Chloroform Contamination in the Louisville Aquifer: An Investigation of Its Occurrence and Propagation

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Sergio E. Serrano

University of Kentucky

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CHLOROFORM CONTAMINATION IN THE LOUISVILLE AQUIFER: AN INVESTIGATION OF ITS OCCURRENCE AND PROPAGATION

By

Sergio E. Serrano
Principle Investigator

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Water Resources Research Institute
University of Kentucky
Lexington, KY

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The contents of this report do not necessarily reflect the views and policies of the United States Department of the Interior, Washington, D.C., nor does mention of trade names or commercial products constitute their endorsement or recommendation for use by the U.S. Government.
This report presents the main results of an investigation on the nature and propagation of an accidental spill of chloroform in the Louisville aquifer, Kentucky. Much of the effort is concentrated on the development of mathematical models to either reconstruct the history of evolution of the plume, or forecast its propagation in the future. Chloroform is a dense halogenated solvent which exhibits a special migration pattern in porous media. Because of this and the relative absence of a conceptual theory on its hydrodynamics in porous media, meaningful predictive models will have to deal with many unresolved theoretical aspects of contaminant migration. Much of this report is devoted to the exploration of the theoretical aspects of migration of dense non-sorbing constituents in aquifers.

Chapter I formulates the fundamental models of propagation of chloroform in the Louisville aquifer. Two models that reconstruct the evolution of chloroform concentration in the unsaturated and the saturated zone are developed and verified with respect to the limited information provided by a field investigation performed by the U.S. Geological Survey. A measure of statistical uncertainty in the data and the models is also introduced as a tool useful for future forecasting problems. Chapter II analyses the effect of recharge from rainfall on the functional form of the dispersion coefficient and the groundwater velocity in mathematical models in an attempt to reduce the artificial estimation (guessing) of these parameters in propagation models of inert constituents. The problem of scale dependency of the parameters is studied in detail. Chapter III analyses the effect of aquifer heterogeneity on the functional form of propagation parameters and successfully derives practical expressions for their calculation as functions of the regional hydrology, aquifer hydrogeologic properties, and aquifer heterogeneity statistical properties.
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CHAPTER I

MIGRATION OF CHLOROFORM IN THE LOUISVILLE AQUIFER

1. Introduction

Chloroform (CHCl₃) is a chemical constituent which falls into the category of chlorinated hydrocarbons (CHCs), commonly known as dense chlorinated solvents. These compounds have a wide range of industrial and domestic applications and its enormous production in the United States has generated a large portion of the contemporary groundwater pollution problems. It has been known for sometime that CHCs are in general more dense and less viscous than water, not nearly as biodegradable as other organic compounds, quite soluble relative to the low levels which require regulatory action, largely nonsorbing and therefore quite mobile in groundwater systems, and rather volatile. CHCs have a distinct migratory pattern in porous media and until relatively recently they were not recognized to pose a serious threat to groundwater systems nor was there available experimental information which could help in the development of predictive field models (Schwille, 1988).

Since an understanding of the time and space evolution of chloroform in unsaturated and saturated porous media is a requisite for adequate forecasting and field remedial strategies, the present chapter attempts to contribute to the fluid dynamics knowledge on the migration of CHC's in groundwater systems and to complement the existing qualitative information with the analysis of two exploratory quantitative models for a case study. The author is inspired by the results of the extensive experimentation of Schwille (1988) on the behavior of CHCs in porous and fractured media. Many of the simplifying model assumptions adopted in this study are based on different experimental observations of the above study. Related studies of transport of other organic constituents in the unsaturated zone are Jury et al. (1983), Baehr (1987), Weeks et al. (1982), Metcalfe and Farquhar (1987), and Mendoza and Frind, (1990).

The selected case study was the chloroform contamination in the Louisville aquifer, Kentucky. On July 2, 1975, well 22 at the Louisville Works of E.I. DuPont de Nemours and Company began producing water
initially containing 25 mgr/l of chloroform from the sand and gravel alluvial aquifer in southwestern Louisville (Fig. 1). The well was pumping water for cooling at a rate of about 40 l/s. An accidental spill of about 20 m³ of chloroform in August, 1970, 37 m from the well, is probably the source of contamination (Fig. 2). In March, 1978, the U.S. Geological Survey began an investigation aimed at determining the source of contamination and the areal extent of groundwater contaminated by chloroform. Initial attempts at locating the contamination plume at the bottom of the saturated zone failed since no trace of chloroform was found in samples taken from the research wells (Davis and Matthews, 1983). An observation noting strong chloroform odors coming from the test wells prompted the U.S.G.S. team to concentrate the investigation to the unsaturated zone. A series of test wells drilled around the spilling tank and the corresponding soil-sample analysis for chloroform produced the concentration distribution maps reproduced in Figs. 2 and 3. Fig. 2 illustrates the U.S.G.S. concentration field in mgr/kg of bulk soil at 127.4 m altitude (11 m of depth below the ground surface), and Fig. 3 illustrates the corresponding concentration field from the samples taken at 121.6 m altitude (17 m below the ground surface, just above the water table elevation). Although these data were produced from only 16 samples, the maps provide valuable preliminary information on the spatial distribution of chloroform in the unsaturated zone on November, 1978. The second source of information, the only one available from the saturated zone, is the monthly report on daily chloroform concentration in mg/l at the DuPont well 22 reported by the company to the U.S.G.S. during the period of 1975 to 1986, and available through the U.S.G.S. open file system.

Since the mechanism of dispersion in the saturated zone is somewhat different from that in the unsaturated zone, I state the specific objectives of the present study as follow: (1) to develop a quantitative model capable of reproducing the typical field-scale migration pattern of chloroform in the unsaturated zone; and (2) to use the unsaturated transport model to characterize the non-point source of chloroform reaching the water table to develop a transport model of chloroform for the saturated zone capable of reproducing the historical data at the DuPont well 22. The first objective is accomplished in section 2.
The contamination scenario assumes that the chloroform liquid percolated into the ground and remained suspended in the unsaturated zone, where it formed an immobile source of residual saturation. Once residual saturation was attained, transport occurred only in the aqueous and specially in the gaseous phase with transport primarily by gaseous phase advection and dispersion. Since the gas mixture is in contact with the soil moisture, organic mass was transferred to the water by phase partitioning. Vapor mass left the unsaturated zone either by escaping to the atmosphere from the top boundary or by dissolution into the groundwater at the water table. Infiltration events periodically transported dissolved chloroform to the saturated zone (Schwille, 1988).

The second objective is accomplished in section 3. The complexity of the problem of representing chloroform migration in the saturated zone is increased by the fact that the chemical load reaching the water table is a non-point source. In this respect the model developed in section 2 was used as a forcing function. The modeling procedure consisted of the solution of the governing differential equation along an axis passing through well 22 and parallel to the average regional groundwater flow velocity. It was assumed that the dominant transport mechanisms are horizontal advection due to the high regional groundwater flow velocity, and longitudinal and transverse dispersion mainly controlled by mechanical dispersion due to the high filtration velocity in the Louisville aquifer. Molecular diffusion is considered of secondary importance. A three-dimensional model with horizontal advection and dispersion along the regional flow direction, and transverse horizontal and vertical dispersion would be appropriate. However a two-dimensional or a three-dimensional model is not possible since only one well, well 22, produced data for verification. It was found that the fluctuation in the groundwater table elevation was a key factor in characterizing the quantitative variability of the concentration reaching the saturated zone. This suggests that even a small solubility of chloroform may be an important element of mass transfer when the saturated zone invades a portion of contaminated unsaturated soil after a seasonal rise in the water table.
Since it is known that chloroform is quite mobile in porous media and due to the relatively coarse nature of the soil in the Louisville alluvium, it is assumed that adsorption of chloroform molecules by the solid surfaces is negligible in both saturated and unsaturated media.

One important feature of the present modeling effort is an uncertainty analysis conducted at the end of section 2. This was done for two reasons: first, it was judged necessary to investigate the quantitative combined effect of the many uncertainties present in the results originated from measurement errors, data alterations, model approximations and assumptions, and computational errors; second, it is important to obtain an objective measure of the uncertainty associated with the predictability of the model, that is to say that any predictive model developed on the present results should have a measure of reliability, and this reliability is best observed in a statistical sense. Finally, the methodology used in the present study applies recent contributions by the author on the theory of stochastic partial differential equations (Serrano, 1988(1), 1988(2), 1990) in hydrology. The methodology involves the treatment of the differential equations as abstract evolution equations for which a strongly continuous semigroup can be easily found, and solving them by convolution. The uncertainty term is treated as a random process forcing the differential equation as a result of the combined errors from the different sources of uncertainty, each having a different probabilistic behavior. The solution of the random differential equation is used as a criterion for the parameter estimation and moments evaluation.

