_T^2 \exp(-\rho|x_1 - x_2|) \exp(-\rho|y_1 - y_2|)$, σ_T^2 is the transmissivity variance parameter ((m^2 month)^2), and ρ is a correlation decay parameter (m^{-1}). The above simplified representation of aquifer heterogeneity in the transmissivity attempts to be in line with current research in the stochastic analysis of groundwater flow and contaminant transport, while reducing the mathematical complexity.

Without loss of generality we assume knowledge of the boundary conditions at a point in the aquifer, $h(0,\ 0) = h_0$,

$$\frac{\partial h}{\partial x}(0,\ 0) = h_0'$$

and

$$\frac{\partial h}{\partial y}(0, \ 0) = 0$$

The flow equation becomes

$$\frac{\partial^2 h}{\partial x^2} = -\frac{1}{\bar{T}}\frac{\partial T'}{\partial x}\frac{\partial h}{\partial x}, \quad 0 \leqslant x < \infty, \quad h(0) = h_0, \quad \frac{\partial h}{\partial x}(0) = h_0' \tag{2}$$

In deriving Eq. (2), the term

$$T'\frac{\partial^2 h}{\partial x^2}$$

has been neglected, since numerical calculations indicate it is very small compared with others in the equation. The solution to Eq. (2) is

$$h(x) = h_0 + h_0'x - \frac{1}{\bar{T}}\int\limits_0^{\infty} G(x; \ \xi)\frac{\partial T'(\xi)}{\partial \xi}\frac{\partial h}{\partial \xi}\,\mathrm{d}\xi \tag{3}$$

where $G(x; \ \xi)$ is the Green's function associated with Eq. (2). It is given by (Serrano, 1992b)

$$G(x, \ \xi) = U(x, \ \xi)(x - \xi) \tag{4}$$

where U is the unit step function. Substituting Eq. (4) into Eq. (3)

$$h(x) = h_0 + h_0'x - \frac{1}{\bar{T}}\int\limits_0^{x}(x - \xi)\frac{\partial T'(\xi)}{\partial \xi}\frac{\partial h}{\partial \xi}\,\mathrm{d}\xi \tag{5}$$

A Neumann expansion of Eq. (5) could be built as (Serrano, 1992a) $h(x) = h_0 + h_1 + h_2 + \ldots$, where h_0 is again the head with respect to the bottom of the aquifer at the origin

$$h_1(x) = h_0'x \tag{6}$$

$$h_2(x) = -\frac{1}{\bar{T}}\int\limits_0^{x}(x - \xi)\frac{\partial T'(\xi)}{\partial \xi}\frac{\partial h_1(\xi)}{\partial \xi}\,\mathrm{d}\xi \tag{7}$$

and in general

$$h_i(x) = -\frac{1}{\bar{T}}\int\limits_0^{x}(x - \xi)\frac{\partial T'(\xi)}{\partial \xi}\frac{\partial h_{i-1}(\xi)}{\partial \xi}\,\mathrm{d}\xi \tag{8}$$

The convergence of the Neumann expansion of Eq. (5) requires that $\max[T'(x)] < 1$ for the sample functions, where max( ) is the maximum operator, and that

$$C_v = \frac{\sigma_T}{\bar{T}} < 1$$

for the expected heads, where C_v is the coefficient of variability of the transmissivity (Serrano, 1992a). Unless the transmissivity is assumed to follow a Gaussian random field, its third moment is usually unknown. Usually, however, only the first two moments are available from field measurements conducted with reasonable detail, and therefore it is only possible to calculate the first three terms in the Neumann expansion. It is known that this represents an accurate scheme for most practical applications (Serrano and Unny, 1987).

Substituting Eqs. (6) and (7) into Eq. (5) and differentiating with respect to x one obtains the hydraulic gradient in the direction of the regional groundwater flow

$$\frac{\partial h}{\partial x} \simeq \frac{\partial}{\partial x}(h_0 + h_1 + h_2) = h_0' - \frac{h_0'}{\bar{T}}\frac{\partial}{\partial x}\left[x\int_0^x \frac{\partial T'(\xi)}{\partial \xi}\,\mathrm{d}\xi\right] + \frac{h_0'}{\bar{T}}\frac{\partial}{\partial x}\left[\int_0^x \xi\frac{\partial T'(\xi)}{\partial \xi}\,\mathrm{d}\xi\right]$$

(9)

Applying Leibnitz rule for differentiation under integrals and solving

$$\frac{\partial h}{\partial x} = h_0' - \frac{h_0'}{\bar{T}}\int_0^x \frac{\partial T'(\xi)}{\partial \xi}\,\mathrm{d}\xi$$

(10)

The large-scale component of the pore velocity, u_x, averaged over the vertical, may be estimated as

$$u_x(x) = -\frac{T}{nh_0}\frac{\partial h}{\partial x}$$

On using Eq. (10)

$$u_x(x) = -\frac{h_0'}{nh_0}\left[\bar{T} + T' - \int_0^x \frac{\partial T'(\xi)}{\partial \xi}\,\mathrm{d}\xi - \frac{1}{\bar{T}}\int_0^x T'(x)\frac{\partial T'(\xi)}{\partial \xi}\,\mathrm{d}\xi\right]$$

(11)

We remark that this is the large-scale component of the pore velocity, that is the one controlled by the random variability in the transmissivity at the large scale. Taking expectations on both sides of Eq. (11) we obtain the mean pore velocity, $\bar{u}_x$

$$\bar{u}_x = E[u_x(x)] = -\frac{h_0'}{nh_0}\left\{\bar{T} - \frac{\sigma_T^2}{\bar{T}}[1 - \exp(-\rho x)]\right\}$$

(12)

This is the same expression obtained by Serrano (1993) when the recharge rate is set to zero. It was noted there that the relative magnitude of the second term in the right-hand side of Eq. (12) is small compared with that of the first. In other words the effect of the correlation decay parameter of the transmissivity on the average pore velocity is small compared with that of the aquifer regional hydraulic gradient in the absence of recharge. With this approximation

$$\bar{u}_x \simeq -\frac{h_0'\bar{T}}{nh_0}$$

(13)

Similarly, from Eq. (11) the random component of the pore velocity is

$$u_x'(x) = u_x - \bar{u}_x = -\frac{h_0'}{nh_0} \left[T' - \int_0^x \frac{\partial T'(\xi)}{\partial \xi} \, \mathrm{d}\xi \right] \tag{14}$$

The right-hand side of this equation illustrates the concept of two scales of motion: one small scale operating at short distances, and one of increasing importance as the distance from the source increases (the integral term). From Eq. (14) the two point correlation function of the pore velocity, R_{uu}, at locations x_1 and x_2 may be derived. Substituting for the assumed exponentially decaying form of the transmissivity correlation function, differentiating under the integrals, calculating the correlation of the derivatives and solving, one obtains

$$E[u_x'(x_1)u_x'(x_2)] = R_{uu}$$

$$= \left(\frac{h_0'\sigma_T}{nh_0}\right)^2 \{\exp(-\rho x_2) + 2\rho x_1 - 2\exp[-\rho(x_2 - x_1)] + 2\},$$

$$\times \; x_1 \leqslant x_2 \tag{15}$$

Finally, set $x_1 = x_2 = x$ to obtain the variance of the pore velocity, σ_u^2, as

$$\sigma_u^2 = r[2\rho x + \exp(-\rho x)], \quad r = \left(\frac{h_0'\sigma_T}{nh_0}\right)^2 \tag{16}$$

This equation indicates that the variance of the pore velocity increases with distance. For large values of ρ the increase is linear with distance, whereas for small values of ρ the increase is non-linear with distance. Eq. (16) further illustrates the concept of two scales of motion: a small scale controlled by the exponential term, and a large scale which grows with distance.

3. Solute dispersion in a heterogeneous aquifer

In this section we study the form of the dispersion equation in a two-dimensional unconfined aquifer with Dupuit assumptions subject to a random transmissivity. In the previous section we investigated the statistical properties of the pore velocity in such an aquifer and now the parameters of the dispersion equation are derived in terms of those properties. The solute mass continuity equation is (Bear, 1979)

$$\frac{\partial C}{\partial t} + \frac{\partial(u_x C)}{\partial x} + \frac{\partial(u_y C)}{\partial y} = 0 \tag{17}$$

where C represents solute concentration (mg l^{-1}); t is the time coordinate (months); u_x, u_y are the x, y components of the pore velocity vector, respectively; and the rest of the terms are as before.

From the observation that the dispersion parameters are functions of distance, and after the results in Section 2, particularly Eqs. (11), (12) and (14), it is assumed in the present work that two mechanisms of dispersion are present: one primarily operating

at the small scale where the dispersion is controlled by the variability in the pore size and the pore velocity at this scale; and one operating at large scale where the dispersion in controlled by the aquifer heterogeneity in the transmissivity at this scale. At the small-scale level the effect of the second mechanism would be negligible, because of the small distances involved, while at the large-scale level both mechanisms are present but the second is the dominant one, because of the large distances involved. Thus we define the large-scale pore velocity in the x direction as $u_x(x) = \bar{u}_x + u'_{px} + u'_x$, where u'_{px} represents the random component of the small-scale pore velocity, and u'_x represents the random component of the large-scale pore velocity as before.

With the x coordinate coinciding with the (mean) regional groundwater pore velocity, the mean y component, $\bar{u}_y$, of the pore velocity is zero. Thus the y (transverse) component of the pore velocity is defined as $u_y = u'_{py} + u'_y$, where u'_{py} represents the random component in the y direction of the pore scale velocity, and u'_y represents the random component of the large-scale pore velocity in the y direction. For an infinite aquifer and an instantaneous point source (a spill) at the origin, Eq. (17) becomes

$$\frac{\partial C}{\partial t} + \frac{\partial(\bar{u}_x C)}{\partial x} + \frac{\partial(u'_{px} C)}{\partial x} + \frac{\partial(u'_x C)}{\partial x} + \frac{\partial(u'_{py} C)}{\partial y} + \frac{\partial(u'_{py} C)}{\partial y} = 0 \tag{18}$$

subject to

$$-\infty < x < \infty, \quad -\infty < y < \infty, \quad 0 < t,$$

$$C(\pm\infty, \ y, \ t) = C(x, \pm\infty, \ t) = 0, \quad C(x, \ y, \ 0) = C_i \delta(x)\delta(y) \tag{19}$$

where C_i is the magnitude of the initial concentration; and $\delta(\ )$ is Dirac's delta function.

Adopting the Fickian approximation at the small scale

$$u'_{px} C \simeq -D_x \frac{\partial C}{\partial x}$$

and

$$u'_{py} C \simeq -D_y \frac{\partial C}{\partial y}$$

where D_x and D_y are the small-scale dispersion coefficients in x and y, respectively, defined as the product of a small (laboratory) scale dispersivity times the mean longitudinal pore velocity. The large-scale concentration may be written as

$$C(x, \ y, \ t) = C_i X(x, \ t) \ Y(y, \ t) \tag{20}$$

where $X(x, \ t)$ satisfies

$$\frac{\partial X}{\partial t} + \bar{u}_x \frac{\partial X}{\partial x} = D_x \frac{\partial^2 X}{\partial x^2} - \frac{\partial(u'_x X)}{\partial x}, \quad X(\pm\infty, \ t) = 0, \quad X(x, \ 0) = \delta(x),$$

$$-\infty < x < \infty, \quad 0 < t \tag{21}$$

and satisfies

$$\frac{\partial Y}{\partial t} = D_y \frac{\partial^2 Y}{\partial y^2} - \frac{\partial(u_y' Y)}{\partial y}, \quad Y(\pm\infty, \ t) = 0, \quad Y(y, \ 0) = \delta(y),$$