2. Modeling Chloroform Evolution in the Unsaturated Zone

A general equation describing chloroform migration in the unsaturated zone can be treated as an evolution equation of the form
\[
\frac{\partial C}{\partial t} - AC = g, \quad t \geq 0,
\] (1)

where \(C(x, y, z, t)\) is the concentration in mg of chloroform per kg of bulk soil; \(t\) is the time coordinate in months; \(A(x, y, z)\) is the three-dimensional spatial partial differential operator given by

\[
AC = (-D_1 \frac{\partial^2}{\partial x^2} - D_1 \frac{\partial^2}{\partial y^2} - D_2 \frac{\partial^2}{\partial z^2} + u \frac{\partial}{\partial z})C; \quad (2)
\]

\(-\infty < x < \infty\) and \(-\infty < y < \infty\) represent horizontal distance (\(m\)) from the chosen origin (one which would minimize the mathematical complexity) located underneath the spilling tank at the ground surface level (see Fig. 2); \(0 \leq z \leq \alpha\) is vertical distance from the origin (\(m\)); \(\alpha\) is the average depth of the unsaturated zone, estimated as less than 20 m; \(D_1, D_2\) are effective (bulk) horizontal and vertical dispersion coefficients respectively (\(m^2/\text{month}\)); \(u\) is the average rate of infiltration of water (\(m/\text{month}\)); and \(g(x, y, z, t)\) is the forcing function given by

\[
g(x, y, z, t) = C_0 U(h - x)U(h - y)U(v - z)\delta(t), \quad (3)
\]

where \(C_0\) is the initial concentration of chloroform (\(mg/kg\)); \(U(\ )\) is the unit step function; \(h\) is the horizontal extent of soil saturated with chloroform at the time of the spill \((t = 0, \text{on August, 1970})\), as measured from the origin (\(m\)); \(v\) is the vertical extent of soil saturated with chloroform at the time of the spill, as measured from the origin located at the ground surface (\(m\)); and \(\delta(\ )\) is the Dirac's delta function.

The boundary and initial conditions imposed on eq.(1) are
\[ C(x,\pm\infty,0,t) = C(\pm\infty,y,0,t) = C(x,y,z,0) = 0, \quad C(x,y,z,t) = 0. \]

With the vertical axis coinciding with the average net infiltration of water, the following assumptions are behind eqs.(1)-(4): The dominant transport processes at the field (bulk) scale are vertical advection driven by the gravitational forces acting on infiltrated water and chloroform molecules, vertical dispersion controlled by the average vertical infiltration velocity and molecular gaseous and liquid diffusion, and horizontal dispersion controlled by transverse dispersion of the vertical transport and molecular diffusion (Bear and Verruijt, 1987). Since the medium horizontal permeability is significantly greater than the vertical one, because of the sedimentary nature of the alluvium, clearly the horizontal component of molecular diffusion is more important than its vertical component. An additional effect on horizontal diffusion may be vapor mass flux caused by compound vaporization at the source, although this factor is not specifically accounted for in the present formulation (Mendoza and Frind, 1987). On the other hand, the presence of a vertical advection term, and no net horizontal advection, would indicate that mechanical dispersion is more important in the vertical sense. It is usually reported that longitudinal dispersivity along the main flow direction is greater than transverse dispersivity, but due to the significant difference in the horizontal and vertical tortuosities the horizontal transverse component of mechanical dispersion may be as important as its vertical component. This would imply that the overall magnitude of the horizontal component of the hydrodynamic dispersion coefficient in the unsaturated zone is greater than its vertical component. This is an interpretation of the greater horizontal dispersion of chloroform reported by the data. The above assumptions are in agreement with results on similar organic volatile constituents (Metcalfe and Farquhar, 1987).

No specific mass transport assumptions have been made with the vertical transport term. The transporting velocity simply results from the movement of percolating water. The units of concentration are given in terms of mass of soil to be consistent with the data supplied by the
Since the value of \( a \) is large (unsaturated zone is deep), it is assumed that the boundary condition at \( z = a \) does not affect significantly the magnitude of \( C \) in the unsaturated domain. This justifies a continuous spectrum for the operator \( A \) in the \( z \) direction (i.e., \( z \) is treated as varying from \( -\infty \) to \( \infty \)). To be consistent with this mathematical assumption of an infinite vertical aquifer, the chloroform initial concentration is maintained equal to zero at \( z = 0 \), since the volatile constituent rapidly evaporated from the top layers of the soil. Therefore, an imaginary initial concentration equal to \( -C_0 \) is assumed for \( -v < z \). The above implies that the presence of a water table at \( z = a \) should not affect the concentration at points \((x, y, z < a)\) and that eq.(1) is only valid for the unsaturated domain \((z < a)\). An improvement of this scheme would consider the water table as a mass transfer boundary condition, although it is not possible to determine the flux across the water table from the available data. Keeping in mind that the aim is to develop a descriptive model of the time and space distribution of chloroform as it reaches the water table, eq.(1) seems a reasonable approximation.

The time 20 \( m^3 \) of chloroform took to saturate a volume of soil equal to \( 2h \times 2h \times v \) was probably several days. This interval is so small as compared with the time scale of observation of about 99 months, that an assumption of an instantaneous source function is justified.

The solution to eq.(1) is given by the convolution integral (see Serrano, 1988(1), (2))
where \( J \) is the strongly continuous semigroup associated with the operator \( A \) in eq.(2) and is given by (Serrano, 1988(1), (2))

\[
J(x,y,z,t-t)g(t) = \int \int \int \exp[-\frac{(x-x')^2}{4D_1(t-\tau)} - \frac{(y-y')^2}{4D_1(t-\tau)} - \frac{(z-u(t-\tau)-z')^2}{4D_2(t-\tau)}]g(x',y',z',\tau)dz'dy'dx',
\]

where \( x' \), \( y' \) and \( z' \) are dummy integration variables in the \( x \), \( y \) and \( z \) directions, respectively.

Substituting eq.(3) and eq.(6) into eq.(5), using the properties of the delta function to solve the time integral, and using the properties of step functions to transform the limits of the spatial integrals, this reduces to

\[
C(x,y,z,t) = \frac{C_0}{\sqrt{8(\pi^3D_1^2D_2^2)^{\frac{3}{2}}} \int \int \int \exp[-\frac{(x-x')^2}{4D_1(t-\tau)} - \frac{(y-y')^2}{4D_1(t-\tau)} - \frac{(z-u(t-\tau)-z')^2}{4D_2(t-\tau)}]} \int \int \int \exp[-\frac{(x-x')^2}{4D_1(t-\tau)} - \frac{(y-y')^2}{4D_1(t-\tau)}]
\]
Solving the spatial integrals the general solution of eq.(1) is:

\[
C(x,y,z,t) = \frac{C_0}{8} \left[ \text{erf}(x + \frac{h}{\sqrt{4D_1 t}}) - \text{erf}(x - \frac{h}{\sqrt{4D_1 t}}) \right] \left[ \text{erf}(y + \frac{h}{\sqrt{4D_1 t}}) - \text{erf}(y - \frac{h}{\sqrt{4D_1 t}}) \right] \left[ \text{erf}(z - \frac{ut}{\sqrt{4D_2 t}}) - \text{erf}(z - \frac{ut + v}{\sqrt{4D_2 t}}) \right] - \frac{(z-u(t-t)-z)^2}{4D_2(t-t)} dz'dy'dx',
\]

Eq.(8) represents the three-dimensional space and time evolution of chloroform in the unsaturated zone.

The parameters of model eq.(8) were preliminary estimated based on the information supplied by Davis and Matthews (1983) on chloroform concentration in about 16 soil samples taken in the unsaturated zone underneath the spilling tank (at 127.4 m of altitude, which corresponds to a depth of \( z = 11 \) m, and 121.6 m of altitude, which corresponds to a depth of \( z = 17 \) m) during October-November, 1978. These values were such that the simulated shape of the concentration plume would approximately follow that generated by the observed samples. The parameter values are as follow: The horizontal and vertical dispersion coefficients are \( D_{subl} = 4.0 \) m\(^2\)/month and \( D_2 = 0.115 \) m\(^2\)/month, respectively; the deep percolation velocity, which is related to the average vertical infiltration rate of water, is \( u = 0.0982 \) m/month; an estimated soil volume covered by the spill during the first few hours gives the value
of \( h = 8.0 \) m and the value of \( v = 1.05 \) m, which would amount a net volume of about \( 40 \, m^3 \) of chloroform which is twice as much the amount reported originally, as pointed by Davis and Matthews, 1983; the value of the initial concentration within the soil saturated with chloroform was estimated based on a reported density of the alluvium of \( 1,602 \, kg/m^3 \), a chloroform density of \( 1,490 \, kg/m^3 \), and an assumed porosity of 0.3, giving a value of \( C_0 = 218,200 \) mg of chloroform per kg of bulk soil (to use the same units reported by Davis and Matthews, 1983).

After writing and executing a short program in C, eq.(8) was used to observe the plume evolution in the unsaturated zone, to re-construct the history of contamination, and finally to compute the source pollution entering the saturated zone, as described in section 3. Fig. 4 shows the simulated chloroform concentration in the unsaturated zone at 127.4 m of altitude on October, 1978. Fig. 5 shows the simulated chloroform concentration in the unsaturated zone at 121.6 m of altitude on October, 1978. Comparison between Figs. 4 and 2, and Figs. 5 and 3, respectively, indicate that the simulated values only approximately conform to the corresponding observed ones. In order to obtain a better fit a substantially higher number of soil samples would be required. In section 3 an investigation of the uncertainty incurred after adopting this model, in addition to other sources of variability, will be attempted. Finally Fig. 6 illustrates a model-reconstructed chloroform concentration evolution in profile in the unsaturated zone on June, 1971 (\( t = 10 \) months after the spill reported on August, 1970), October, 1974 (\( t = 50 \) months), and November, 1978 (\( t = 99 \) months, the time of the USGS investigation). Note the general plume evolution resembles that of reported laboratory experimentation as discussed in section 1.

It was concluded that the above modeling procedure constitutes a simple tool the planner can use to design needed monitoring wells and sampling timing and spacing. With an adequate set of parameters the model can be used to reconstruct the history of the contamination (to aid in legal procedures), and to forecast the concentration evolution to design remedial or restoration tasks. The primary purpose, however, is to use eq.(8) as a forcing function for the saturated zone model.
3. Modeling of Chloroform Evolution in the Saturated Zone

The migration of chloroform in the saturated zone in this case should be interpreted as the contaminant evolution due to a non-point source of chloroform entering the water table. The spatial distribution and timing of the source coming from the unsaturated zone is described by eq.(8) after consideration for the units. Since the only means of model verification in the saturated zone is the chloroform concentration measurements at DuPont well 22, it seems natural to develop the simplest possible model able to forecast chloroform concentration at this well. From the mathematical point of view the simplest model involves the solution of the advective-dispersive differential equation in a one-dimensional spatial domain. Since concentration data are not available from any other well in the field, a two-dimensional or a three-dimensional model is not appropriate.

Assuming that advection and dispersion are the main transport processes in the saturated zone, the governing differential equation describing chloroform evolution with respect to distance along an axis coinciding with the regional groundwater flow is

\[
\frac{\partial C_1}{\partial t} - D \frac{\partial^2 C_1}{\partial x_1^2} + \bar{u} \frac{\partial C_1}{\partial x_1} = g_1(x_1, t) \quad (9)
\]

\[
C_1(-\infty, t) = C_1(\infty, t) = C_1(x_1, 0) = 0,
\]

where \( C_1(x_1, t) \) represents chloroform concentration in the saturated zone (mg/l); \( x_1 \) is distance from the new origin, now located at DuPont well 22 (m), in a direction parallel to the regional groundwater flow (see Fig. 7);
D is the saturated aquifer dispersion coefficient \((m^2/\text{month})\); \(\bar{u}\) is the average magnitude of the regional groundwater pore velocity (m/month); and \(g_1(x_1, t)\) is the chloroform source reaching the water table from the unsaturated zone. A new coordinate system was chosen in order to minimize the mathematical complexity of the governing differential equation. Fig. 7 illustrates the new coordinate system adopted for the modeling in the saturated zone and its relationship to that of the unsaturated zone. Note that the new origin is at the DuPont well 22, which is located at \(x = X = -17.0\) m, and \(y = Y = 54.0\) m. The orientation of the axis \(x_1\) tilts an angle \(22.4^\circ\) with respect to \(x\), and its direction is parallel to the average regional groundwater flow direction, \(u\) bar. The average direction of the groundwater velocity, was estimated based on water table maps of the Louisville alluvium (Davis and Matthews, 1983). The source function in eq.(9), \(g_1(x_1, t)\), is given by eq.(8) with \(x = X - x_1 \cos(\theta)\), \(y = Y + x_1 \sin(\theta)\) and \(z\) the current depth of the water table with respect to the ground surface. The source concentration values are given in mgr of chloroform per kg of dry soil sample, and must be transformed to mgr of chloroform per liter of voids volume. The voids volume is filled with the mixture of water and chloroform once the chemical reaches the saturated zone. Using again a value of alluvium density of 1602 \(\text{kg/m}^3\) and an average porosity of 0.3, it is found that \(g_1(x_1, t) = 1.602C(x, y, t)\), where \(C\) is given by eq.(8) in mg/kg and \(g_1\) is given in mg/l. Given the resolution time scale of the model (one month) and the relatively slow movement of the water table, it is assumed that the mass transfer between the saturated and unsaturated zone is instantaneous.

Eq.(9) models the average concentration along the vertical line as sampled by the DuPont well 22. Following a similar procedure as in section 2 (see Serrano, 1988(1), (2)), the solution to this equation is
\[ C_1(x_1,t_1) = \int_{0}^{t_1} J(x_1,t_1 - \tau)g_1(\tau) d\tau, \quad (10) \]

where \( t_1 \) is the time interval (months) from a more convenient time origin now located on January, 1974, which is the time when DuPont began sampling well 22 with no traces of chloroform; \( J \) is the semigroup operator associated with the spatial partial differential operator of eq.(9), which by analogy with eq.(6) is given as

\[
J(x_1,t_1 - \tau)g_1(\tau) = \frac{1}{\sqrt{4\pi D(t_1 - \tau)}} \int \exp\left[-\frac{(x_1 - \bar{u}(t_1 - \tau) - s)^2}{4D(t_1 - \tau)}\right]g_1(s, \tau). \quad (11)
\]

The solution of eq.(10) was carried on a monthly basis by using a 24-point Gauss-Legendre quadrature for the double integral. In order to keep \( C_1 \) bounded and to guarantee the uniform convergence of the infinite integral, several numerical tests were conducted to observe the smooth spatial distribution of the concentration along \( x_1 \), month after month. It was found that instability was minimized after subdividing the spatial integral into reaches no longer than 30.0 m. Preliminary simulations indicated, as expected, that the concentration time evolution at well 22 was a very smooth wave with a peak magnitude around April, 1978 and a very slow recession afterwards. These results were obtained when the value of \( z \) in the source, \( g_1 \), was kept constant and equal to the observed mean water table depth. However Davis and Matthews (1983) noted a strong relationship between the water table elevation and the chloroform concentration at well 22. This would suggest that higher elevations in the water table would give the saturated zone a better
opportunity to transport greater quantities of the contaminant than would normally arrive via the natural load from the unsaturated zone to a static water table level. Since chloroform seems to travel more efficiently in the saturated zone, because of the combined effect of dispersion and advection, higher water table elevations should produce higher concentrations in the well. This phenomenon, along with the inherent measurement errors, would explain the high variability of chloroform concentration observed at the well.

After the water table elevation fluctuation was introduced in the model (Faust and Lyons 1989), simply by making $z$ in the source function, $g_1$, equal to the recorded mean monthly water table depth at DuPont well 19T, the monthly variability of the simulated concentration at well 22 corresponded closely with the observed mean monthly variability. The exact form of the simulated concentration, however, depends on the values of the parameters $D$ and $\bar{u}$. Following a new parameter estimation procedure described below, the optimal values were found to be $D = 0.9 \text{ m}^2/\text{month}$ and $\bar{u} = 0.9 \text{ m/month}$. Fig. 8 illustrates the observed mean monthly chloroform concentration at well 22 (as supplied by the U.S.G.S. open file system) as compared to the simulated (reconstructed) concentration. Generally the agreement between observed and simulated concentration is good, particularly in the latter years. The disagreement during the initial stages may be due to several reasons, including the high values registered soon after DuPont decided to continuously pump well 22 thereby attracting contaminant from directions transverse to the regional groundwater flow. Since the present model assumes the concentration evolves due to the natural field velocities and dispersion in the main direction of flow, and since the effect of pumping is not yet considered, these may indicate the possible causes for the discrepancies between model and observed concentration during the initial stages.