$$-\infty < y < \infty, \quad 0 < t \tag{22}$$

The solution to Eq. (21) may be expressed as the Neumann series (Serrano, 1992a) $X = X_0 + X_1 + X_2 + \ldots$, where the first term, X_0, satisfies

$$\frac{\partial X_0}{\partial t} + \frac{\partial(\bar{u}_x X_0)}{\partial x} = D_x \frac{\partial^2 X_0}{\partial x^2}, \quad X_0(\pm\infty, \ t) = 0, \quad X_0(x, \ 0) = \delta(x),$$

$$-\infty < x < \infty, \quad 0 < t \tag{23}$$

which indicates that the first approximation to a scale-dependent solute dispersion is a convection dispersion equation with a constant small-scale dispersion coefficient. Its solution is (Serrano, 1992a)

$$X_0(x, \ t) = \frac{\exp\left[-\dfrac{(x - \bar{u}_x t)^2}{4D_x t}\right]}{\sqrt[2]{4\pi D_x t}} \tag{24}$$

Any subsequent term, X_i, in the Neumann expansion of Eq. (21) satisfies

$$\frac{\partial X_i}{\partial t} + \bar{u}_x \frac{\partial X_i}{\partial x} = -\frac{\partial(u_x' X_{i-1})}{\partial x}, \quad X_i(\pm\infty, \ t) = 0, \quad X_i(x, \ 0) = 0,$$

$$-\infty < x < \infty, \quad 0 < t, \quad i \geqslant 1 \tag{25}$$

In view of Eqs. (23) and (25), Eq. (21) for the first two terms in the series could be written as

$$\frac{\partial X}{\partial t} + \bar{u}_x \frac{\partial X}{\partial x} = D_x \frac{\partial^2 X}{\partial x^2} - \frac{\partial(u_x' X_0)}{\partial x} + \frac{\partial}{\partial x}\left[u_x' \frac{\partial}{\partial x}(u_x' X_0)\right] \tag{26}$$

More terms in the series solution could be included. However the expectation of such terms would require information on the moments of order greater than two and, as stated before, this information is not usually available in most applications. Taking expectations on Eq. (26), using Eq. (16), and approximating

$$\frac{\partial \bar{X}}{\partial t} + \bar{u}_x \frac{\partial \bar{X}}{\partial x} - D_x \frac{\partial^2 \bar{X}}{\partial x^2} = 2r\rho x \frac{\partial^2 X_0}{\partial x^2}, \quad \bar{X}(x, \ 0) = \delta(x) \tag{27}$$

where $\bar{X} = E\{X\}$. The solution to this equation has the shape of a Gaussian distribution with a time-dependent plume variance. The plume variance may be obtained easily after multiplying Eq. (27) by $(x - \bar{u}_x t)$ and integrating with respect to x. Thus the longitudinal component of the mean concentration variance is $\phi_x = 2D_x t + 2r\rho\bar{u}_x t^2$, which would produce a time-dependent dispersion coefficient, $\bar{D}_x$, given by

$$\bar{D}_x(t) = D_x + 2r\rho\bar{u}_x t \tag{28}$$

A similar analysis may be performed on Eq. (22) to obtain an expression for the time-dependent dispersion coefficient in the y direction

$$\bar{D}_y = D_y + \frac{r}{2}\rho^2 D_y t \tag{29}$$

An analysis of convergence on the above Neumann series solution to Eq. (21) indicates that solution is strictly valid for $t < t_m$ (Serrano, 1992a), where t_m is the maximum simulation time given by

$$t_m = \frac{1}{\rho x_m r}$$

where x_m is the maximum longitudinal scale in the simulations. Using the shifting properties of Gaussian curves, the longitudinal plume variance is calculated as

$$k\phi_x(t_m), \quad k = \frac{t}{t_m}$$

This restriction does not affect the transverse component.

In summary, the mean concentration distribution for a point source initial condition is given by

$$\bar{C}(x, \ y, \ t) = C_i \bar{X}(x, \ t)\bar{Y}(y, \ t), \quad \bar{X}(x, \ t) = \frac{\exp\left[-\dfrac{(x - \bar{u}_x t)^2}{4k\bar{D}_x(t_m)t_m}\right]}{\sqrt[2]{4\pi k \bar{D}_x(t_m)t_m}},$$

$$\bar{Y}(y, \ t) = \frac{\exp\left[-\dfrac{y^2}{4k\bar{D}_y(t_m)t_m}\right]}{\sqrt[2]{4\pi k \bar{D}_y(t_m)t_m}} \tag{30}$$

$$k = \frac{t}{t_m}, \quad t_m = \frac{1}{\rho x_m r} \tag{31}$$

and $\bar{D}_x(t_m)$, $\bar{D}_y(t_m)$ are the dispersion coefficients evaluated at t_m from Eqs. (28) and (29), respectively. The form of Eq. (30) suggests that the scale-dependent mean concentration, $\bar{C}$, owing to a point source in an aquifer satisfies an equation of the form of (37) when the forcing function is zero. Thus Eq. (30) is actually the (approximate) Green's function, of Eq. (37). Knowledge of the form of the Green's function is essential for more complex applications such as groundwater pollution forecasting owing to non-point sources.

4. Applications to spills originated in the unsaturated zone

Most simulation models of groundwater pollution limit their attention to the solution of contaminant transport problems at either the unsaturated zone or the saturated zone. This is due in part to the conceptual difficulties in representing mass

transfer at the interface between the saturated zone and the saturated zone, and the mathematics of subsequent propagation in the saturated zone subject to a non-point source at the interface. Yet an accidental chemical spill at the ground surface, which becomes a point source of contaminants in the unsaturated zone which eventually penetrate and propagate within the saturated zone, constitutes a frequent problem of practical importance.