After the development described above, I would like to improve the prediction capability of the model by including a term which will account for the random differences between the observed and simulated values of concentration. These random differences are originated, as stated above,
from the inaccuracies in the model development, the errors incurred by adopting many of the simplifying assumptions, both in the unsaturated and the saturated zone, measurement errors in geometry, water table depths and chloroform concentration. The new random term will not only offer an objective, quantitative, measure of the model uncertainty and variability, but will also provide a concrete mathematical criterion for the optimal estimation of the parameters D and $\bar{\mu}$.

Re-writing the solution eq.(10) in a form which includes the uncertainty term, one obtains

$$C_1(x_1,t_1,\omega)=\int_0^{t_1} J(x_1,t_1-\tau)g_1(\tau)d\tau + f(t_1,\omega),$$

where the function $f(t_1, \omega)$ is a time stochastic process which accounts for the variability of the difference between the observed and predicted chloroform concentration at well 22; $\omega$ denotes the probability space; and the rest of the terms as before. The function $f$ results from the convolution integral of the known semigroup operator, $J$, with an unknown perturbing random process. Presumably this function is a zero-mean process since $C_1$ now represents the stochastic transient component which will produce the average concentration given by eq.(10). This provides a mathematical criterion for the optimal estimation of the parameters D and $\bar{\mu}$. The estimation problem is simply to find the numerical value of the parameters such that the expected value of the concentration follows eq.(10). In other words, find the values of D and $\bar{\mu}$ such that the following equation holds:
\[
E(C_1(0,t_1)) = E(C_1(0,t_1) - C_1(0,t_1)) = E(f(t_1)) = 0, \quad 0 \leq t_1 < \infty
\] (13)

where \(E\{\quad\} \) denotes the expectation operator; and \(\hat{C}_1(0,t_1)\) is the observed concentration at well 22 \((x_1 = 0)\). An assumption behind this criterion is that the random variability of the observed concentration follows the same stochastic process as that of the simulated concentration. Eq. (13) also implies stationarity in \(f\) (see Jazwinski, 1970). Following this condition, the optimal values of the parameters were found. Thus eq. (10) and the simulated values shown in Fig. 8 are indeed the expected value of the concentration as a function of time.

The residual \(\hat{C}_1(0,t_1) - C_1(0,t_1)\) is a sample realization of the random process \(f(t_1, \omega)\). The last modeling task is the investigation of the statistical properties of this process. It is already known it is a zero-mean process, that is \(E[f(t_1)] = 0\). Investigation of the correlation structure of the \(f\) process indicated some rather interesting properties. Fig. 9 shows the observed serial correlation coefficient of the random sample of \(f\), \(r_f(k)\), at the DuPont well 22 for lags \(k = 1\) through \(k = 24\) months. The correlation was computed after applying the standard formula. Note that the serial correlation gradually decays to an almost zero magnitude at lag 8, and then oscillates around values of less than \(\pm 0.22\) at lags greater than 8. This clearly shows that no seasonal component in the uncertainty term is present, which indicates a good deterministic model, and that \(f\) could be described by a colored-noise random process. Fig. 9 also shows the theoretical correlation coefficient of a colored-noise random process with a correlation coefficient given by

\[
r_f(k) = e^{-\rho|k|},
\] (14)
with parameter $p = 0.5$. This implies a two-point autocorrelation function given by

$$E[f(t_i)|f(t_i+k)] = \sigma_f e^{-p|k|}, \quad (15)$$

where $\sigma_f$ is the variance parameter of $f$. With the assumption of stationarity one obtains $\delta_f = S_f = 4.80 \text{ mg/l}$, where $S_f$ is the sample standard deviation of $f$. Fig. 10 illustrates the sample function of the uncertainty term $f$ plus and minus one standard deviation as estimated from above.

The correlation function is a key element in identifying the variance, the standard deviation, and covariances measures, all of which contribute to produce an objective quantitative measure of the combined model uncertainty. One can further fit a particular analytical form for the random process $f$, after adopting certain assumptions. This random process would be helpful in the generation of sample functions of $f$ and in the synthesis of concentration data for forecasting purposes. This last step was not attempted since the size of the concentration data from well 22 will not allow a reliable fit.

4. Chapter Summary

The enormous production, wide variety of uses, and distinct migratory pattern in porous media of dense chlorinated solvents have created serious problems of contamination to the groundwater systems.

An understanding of the time and space evolution of chloroform in unsaturated and saturated porous media is a requisite for adequate forecasting and field remedial strategies. The present study attempted to
contribute to the fluid dynamics knowledge on the migration of chloroform in groundwater systems and to complement the existing qualitative information with the development and analysis of two exploratory quantitative models for the case of chloroform contamination in the Louisville aquifer. Two exploratory models were developed and tested as to their ability to reproduce the limited historical information on the evolution of the contaminant concentration in the unsaturated and the saturated zone of the alluvial aquifer. It was found that for the unsaturated zone the controlling field-scale transport processes are diffusion in the gaseous phase (for small quantities of the spill) and vertical advection caused probably by deep percolation of infiltrated water. For the saturated zone, it was found that the complexity of the model is significantly increased because the concentration of chloroform reaching the water table constitutes a non-point source. It was found that the dominant transport process in the saturated zone was advection along the average regional horizontal groundwater flow velocity, and dispersion. It was also found that a key element explaining the wide range of variability of concentrations in the saturated zone was the seasonal fluctuation of the water table elevation. This suggests that even a small solubility of chloroform may be an important element of mass transfer when the saturated zone invades a portion of contaminated unsaturated soil after a seasonal rise in the water table. An uncertainty analysis was conducted at the end in order to obtain an objective measure of the reliability of the models.

The methodology of analysis consisted in the gradual construction of a stochastic partial differential equation, the solution of which was used for the estimation of parameters and the statistical measures of uncertainty.

5. Chapter References


CHAPTER II
SCALE DEPENDENT MODELS OF DISPERSION

1. Introduction

In the previous chapter we developed models to predict the propagation of chloroform, or of dense halogenated solvents, in the saturated and the unsaturated zone. An important difficulty we encountered was the accurate estimation of the dispersion parameters, namely the dispersion coefficient and the mean pore velocity. It was noted that the calibrated parameters were substantially greater in magnitude than reported laboratory scale parameters. It is suspected that behind this enhanced values of the parameters is the so called scale dependency reported in the literature. Recent theoretical and field studies have demonstrated that the movement of inert solutes in aquifers is governed by a dispersion equation whose dispersion coefficient is a function of the spatial coordinates or travel time and that only under ideal circumstances, i.e., usually at the laboratory scale, the classical form of the convection dispersion equation (CDE) with constant coefficients is adequate for describing contaminant transport (Fried, 1975; Sudicky, 1986; Dagan, 1984).

In the search for the definition of transport equations which adequately represent the evolving nature of the dispersion parameters at large scales, stochastic analyses have played an important role with a variety of studies investigating 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 Cushman, 1987 and Sposito and Jury, 1986. Other researchers have conceived the variability of the dispersion parameters as deterministic evolving or periodic functions of space or time (Pickens

Much of the previous stochastic analyses relies on a logarithmic transformation of the hydraulic conductivity data to reduce its variance and solves the resulting flow and contaminant transport equations using the small perturbation theory. Although many fundamental results have been obtained, this approach limits the spatial variability in the physical parameters to cases of small variances, that is to cases where only small deviations from the deterministic problem are solved.

Recently Serrano (1992b) attempted to incorporate aquifer physical variables in the definition of the functional form of dispersion parameters. A new equation of dispersion in a one-dimensional homogeneous aquifer with scale dependent parameters given as functions of natural recharge rate from rainfall, aquifer transmissivity, head hydraulic gradient, aquifer thickness, and aquifer soil porosity was derived (the variable dispersion equation, VDE).

The present study reports an improvement over the above work by including in the analysis the aquifer heterogeneity, as measured by the stochastic spatial variability in the transmissivity in a two-dimensional aquifer, comparing the relative impact of hydrologic-hydraulic variables with respect to aquifer heterogeneity on the magnitude of the dispersion coefficient, and verifying the results with other theoretical and field studies. A hypothetical phreatic aquifer at the regional scale is considered (Dagan, 1986) 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. A differential equation governing the flow in this aquifer with the above properties is written and solved for the expected groundwater pore velocity.
Subsequently the solute transport dispersion coefficient is written in terms of the above hydrologic and hydraulic properties, and the corresponding dispersion equation is derived. Subsequently, a Neumann expansion solution for the expected concentration is built based on the characteristics of a particular analytical solution. Finally, comparison tests of the solution to the expected VDE with the classical CDE and the Dagan's solution (Dagan, 1984) as applied to the Borden site experiment (Mackay et al., 1986) are given.

Important features of the present work include the consideration of the "raw" hydraulic conductivity in the flow equation, rather than its logarithm, and the implementation of the Neumann expansion method in the solution of the groundwater flow and groundwater transport equations.

The Neumann expansion method has been shown as an accurate, systematic and flexible tool capable of handling large variances in the physical parameters. An interesting characteristic of the Neumann expansion solution is that any term in the series may be computed after a convolution integral of the system impulse response function times a function of the previous term in the expansion. For a system with a well known impulse response, a computationally efficient algorithm may be constructed with a subroutine questioning the convergence rate (Serrano, 1992a). The time step in the calculations may be adjusted to assure uniform convergence in cases of very large variances in the random terms (Serrano, 1992a). Statistical separability of the moments series is another important advantage of the Neumann series over the small perturbation techniques. A Neumann expansion series may be constructed in several different ways to sequentially approximate a non-linear stochastic partial differential equation towards its exact non-linear solution (Serrano, 1988b). This would avoid the need to "linearize" the differential equation in order to solve it.
Comparison between exact and Neumann expansion solutions of groundwater flow equations are presented in Serrano (1992a) and Serrano and Unny (1987). A theorem with proof stating the conditions for uniform convergence of the Neumann series is presented in Serrano (1992a). Applications to problems involving the modeling of horizontal infiltration (Serrano, 1990a), and the modeling of infiltration in hysteretic soils (Serrano, 1989) have shown potential. Applications to various cases of stochastic analysis of groundwater pollution (Serrano, 1992a, 1988a, 1988b) have illustrated the versatility of the method. Finally, a computational algorithm with a code in C is presented by Serrano (1990b).

2. The Velocity Field in a Heterogeneous Aquifer Under Recharge

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 under steady recharge from rainfall. The governing flow equation with Dupuit assumptions is (Bear, 1979)

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

where \(h(x, y)\) is the hydraulic head (m) above a specified datum; \(T(x, y)\) is the aquifer transmissivity \((m^2/month)\); \(x, y\) are the planar Cartesian coordinates (m); and \(I\) is the mean monthly recharge rate (m/month).

For an aquifer with a regional groundwater velocity coinciding with \(x\) and negligible net velocity in the \(y\) direction, we may assume the aquifer transmissivity as \(T = \overline{T} + T'\), where \(\overline{T} = E\{T\}\), \(E\{\}\) is the expectation operator, the random field \(T'\) has the properties...
\( E\{T'\} = 0, \) \( E\{T'(x_1)T'(x_2)\} = \sigma_T^2 e^{-\frac{|x_1-x_2|}{L}}, \) \( \sigma_T^2 \) is the transmissivity variance parameter \((m^2/month)^2\), L is a typical length (m), and rho is a correlation decay parameter. 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.

With the above assumptions, imposing the boundary conditions \( h(0) = h_0 \) and \( \frac{\partial h}{\partial x}(0) = h'_0 \), and choosing a dimensionless spatial coordinate \( \chi = x/L \), Equation (1) reduces to

\[
\begin{aligned}
&h_{xx} = -\frac{IL^2}{T} - \frac{T'}{T}h_{xx} - \frac{1}{T}h_x, & &0 < \chi < \infty, \quad (2)
\end{aligned}
\]

where the notation \( h_{xx} = \frac{\partial^2 h}{\partial \chi^2} \) convenient for partial differential equations has been adopted.

The boundary condition on Equation (2) are \( h(0) = h_0 \) and \( h_x(0) = Lh_0 \).

The solution to Equation (2) may be expressed as \( h = V + W \), where \( V \) satisfies

\[
\begin{aligned}
&V_{xx} = -\frac{IL^2}{T}, & &V(0) = h_0, \quad V_x = Lh_0. \quad (3)
\end{aligned}
\]
and $W$ satisfies

$$W_{xx} - f(x) = -\frac{T'}{T}W_{xx} - \frac{1}{T}T_xW_x. \quad (4)$$

The solution to Equation (3) is simply

$$V(x) = h_0 + Lh_0x - \frac{HH^2x^2}{2T}. \quad (5)$$

The solution to Equation (4) may be expressed as

$$W(x) = \int_0^x G(x, \xi)f(\xi)d\xi. \quad (6)$$

Since the Green’s function associated with Equation (4) is $G(x, \xi) = U(x-\xi)(\chi-\xi)$, where $U(\cdot)$ is the unit step function, then the potential distribution in the aquifer is given by

$$h(x) = V(x) - \frac{1}{T} \int_0^x (x - \xi)R(\xi)h(\xi)d\xi, \quad (7)$$

where the random operator $R$ is given by
A Neumann expansion (Serrano, 1988) of (7) will yield the series 

\[ h(x) = v_1 + v_2 + v_3 + \ldots, \]

where

\[ v_1(x) = V(x), \]  

and any subsequent term

\[ v_i(x) = -\frac{1}{T} \int_0^x (x - \xi)R(\xi)v_{i-1}(\xi)d\xi, \quad i > 1. \]  

Numerical tests on the convergence rate of the series indicated that with moderately large realizations of the transmissivity of about 50% above or below an average of 1000.0 m²/month, two terms in the series will generate a relative error of about 0.25% For more rigorous tests on the convergence rate of Neumann expansion solutions to transport equations subject to large-variance parameters the reader is referred to Serrano (1992a).

With two terms in the series Equation (7) reduces to
The total discharge in the \( \chi \) direction per unit width is given by 
\[
q(\chi) = -(T + T'(\chi)) h_\chi.
\]
Differentiating Equation (11), using Leibnitz's rule for differentiation of integrals, and substituting into the above expression, we find that the specific discharge could be written as
\[
q(\chi) = q(\chi) + q'(\chi),
\]
where
\[
r = 1 - C_v^2, C_v = \sigma_t/\overline{T}, \text{ the coefficient of variability of the transmissivity.}
\]
Expressing the discharge in terms of the scalar distance, \( x \), and taking expectations, the mean discharge is given by

\[
E(q(x)) = \bar{q}(x) = -h_0 \bar{T} + lrx + \frac{h_0 \sigma_T^2}{T} (1 - e^{-\rho dL}). \tag{14}
\]

Finally, the seepage velocity is given as

\[
u(x) = \bar{u}(x) + u'(x), \bar{u}(x) = \bar{q}(x)/(n h_0), u'(x) = q'(x)/(n h_0), n = \text{the mean aquifer porosity.}
\]

Equation (14) indicates that the groundwater velocity varies with distance, with the recharge intensity and with the degree of variability and correlation of the transmissivity. A few numerical tests further suggest that the aquifer geohydrologic variables play a more important role in determining the magnitude and evolution of the mean velocity field than the statistical variability and spatial correlation in the transmissivity. For example, Fig. 1 shows the spatial distribution of the seepage velocity of an aquifer with the following properties:

- \( h_0 = 10.0 \text{ m}, L = 100.0 \text{ m}, h_0 = -0.001, n = 0.3, l = 0.01 \text{ m/month (10.0 mm/m).} \]

Large variations in the correlation decay parameter, rho, appear to have very little effect on the velocity distribution, which would support an assumption neglecting the third term in Equation (14). The magnitude of the coefficient of variability of the transmissivity is relatively more important, but the recharge rate, the hydraulic gradient the porosity and the mean transmissivity seem to be the determinant elements of the magnitude and distribution of the mean seepage velocity. An interesting result is that a higher degree of
variability in the transmissivity, as expressed by higher values in $C_v$, tend to decrease the overall value of the mean seepage velocity, which suggests that groundwater velocities in heterogeneous aquifers are controlled by the sections with the lower, rather than the higher, transmissivities. However, these results need to be field verified.