In this section we attempt to extend the scale-dependent fundamental solution of a point source problem in saturated media to the case of a distributed source coming from the unsaturated zone. First, a description of contaminant propagation in the unsaturated zone is needed in order to define the functional variability of the source concentration at the interface. For that purpose we focus our attention on the case of a shallow aquifer, that is one whose unsaturated zone depth is small compared with the horizontal dimensions of the aquifer. In such a case the large scale dependency of the dispersion parameters is controlled by the aquifer dimensions, rather than the unsaturated zone dimensions.

We assume that the source at the ground surface is instantaneous and punctual; the unsaturated soil is homogeneous and anisotropic in the dispersion coefficient; the contaminant loss through evapotranspiration is negligible; the concentration at the water table does not affect that of the unsaturated zone; the center of mass of contaminant plume moves as a result of mean percolation (recharge) rate from rainfall; and the dispersion in the horizontal direction is greater than that in the vertical direction.

The governing differential equation is (Serrano, 1992c)

$$\frac{\partial C'}{\partial t} - D'_x \frac{\partial^2 C'}{\partial x^2} - D'_x \frac{\partial^2 C'}{\partial y^2} - D'_z \frac{\partial^2 C'}{\partial z^2} + \bar{u}_z \frac{\partial C'}{\partial z} = 0 \tag{32}$$

$$-\infty < x < \infty; \quad -\infty < y < \infty; \quad -\infty < z < \infty; \quad 0 < t \tag{33}$$

subject to

$$C'(\pm\infty, \ \pm\infty, \ \pm\infty, \ t) = 0; \quad C'(x, \ y, \ z, \ 0) = C_i\delta(x)\delta(y)\delta(z) \tag{34}$$

where C' is the solute concentration (mg kg^{-1}); x, y are the spatial horizontal coordinate axis (m), with x parallel to the regional saturated groundwater flow direction; z is the vertical spatial coordinate (m), positive downwards; t is the temporal coordinate (months); D'_x is the horizontal dispersion coefficient (m^2 month^{-1}); D'_z is the vertical dispersion coefficient (m^2 month^{-1})

$$\bar{u}_z = \frac{I}{n}$$

is the mean seepage velocity (m month^{-1}), where I is the mean monthly recharge rate from rainfall (m month^{-1}), and n is the soil porosity; and C_i is the initial solute concentration at the time of the spill (mg kg^{-1}).

It is easy to show the solution to Eq. (32) (Serrano, 1988a)

$$C'(x, \ y, \ z, \ t) = C_i X'(x, \ t) Y'(y, \ t) Z'(z, \ t) \tag{35}$$

where

$$X'(x, t) = \frac{\exp\left[-\dfrac{x^2}{4D_x't}\right]}{\sqrt[2]{4\pi D_x't}}, \quad Y'(y, t) = \frac{\exp\left[-\dfrac{y^2}{4D_x't}\right]}{\sqrt[2]{4\pi D_x't}},$$

$$Z'(z, t) = \frac{\exp\left[-\dfrac{(z - \bar{u}_z t)^2}{4D_z't}\right]}{\sqrt[2]{4\pi D_z't}} \tag{36}$$

Eq. (35), with the appropriate change in units and with $z = w$, where w is the water table depth from the ground surface (m), represents the space–time evolution of the contaminant concentration at the interface between the unsaturated and the saturated zone. If we interpret the transport problem of the saturated zone as one of a contaminant evolution owing to a non-point source entering the water table, and using the results of the previous section, then the scale-dependent differential equation governing solute dispersion in the saturated zone could be written as (Serrano, 1988a)

$$\frac{\partial \bar{C}}{\partial t} - \bar{D}_x \frac{\partial^2 \bar{C}}{\partial x^2} + \bar{u}_x \frac{\partial \bar{C}}{\partial x} - \bar{D}_y \frac{\partial^2 \bar{C}}{\partial y^2} = g(x, y, t) \tag{37}$$

$$-\infty < x < \infty, \quad -\infty < y < \infty, \quad 0 < t,$$
$$\bar{C}(\pm\infty, \pm\infty, t) = 0 = \bar{C}(x, y, 0) \tag{38}$$

where $g(x, y, t)$ is the distributed source at the interface given by Eq. (36) as

$$g(x, y, t) = f \; X'(x, t)Y'(y, t)Z'(w, t) \tag{39}$$

and f is a units conversion factor accounting for the change in concentration units (from mg kg^{-1} in the unsaturated zone to mg l^{-1} in the saturated zone)

$$f = \frac{\gamma_s}{1000n} \tag{40}$$

where γ_s is the soil dry bulk density.

The solution to Eq. (37) may be written as (Serrano, 1988a)

$$\bar{C}(x, y, t) = \int_0^t \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} G(x - x', y - y', t - t')g(x', y', t')\mathrm{d}x'\mathrm{d}y'\mathrm{d}t' \tag{41}$$

Interpreting the Green's function, G, as given by Eq. (30), using Eq. (39), and applying the shifting properties of integrals of Gaussian curves, one may eliminate

the spatial integrals

$$
\bar{C}(x,\ y,\ t) = C_i f \int_0^t \frac{\exp\left\{ -\dfrac{[x - \bar{u}_x(t - t')]^2}{4[\bar{D}_x(t - t')(t - t') + D_x' t']} \right\}}{\sqrt[2]{4\pi[\bar{D}_x(t - t')(t - t') + D_x' t']}}
$$

$$
\times \frac{\exp\left\{ -\dfrac{y^2}{4[\bar{D}_y(t - t')(t - t') + D_y' t']} \right\}}{\sqrt[2]{4\pi[\bar{D}_y(t - t')(t - t') + D_y' t']}} \frac{\exp\left[-\dfrac{(w - \bar{u}_z t')^2}{4D_z' t'} \right]}{\sqrt[2]{4\pi D_z' t'}} \, dt'
$$

(42)

An algorithm for a Gaussian quadrature may be easily constructed for the approximation of Eq. (42).