3. The Dispersion Equation in a Heterogeneous Aquifer

In this section we derive the form of the two-dimensional solute dispersion equation in the same hypothetical aquifer studied in the previous section. Assuming that the fundamental physical principles of convection, mechanical dispersion and molecular diffusion hold, the general dispersion equation is (Bear, 1979)

$$\frac{\partial nC}{\partial t} - \nabla (nD \nabla C) + \nabla \cdot (uC) = 0,$$  \hspace{1cm} (15)

where $C$ represents solute concentration (mg/l); $t$ is the time coordinate (months); $D$ is the dispersion tensor ($m^2$/month); $u$ is the velocity vector (m/month); $\nabla$ is the gradient operator; and the rest of the terms as before. In a two-dimensional aquifer with Dupuit assumptions, regional groundwater velocity coinciding with $x$, principal dispersion components (longitudinal and transverse respectively) coinciding with $x$ and $y$, and the dispersion coefficients expressed as functions of the variable field velocity, $\alpha_l$, $\alpha_t$ (advection-dominated transport), where $\alpha_l$, $\alpha_t$ are the longitudinal and transverse dispersivities respectively, Equation (15) becomes
\[ C_t - \alpha \mu C_{xx} + (u - \alpha \mu_x)C_x + u_x C - \alpha \mu C_{yy} = 0, \quad (16) \]

\[-\infty < x < \infty, -\infty < y < \infty, 0 < t.\]

This is the two-dimensional version of the VDE in a heterogeneous aquifer. It reiterates the dependence of the dispersion coefficient on distance in an aquifer with non-uniform velocity. In this case the dispersion coefficient does not appear to reach an asymptotic value, and physically it will continue to grow to the end of the recharge zone. Equation (16) is subject to \( C(\pm \infty, \pm \infty, t) = 0 \), \( C(x, y, 0) = C_i \delta(x) \delta(y) \), where \( C_i \) is a constant and \( \delta(\cdot) \) is the Dirac's delta function (an instantaneous spill at \( t = 0 \)). Substituting the deterministic and random components of \( u \) into Equation (16) and placing the random terms on the right side we obtain

\[ C_t - \alpha \mu \bar{C}_{xx} + (\bar{u} - \alpha \mu_x)\bar{C}_x + \bar{u}_x \bar{C} - \alpha \mu \bar{C}_{yy} = Q(x, y)\bar{C}, \quad (17) \]

where the operator \( Q \) is given by

\[ Q(x, y)\bar{C} = \left[ \alpha \mu' \frac{\partial^2}{\partial x^2} - (u' - \alpha \mu_x) \frac{\partial}{\partial x} - u_x + \alpha \mu' \frac{\partial^2}{\partial y^2} \right] \bar{C}. \quad (18) \]

The solution to Equation (17) can be written as

\[ C(x, y, t) = C_i G(x, 0; y, 0, t, 0) \quad (19) \]
where \( G(x, x'; y, y'; t, t') \) is the Green's function associated with Equation (17). A Neumann expansion solution to this equation may be expressed as (Serrano, 1992a, 1988b)

\[
C = g_1 + g_2 = ..., \tag{20}
\]

with

\[
g_1(x, y, t) = C_t G(x, 0; y, 0, t, 0), \tag{21}
\]

and in general

\[
g_i(x, y, t) = \int \int \int G(x, x'; y, y'; t, t')Q(x', y', t')C(x', y', t')dt'dx'dy', \tag{22}
\]

Truncating the series at \( i = 2 \), which is a level found acceptable in most previous applications, and taking expectations on Equation (19), we found that the mean concentration is \( E\{C(x, y, t)\} = \bar{C} = g_1 \), which implies that the mean concentration satisfies Equation (17) with the right side set to zero. Substituting for the terms containing \( u \) bar and its derivatives, using Equation (14), into Equation (17) we obtain the differential equation satisfying the mean
concentration:

\[
\bar{C}_t - \frac{\alpha}{n}(Ir - h_0 T)\bar{C}_{xx} + \frac{1}{n}(Ir - h_0 T - \alpha_r T_0)\bar{C}_x 
\]

\[
+ \frac{Ir}{n} \bar{C} - \frac{\alpha}{n}(Ir - h_0 T)\bar{C}_{yy} = 0. \tag{24}
\]

Now choosing a dimensionless time coordinate \( \tau = \frac{It}{nh_0} \), dimensionless spatial coordinates \( \chi = x/L, \eta = y/L, \xi = r \chi + b \); dimensionless dispersivities \( a = a/L, \beta = \alpha_r/L \); and the dimensionless velocity at the origin \( b = -\frac{h_0 T}{L} \), the dimensionless form of Equation (23) is

\[
\bar{C}_t - ar^2 \xi \bar{C}_{\xi\xi} + r(\xi - ra)\bar{C}_\xi + r\bar{C} - \beta \xi \bar{C}_{\eta\eta} = 0, \tag{25}
\]

\(-\infty < \xi < \infty, -\infty < \eta < \infty, 0 < \tau, \)

Subject to

This is the two-dimensional version of the dimensionless VDE.
\[ \bar{C}(\pm \infty, \eta, \tau) = C(\xi, \pm \infty, \tau) = 0; \bar{C}(\xi, \eta, 0) = \delta(\xi - b)\delta(\eta). \]
derived by Serrano (1992b).

4. Solution to the Variable Dispersion Equation

An exact solution of Equation (24) may be initially approached via defining the Fourier transform of the mean concentration as

\[ F\{\bar{C}\} = c(\xi, \lambda, \tau) = \int_{-\infty}^{\infty} e^{j\eta} \bar{C}(\xi, \eta, \tau) d\eta, \quad j = \sqrt{-1}, \quad (25) \]

which reduces Equation (24) to

\[ c_\tau - ar^2 \xi c_{\xi \xi} + r(\xi - ra)c_\xi + (r + \lambda^2 \beta \xi)c = 0, \quad (26) \]

subject to

\[ c(\pm \infty, \lambda, \tau) = 0, \quad c(\xi, \lambda, 0) = \delta(\xi - b). \]

Now define the Laplace transform as

which reduces Equation (26) to
After solving this equation and inverting the Laplace transform (see Serrano, 1992b),

\[ C'(\xi, \lambda, s) = 0. \]  

Fourier inverting Equation (29) will yield the desired solution for the mean concentration, which may be expressed as
\[ C(\xi, \eta, \tau) = C \Psi(\xi, \tau). \Phi(\eta, \tau), \quad (30) \]

\[ \Psi(\xi, \tau) = e^{\frac{(1-\alpha \tau)(\xi-b)}{2}} \frac{e^{-[\alpha \tau^2(1-\alpha \tau)^2+\tau]}}{\sqrt{4\pi \alpha \tau^3}} \quad (31) \]

\[ \Phi(\eta, \tau) = \frac{1}{\sqrt{4\pi \beta \tau}} e^{-\frac{\eta^2}{4\beta \tau}} \quad (32) \]

Serrano (1992b) used the one-dimensional deterministic version of the above solution to investigate the relative effect of recharge rate, transmissivity, hydraulic gradient, aquifer thickness and soil porosity on contaminant distribution in an aquifer.

However, it has been found that this solution exists and is stable for only a few values of the parameter \( \alpha \), which limits its applicability to only a few theoretical results. An alternative Neumann expansion solution to the VDE will offer flexibility with respect to the choice of the parameters while providing the convenience of a recursive computational scheme. From Equation
(30) and Equation (31) it is easy to see that, in terms of $\chi$ and $\tau$, $\Psi$ satisfies

$$
\Psi_x - ab\Psi_{xx} + b\Psi_x = O(\chi, \tau)\Psi,
$$

(33)

where the operator $O$ is given by

$$
O(\chi, \tau)\Psi = \left[a\chi^{\frac{\partial}{\partial \chi^2}} - (\chi - a)\frac{\partial}{\partial \chi} - 1\right]\Psi.
$$

(34)

Formally, the solution to Equation (33) is

$$
\Psi(\chi, \tau) = G(\chi, 0; \tau, 0) + \int_0^\tau \int_0^\tau G(\chi, \chi'; \tau, \tau')O(\chi', \tau')\Psi(\chi', \tau')d\chi'd\tau'
$$

(35)

where $G$ in this case is the well known Green's function of the CDE,

$$
G(\chi, \chi'; \tau, \tau') = \frac{1}{\sqrt{4\pi ab(\tau - \tau')}} e^{-\frac{(\chi - \chi')^2}{4ab(\tau - \tau')}}.
$$

(36)
We now construct a Neumann expansion solution for Equation (35), one which uses the CDE as an initial iteration and its well behaved kernel for subsequent iterations (Serrano, 1992a):

$$\Psi = \psi_1 + \psi_2 + \ldots,$$

where

$$\psi_1(x, \tau) = G(x, 0; \tau, 0)$$

(37)

$$\psi_i(x, \tau) = \int \int G(x, x'; \tau, \tau') O(x', \tau') \psi_{i-1}(x', \tau') dx'd\tau'.$$

(38)

A theorem with proof delineating the convergence conditions of a Neumann expansion series very similar to the above was presented by Serrano (1992a). The most critical criterion would require that

$$r(x_{\text{max}} - \tau_{\text{max}}/2 < 1,$$

where chi sub max and tau sub max are the maximum dimensionless distance and dimensionless time in the simulations respectively. This condition is easily satisfied in the verification tests, as seen in the next section. With two terms in the series (initial numerical tests indicated that additional terms contributed less than 10% to the solution), the integrand in Equation (38) is analytical and the solution to the VDE, in summary, reduces to

$$\bar{C}(x, \eta, \tau) = C_i \Psi(x, \tau). \Phi(\eta, \tau),$$

(39)
\[ \Psi(x, \tau) = G(x, 0; \tau, 0) + \int_0^\tau \int G(x, x'; \tau, \tau') f(x', \tau') dx'd\tau', \quad (40) \]

\[ f(x', \tau') = \frac{e^{-(x'-br')^2}}{\sqrt{4\pi ab\tau^3}} \quad (41) \]

\[ \Phi(\eta, \tau) = \frac{1}{\sqrt{(4\pi \beta(1 + b)\tau)}} e^{-\frac{\eta^2}{4\beta(1 + b)\tau}}, \quad (42) \]

and \( G \) is given by Equation (36).

5. Verifications with Other Theoretical and Field Results

In this section we study a preliminary comparison of the VDE alternative solution, Equations (39) through (42), with the two-dimensional CDE and the two-dimensional Dagan's model as applied the Borden site experiment.

The classical deterministic CDE under constant dispersion coefficient and constant pore velocity resulting from neglecting recharge results from (16) as
\[ C_t - \alpha \mu C_{xx} + u C_x - \alpha \mu C_{yy} = 0, \quad -\infty < x < \infty, \quad -\infty < y < \infty, \quad 0 < t, \quad (43) \]

subject to

\[ C(\pm \infty, y, t) = 0, \quad C(x, y, 0) = C_i \delta(x) \delta(y). \quad (44) \]

Defining the velocity according to Equation (14) with \( I = \sigma_T = 0 \), expressing Equation (43) in dimensionless form and solving,

\[ C(x, \eta, \tau) = C_i \frac{1}{\sqrt{4\pi ab\tau}} e^{-\frac{(x-\beta t)^2}{4ab\tau}} \frac{1}{\sqrt{4\pi \beta b\tau}} e^{-\frac{\eta^2}{4\beta b\tau}}. \quad (45) \]

The two-dimensional version of the Dagan (1984, 1986) model conceives a CDE for the mean concentration with time dependent dispersion coefficients as

\[ \overline{C}_t - D_1(t) \overline{C}_{xx} + u \overline{C}_x - D_2(t) \overline{C}_{yy} = 0, \quad -\infty < x < \infty, \quad -\infty < y < \infty, \quad 0 < t, \quad (46) \]

subject to Equation (44). The longitudinal dispersion coefficient is defined as
\[ D_1(t) = 0.74ul_y \sigma_y^2 \left[ 1 - \frac{1.5}{\gamma} \frac{3e^{-\gamma}}{\gamma^2} + \frac{3}{\gamma^3} (1 - e^{-\gamma}) \right] + D_{dl}, \quad (47) \]

where \( l_y \) and \( \sigma_y^2 \) are the correlation length and variance of the log hydraulic conductivity, respectively; \( \gamma = ul_y/\theta; \) \( D_{dl} \) is the longitudinal pore scale dispersion coefficient. The transverse dispersion coefficient is defined as

\[ D_2(t) = \frac{0.74ul_y \sigma_y^2}{2\gamma} \left[ 1 - \frac{6}{\gamma^2} + 2e^{-\gamma} \left( 1 + \frac{3}{\gamma} + \frac{3}{\gamma^2} \right) \right] + D_{dz}, \quad (48) \]

where \( D_{dz} \) is the transverse pore scale dispersion coefficient.

The solution to (46) has been derived by Barry and Sposito (1989) as

\[ \bar{C}(x, y, t) = C_i \frac{1}{\sqrt{4\pi \Phi_1}} e^{-\frac{(x-u)t^2}{4\Phi_1}} \frac{1}{\sqrt{4\pi \Phi_2}} e^{-\frac{y^2}{4\Phi_2}}, \quad (49) \]

where
\[ \phi_{i}(x) = \int_{0}^{t} D_{i}(t') dt', \quad i = 1, 2. \tag{50} \]

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). Incomplete sampling of the solute plume during the early sampling sessions, as well as assumptions made with respect to the data analysis produced an important degree of uncertainty in the specification of the initial conditions of the model (Barry et al., 1988). In order to assure identical initial conditions that are not affected by measurement uncertainty or by the particular integration procedure used, it was decided to approximate the initial condition for the three models, the CDE, the Dagan's and the VDE, as a delta function. Knowing that this assumption will make it difficult to assess the results with respect to the field data, the main features of peak concentration, peak location and overall plume evolution will be easily observed.

The parameter values for the Borden aquifer are:
\[ \alpha_{x}=0.011m; \alpha_{y}=0.0033m; \sigma_{x}^{2}=0.24; \]
\[ l_{x}=2.8m; \bar{u}=0.091m/day; D_{d1}=0.001m^{2}/day; D_{d2}=0.0003m^{2}/day; \]
\[ h_{0}=6.0m, n=0.33; \text{ the mean hydraulic conductivity } \bar{K}=6.18m/day; h_{0}=0.0056; T=Kh_{0}=1112.4m^{2}/month; \] for a log normal distribution, the variance of the hydraulic conductivity is \[ \sigma_{K}^{2}=-\bar{K}(e^{\sigma_{x}^{2}}-1)=10.36(m^{2}/day)^{2}, \text{ or } \sigma_{K}=3.22m^{2}/day; \] the transmissivity standard deviation is \[ \sigma_{T}=\sigma_{K}h_{0}=19.31m^{2}/day=579.34m^{2}/month; \] the
coefficient of variability for the hydraulic conductivity or the transmissivity, $C_v=\sigma_T/T=0.52$; if we set $L=1$, then $a=\sigma_T/L=0.011, \beta=\sigma_T/L=0.0033$; with a moderate recharge value of $I=0.01$ m/month for South Western Ontario obtained from water balance studies (Serrano et al., 1985), we have $b=-\frac{h_0T}{LI}=622.94$; setting values of $t$ in months, corresponding values of $\tau=\frac{It}{nh_0}$ can be obtained.

Simulations were done using the three models to calculate concentration distributions at times corresponding to the measurement schedule after tracer injection at the Borden site (Mackay et al., 1986). A realistic value of resident initial concentration at the time of injection, $C_I$, may be deduced from the vertically-integrated surfaces fitted to measured data after one day after injection (Barry et al., 1988). For the case of Bromide, 3.87 kg of solute were injected. Knowing that the tracer occupied about $25 m^2$ of surface area, an integrating depth of $6.0 m$, and an average porosity of $0.33$, the initial resident concentration is approximately $78.2$ mg/l.

A comparison with measured results (in particular with those of Barry et al. (1988), Fig. 5, which depict the plume evolution) suggest that the three models approximate well the location of the peak concentration at any time. Fig. 2 shows the simulated Bromide breakthrough curve along the x axis (assumed as coinciding with the regional groundwater flow direction) at $t=260$ days Fig. 3 shows the simulated Bromide areal distribution using the VDE at the same time, and Fig. 4 the corresponding areal distribution using the Dagan’s model.

The models exhibit inherent differences worth noting. The VDE
and the CDE in this case appear to predict well the peak concentration magnitude, but exhibit substantially lower spatial contaminant dispersion, whereas the Dagan's model predicts a lower peak concentration magnitude, but a good spatial contaminant dispersion.

Due to the increasing value of the dispersion coefficient with distance, the VDE produces a shifted plume with somewhat greater spatial dispersion than that of the CDE. This discrepancy will increase as the travel distance increases (see Serrano, 1992b, Fig. 2 for an observation of this effect with the exact dimensionless VDE). The Dagan's model-generated plume increases in dispersion with travel time with a dispersion coefficient reaching an asymptotic value.