As an illustration, let us imagine that a small spill of a certain contaminant accidentally occurred at the ground surface and that we wish to forecast the contaminant concentration in the unsaturated zone and the saturated zone. The following parameters were measured: $C_i = 70$ mg kg^{-1}; $D_x' = 0.03$ m^2 month^{-1}; $D_z' = 0.009$ m^2 month^{-1}; $n = 0.33$; $I = 0.01$ m month^{-1}; $w = 1.0$ m; $\gamma_s = 1600.0$ kg m^{-3}; $h_0' = -0.0056$ m m^{-1}; $\bar{K} = 185.4$ m month^{-1}; $D_x = 0.03$ m^2 month^{-1}; $D_y = 0.009$ m^2 month^{-1}; $\sigma_k = 96.6$ m month^{-1} and $\rho = 0.36$. From Eq. (35) we predict the space–time evolution of the contaminant in the unsaturated zone.
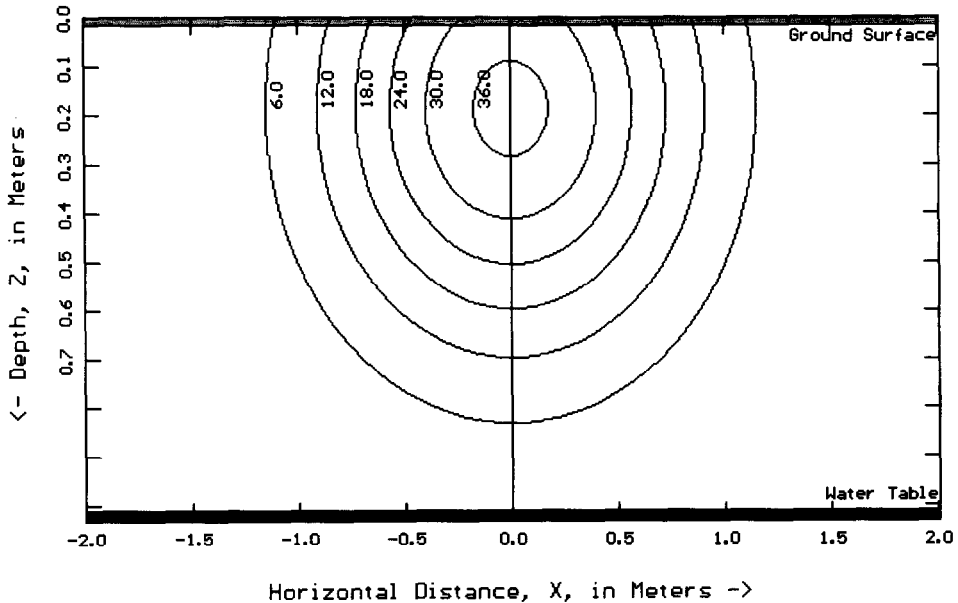

Fig. 1. Unsaturated zone profile concentration contours for the case of a soil spill. Contours in milligrams per kilogram; time, 6 months; plume center, $Z = 0.2$ m.
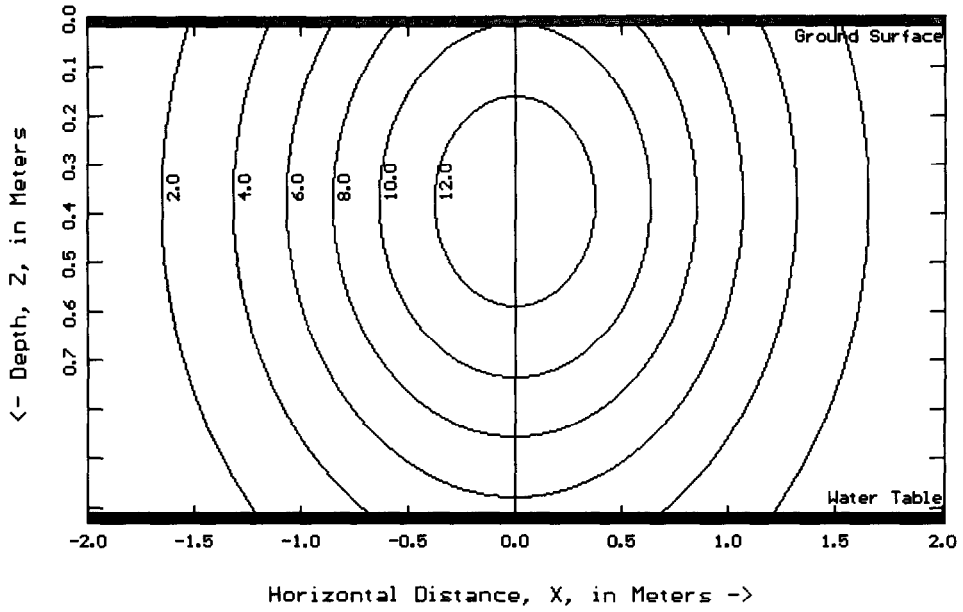
Fig. 2. Unsaturated zone profile concentration contours for the case of a soil spill. Contours in milligrams per kilogram; time, 12 months; plume center, $Z = 0.4$ m.
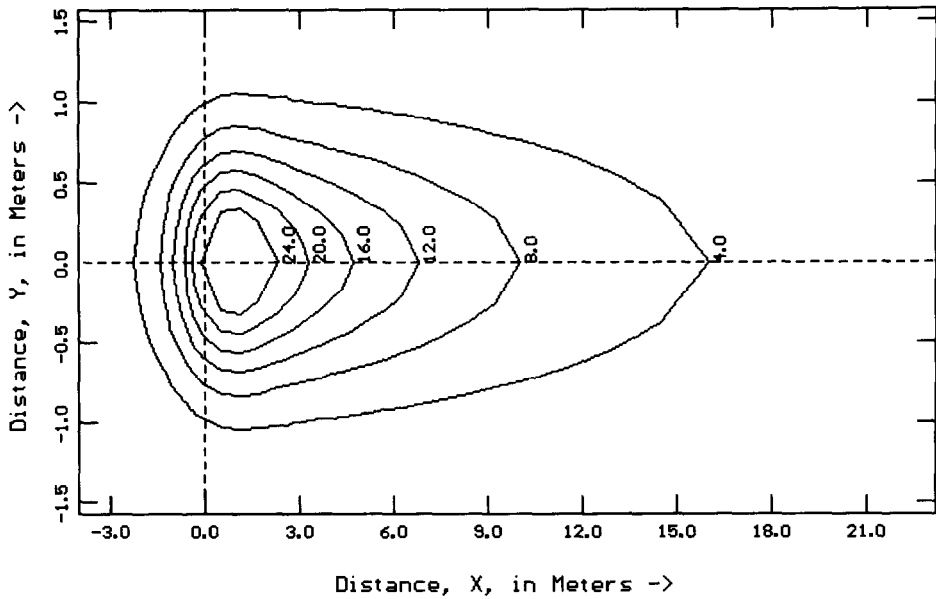

Fig. 3. Saturated zone plan concentration contours for the case of a soil spill. Contours in milligrams per liter; time, 12 months; maximum $C = 29.6$ mg l^{-1} at $X = 0.9$ m.

Figs. 1 and 2 show the unsaturated zone concentration contours 6 and 12 months after the spill, respectively. Using Eq. (42) we predict the saturated zone concentration distribution. Figs. 3 and 4 show the saturated zone concentration contours 12 and 36 months after the spill, respectively. Note that owing to the slow penetration of the source from the unsaturated zone, the saturated zone plume is not symmetrical with respect to the peak in the longitudinal direction. It is also interesting to observe that the maximum concentration remains somewhat close to origin, and that only after prolonged time, when most of the contaminant from the unsaturated zone has entered the saturated zone, the plume will tend to become symmetric. Finally, if one attempts to model this problem with constant, rather than scale-dependent, dispersion parameters, the calculated concentration values become unrealistic.

5. Field verification

Verification between the scale-dependent dispersion equations described in the above sections and existing dispersion models reveals the obvious features of the present theory. A comparison between the classical convection dispersion equation and the variable dispersion equation (VDE) for the case of an instantaneous spill, Eq. (31), indicates that the CDE overestimates the maximum concentration, the peak of the plume, and underestimates the spread of the contaminant, that is the plume variance. Now the main difference between the existing scale-dependent models, such as the widely used Dagan (1984, 1986) model, and the present theory lies in
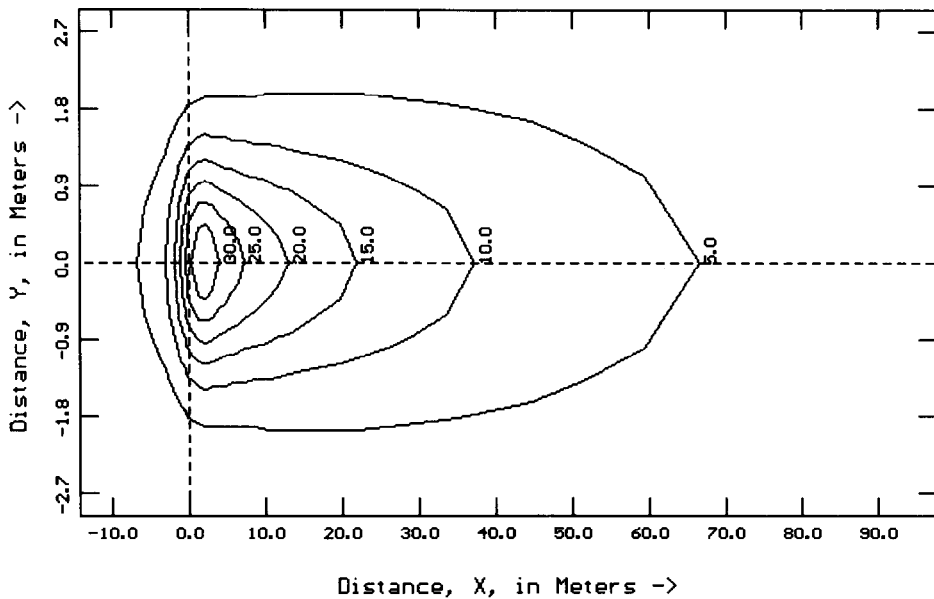

Fig. 4. Saturated zone plan concentration contours for the case of a soil spill. Contours in milligrams per liter; time, 36 months; maximum $C = 33.6$ mg l^{-1} at $X = 1.7$ m.

the functional definition of the time-dependent dispersion coefficient. A comparison between Eqs. (28) and (29) and the corresponding longitudinal and transverse dispersion coefficient equations in the Dagan model shows that the VDE generates a continuously increasing with time dispersion coefficient, in contrast to the Dagan model in which the dispersion coefficient exhibits an asymptotic value. The contrast between the two theories may lie in the different assumptions adopted in each one. The absence of an asymptotic value in the dispersion coefficient may be reinforced physically by recent studies that emphasize the partial effect of recharge on the dispersion parameters. Serrano (1992b, 1993) concluded that, in the presence of recharge, the dispersion coefficient does not appear to have an asymptotic value either, and its value would only be limited by the end of the recharge zone or the presence of a physical aquifer boundary. An independent confirmation of the non-existence of an asymptotic value of the dispersion coefficient was given by Paredes and Elorza (1992). They developed a dispersion model determined by non-stationary random walk techniques, and the concept of Fractal Geometry.

Field verification of groundwater pollution models of chemical spills is a more difficult problem owing to the relative lack of reliable field data bases documenting environmental accidents, the subjective account of certain parameters, particularly the initial concentration and mass, and the inherent inaccuracies of certain measurement strategies. Most field data banks possess a degree of uncertainty comparable with that of the mathematical model after the adoption of many assumptions and approximations. Another problem relates to the verification of the moments of a stochastic model (i.e. the mean concentration, $\bar{C}$) with what appears to be a single realization (a sample function) of the concentration, C, taken in the field. Aware of these obstacles, an attempt at verification may be approached by comparing the simulation results with a controlled tracer experiment. Our objective would then be to observe if the mathematical model reproduces the enhanced dispersion observed in the field, and the general characteristics of the plume.

One of the most widely available tracer experiments is the one performed at the Borden site, Ontario, Canada. The results of the Borden site experiment have been extensively documented in the literature (Mackay et al., 1986). We focus our attention on the implementation of the two-dimensional Dagan's model to vertically averaged bromide and chloride concentrations at the Borden site reported by Barry et al. (1988). The parameter values for the aquifer are the same we adopted for the saturated zone in the examples of the previous section, except that the initial bromide concentration $C_i = 324$ mg l^{-1}. The initial mass amount and the way in which the tracers were initially injected (via a collection of wells) may not resemble a point source, and therefore the following comparison is only approximate.

Figs. 5 and 6 illustrate the saturated zone surface contours of mean bromide concentration at the Borden aquifer, as simulated by Eq. (30), 9 and 15 months after injection, respectively. A comparison with the field analyses on the Borden aquifer reported by Barry et al. (1988) suggests that the VDE reproduce the main features of the measured plume: peak concentration magnitude, peak location and continuously increasing dispersion coefficients. The longitudinal contaminant spread
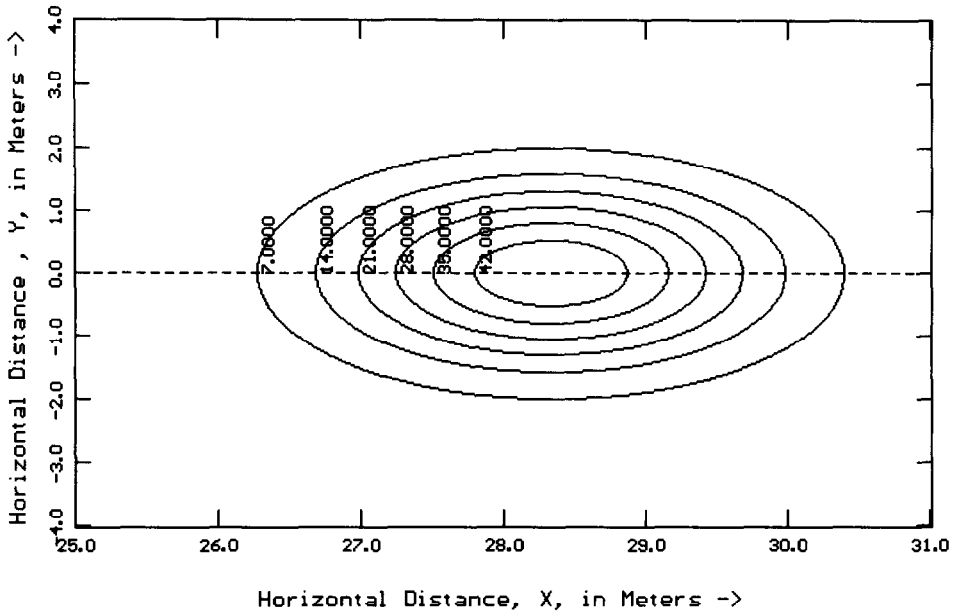
Fig. 5. Simulated saturated zone plan bromide concentration at the Borden aquifer. Contours in milligrams per liter; time, 9 months; maximum $C = 47.986445$ at $X = 28.3$ m.
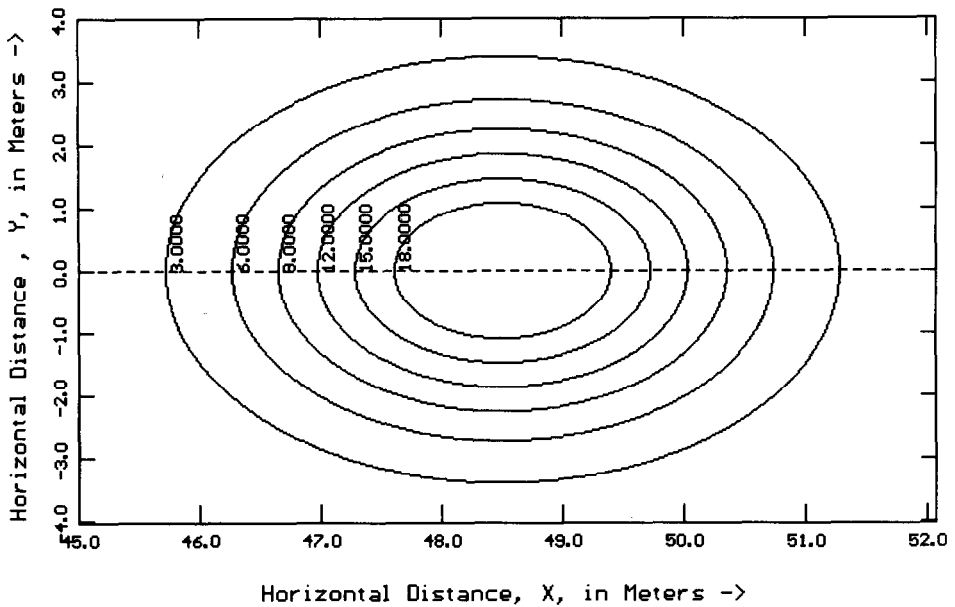

Fig. 6. Simulated saturated zone plan bromide concentration at the Borden aquifer. Contours in milligrams per liter; time, 15 months; maximum $C = 22.165803$ at $X = 48.5$ m.

is somewhat underestimated by the VDE, most probably because the VDE has less mass at the initial injection (instantaneous injection) than that reported in the field test. A simulation with a more realistic step function as initial condition to the VDE was not attempted at this time.

6. Summary and conclusions

Mathematical models designed to predict scale-dependent solute concentration after accidental spills in heterogeneous aquifers were developed and tested. The methodology used does not require the usual restrictive assumptions of small perturbations, logarithmic transformations, specific probability laws in the random quantities, or a disregard for the aquifer hydrology. Two main applications were considered: (1) the case of a well injection directly in the saturated zone; (2) the case of a spill at the ground surface, which considers the contaminant dispersion in the unsaturated zone, and its subsequent dispersion in the saturated zone. The latter involved the solution of a scale-dependent dispersion equation in the saturated zone subject to a non-point source from the unsaturated zone. Two scales of dispersion were assumed: a small scale of the order of less than 10 m, where the dispersion is controlled by the variability in the pore size and the pore velocity at this scale; and one large scale of the order of tens of meters, where the dispersion is controlled by the aquifer heterogeneity in the transmissivity. At the small-scale level the effect of the second mechanism is negligible, because of the small distances involved, while at the large-scale level both mechanisms are present but the second is the dominant one, because of the large distances involved.

Several new features are included in the models: the ability to consider normal, and sometimes large, variability in the aquifer parameters, particularly in the aquifer transmissivity; the inclusion of a specific measure to assure convergence of the series solution. The aquifer statistical parameters are given in linear dimensions rather than in the form of a logarithmic transformation. Assumptions on the underlying probability distribution of the transmissivity are not needed and only a knowledge of the mean and correlation structure is necessary (information more easily available in practical applications). The model's output is the expected concentration as a function of space and time. Aquifer parameters such as mean pore velocity are directly related to the underlying groundwater flow problem, and are expressed in terms of field measurable aquifer hydrogeologic properties such as mean transmissivity, mean hydraulic gradient, mean porosity and aquifer thickness.

Comparison with theoretical models, such as the Dagan's model and the classical convection dispersion equation, and field verification with the tests at the Borden aquifer indicated that the proposed model reproduced the enhanced longitudinal dispersion reported in the literature. The effective dispersion coefficient of the proposed model grows continuously with time and does not exhibit an asymptotic value. The absence of an asymptotic dispersion coefficient has been reported in cases where recharge to the aquifer from rainfall is present.

It is believed that the model could be easily implemented in practical applications of

groundwater pollution forecasting, since the required parameter information is directly related to standard hydrogeologic field measures, and its output is the mean concentration as a function of space and time.

Acknowledgments

References

Barry, D.A. and Sposito, G., 1989. Analytical solution of a convection dispersion model with time dependent transport coefficients. Water Resour. Res., 25(12): 2407–2416.

Barry, D.A., Coves, J. and Sposito, G., 1988. On the Dagan model of solute transport in groundwater: application to the Borden site. Water Resour. Res., 24(10): 1805–1817.

Bear, J., 1979. Hydraulics of Groundwater. McGraw-Hill, New York.

Dagan, G., 1984. Solute transport in heterogeneous porous formations. J. Fluid Mech., 145: 151–177.

Dagan, G., 1986. Statistical theory of groundwater flow and transport: pore to laboratory, laboratory to formation, and formation to regional scale. Water Resour. Res., 22(9): 120S–135S.

Cushman, J.H., 1987. Development of stochastic partial differential equations for subsurface hydrology. Stoch. Hydrol. Hydraul., 1(4): 241–262.

Fried, J.J., 1975. Developments in Water Science, Vol. 4, Groundwater Pollution. Elsevier, New York.

Gupta, V.K. and Bhatthacharya, R.N., 1986. Solute dispersion in multidimensional periodic saturated porous media. Water Resour. Res., 22(2): 156–164.

Mackay, D.M., Freyberg, D.L., Roberts, P.V. and Cherry, J.A., 1986. A natural gradient experiment on solute transport in a sand aquifer, 1, approach and overview of plume movement. Water Resour. Res., 22(13): 2017–2029.

Paredes, C.B. and Elorza, F.J., 1992. Transporte de solutos por aguas subterraneas en medios fractal-heterogeneos. In: Simposio Nacional de Hidrogeologia, Alicante, Spain.

Pickens, J.F. and Grisak, G.E., 1981. Modeling of scale dependent dispersion in hydrogeologic systems. Water Resour. Res., 17: 1701–1711.

Serrano, S.E., 1988a. General solution to random advective–dispersive equation in porous media. Part 1: Stochasticity in the sources and in the boundaries. Stoch. Hydrol. Hydraul., 2(2): 79–98.

Serrano, S.E., 1988b. General solution to random advective–dispersive equation in porous media. Part 2: Stochasticity in the parameters. Stoch. Hydrol. Hydraul., 2(2): 99–112.

Serrano, S.E., 1992a. Semianalytical methods in stochastic groundwater transport. Appl. Math. Model., 16: 181–191.

Serrano, S.E., 1992b. The form of the dispersion equation under recharge and variable velocity, and its analytical solution. Water Resour. Res., 28(7): 1801–1808.

Serrano, S.E., 1992c. Migration of chloroform in aquifers. ASCE J. Environ. Eng., 118(2): 167–182.

Serrano, S.E., 1993. Groundwater flow and contaminant transport in aquifers subject to large parameter uncertainty. In: A.H.-D. Cheng and C.Y. Yang (Editors), Computational Stochastic Mechanics. Elsevier, New York, pp. 475–491.

Serrano, S.E. and Unny, T.E., 1987. Semigroup solutions to stochastic unsteady groundwater flow subject to random parameters. Stoch. Hydrol. Hydraul., 1(4): 281–296.

Sposito, G. and Jury, W.A., 1986. Fundamental problems in the stochastic convection dispersion model of solute transport in aquifers and field soils. Water Resour. Res., 22: 77–78.

Yates, S.R., 1990. An analytical solution for one dimensional transport in heterogeneous porous media. Water Resour. Res., 26(10): 2331–2338.