The Dagan's model appears to be quite sensitive to hydraulic conductivity variability. A moderate coefficient of variability, $C_v = 0.2$ for the raw hydraulic conductivity will cause a reduction of over 50% in peak concentration and a corresponding enhanced spatial dispersion with respect to the CDE. As $C_v \rightarrow 0 (\sigma^2 \rightarrow 0)$, the Dagan's model coincide with the CDE. The VDE produces an opposite effect with respect to variability in the transmissivity. While being substantially less sensitive to $C_v$, the VDE produces a plume with a decreasing shifting and enhanced dispersion effect as $C_v$ increases. As $C_v \rightarrow 1.0$, the VDE coincides with the CDE. However, as $C_v \rightarrow 0.0$, the discrepancy between the CDE and the VDE is maximum. An objective physical explanation of this inverse effect with respect to statistical transmissivity variability is found in section 2 (i.e., Fig. 1), where it was found that the greater the value of $C_v$ the less the mean groundwater velocity.

In a subsequent study on applications a more complete assessment of the VDE with an integration of the measured initial
condition at the Borden site will be conducted. A potential possibility for improvement exists with the incorporation of the true transient effect of aquifer recharge and the hydrologic regime into the analysis, which will produce a general time and space dependent dispersion coefficient. For the moment, however, the VDE appears to be a promising alternative for the practical modeling of plume concentration evolution with parameters defined in terms of hydrologic-hydraulic variables.

6. Chapter Summary

An investigation into the characteristics of the dispersion equation in heterogeneous aquifers subject to recharge and non-uniform velocity was conducted. The results indicated that aquifer regional hydrogeologic variables such as mean transmissivity, hydraulic gradient, mean porosity, aquifer thickness and recharge rate from rainfall generate a variable with distance mean groundwater velocity, which in turn produces a variable with distance dispersion coefficient. Aquifer heterogeneity, as represented by the statistical spatial variability of the transmissivity, appears to play a less important role in the magnitude and spatial variability of the dispersion coefficient. Greater transmissivity variances appear to produce relatively lower values of mean groundwater velocity, in contrast to what is currently accepted, which implies that the mean velocity in a long, thin, aquifer is controlled by the lower realizations, rather than the higher values, and that mean dispersion in a homogeneous aquifer is greater than in a heterogeneous one with the same mean transmissivity.

An equation such as the VDE which includes the functional dependency of the above regional variables on the dispersion coefficient seems to partially explain the spatial evolution of the dispersion coefficient and offers a promising concentration forecasting tool for practical applications.
A preliminary field comparison between the VDE, the CDE and the two-dimensional Dagan's model emphasized the shifting and enhanced dispersion effects of the VDE due to a variable velocity field. These effects are maximum when the statistical variability in the transmissivity is minimum (deterministic), as opposed to the Dagan's model which is very sensitive to statistical variability in the hydraulic conductivity and produces a greater plume dispersion with greater statistical variability. The dispersion coefficient modeled by the VDE increases with distance to the point where recharge ends, whereas the one modeled by the Dagan's model increases with travel time to an asymptotic value.

Future research should be devoted to the transient analysis of regional recharge and its effect on the time and space variability of the dispersion coefficient.

7. Chapter References


CHAPTER III

SCALE DEPENDENT TRANSPORT IN HETEROGENEOUS AQUIFERS

1. Introduction

The previous chapter confirms the results of recent theoretical and field studies which demonstrates 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 convection dispersion equation with constant coefficients is adequate for describing contaminant transport (Fried, 1975; Dagan, 1984).

In the search for the definition of transport equations which adequately represent the evolving nature of the dispersion parameters at large scales, 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 Cushman (1987), and Sposito and Jury (1986). Other 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) attempted to incorporate aquifer physical variables in the definition of the functional form of dispersion parameters. An equation of dispersion in a one dimensional homogeneous aquifer with scale dependent parameters given as functions of natural recharge rate from rainfall, aquifer transmissivity, head hydraulic gradient, aquifer thickness and aquifer
soil porosity was derived. In a subsequent improvement (Chapter II of this report), aquifer heterogeneity, as measured by the stochastic spatial variability in the transmissivity, was included in the analysis. 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. An interesting result showed that a higher degree of variability in the transmissivity, as expressed by higher values in the coefficient of variability, tend to decrease the overall value of the mean pore velocity, which suggests that groundwater velocities in heterogeneous aquifers are controlled by the sections with the lower, rather than the higher, transmissivities. In terms of the dispersion problem, this would imply that a dispersion coefficient, defined as the product of the mean pore velocity times the dispersivity, would be lower in magnitude in aquifers with high recharge rates and high variability in the transmissivity (heterogeneous aquifers). This would contradict the accepted fact that the dispersion coefficient grows with the scale of observation, specially in heterogeneous aquifers, and it probably indicates that the definition of the dispersion coefficient as a direct function of the mean pore velocity is probably inappropriate at large scales.

In the present chapter we attempt to re-examine the problem of dispersion in an aquifer subject to large spatial variability in the transmissivity in the absence of recharge. 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 (section 2). Subsequently, a large scale dispersion equation is derived based on the solute mass conservation and the random nature of the pore velocity (section 3). 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. Finally a comparison with the classical theory, the Dagan’s model and field tracer tests in the Borden aquifer is described with favorable results (section 4).
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, 1988), rather than the small perturbation method, 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)

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

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

For an aquifer with a regional groundwater velocity coinciding with \( x \) and negligible net velocity in the \( y \) direction, we may assume the aquifer transmissivity as \( T = \overline{T} + T' \), where \( \overline{T} = E\{T\}; E\{\} \) is the expectation operator; the random field \( T' \) has the properties \( E\{T'\} = 0; E\{T'(x_1)T'(x_2)\} = \sigma_T^2 e^{-\rho |x_1-x_2|}; \sigma_T^2 \) is the transmissivity variance parameter \((m^2)\); \( T' \) has the properties \( E\{T'\} = 0; E\{T'(x_1)T'(x_2)\} = \sigma_T^2 e^{-\rho |x_1-x_2|}; \sigma_T^2 \) is the transmissivity variance parameter \((m^2)\); and \( \rho \) is the correlation decay parameter \((m^{-1})\). The above simplified representation of aquifer heterogeneity attempts to be in line with current research on the stochastic analysis of groundwater flow and contaminant transport, while reducing the mathematical complexity.

Imposing a set of boundary conditions that require knowledge of the head and the hydraulic gradient at the origin, \( h_0 \) and \( h'_0 \) respectively, (1) reduces to

\[
\frac{\partial^2 h}{\partial x^2} = -\frac{1}{T} \frac{\partial T'}{\partial x} \frac{\partial h}{\partial x}, \quad 0 \leq x < \infty, \quad h(0) = h_0, \quad \frac{\partial h}{\partial x}(0) = h'_0. \tag{2}
\]

The solution to this differential equations is

\[
h(x) = h_0 + h'_0 x - \frac{1}{T} \int_0^x G(x; \xi) \frac{\partial T'(\xi)}{\partial \xi} \frac{\partial h}{\partial \xi} d\xi, \tag{3}
\]

where \( G(x; \xi) \) is the Green's function associated with (2). It is given by (Serrano, 1992b)
\[ G(x, \xi) = U(x, \xi)(x - \xi), \quad (4) \]

where \(U(\cdot)\) is the unit step function. Substituting (4) into (3),

\[ h(x) = h_0 + h_0'x - \frac{1}{T} \int_0^x (x - \xi) \frac{\partial T'(\xi)}{\partial \xi} \frac{\partial h}{\partial \xi} d\xi. \quad (5) \]

A Neumann expansion of (5) could be built as (Serrano, 1992a)

\[ h(x) = h_0 + h_1 + h_2 + ... \]

where \(h_0\) is again the head with respect to the bottom of the aquifer at the origin,

\[ h_1(x) = h_0'x, \quad (6) \]

\[ h_2(x) = -\frac{1}{T} \int_0^x (x - \xi) \frac{\partial T'(\xi)}{\partial \xi} \frac{\partial h_1(\xi)}{\partial \xi} d\xi, \quad (7) \]

and in general

\[ h_i(x) = -\frac{1}{T} \int_0^x (x - \xi) \frac{\partial T'(\xi)}{\partial \xi} \frac{\partial h_{i-1}(\xi)}{\partial \xi} d\xi, \quad (8) \]

The convergence of the Neumann expansion of (5) requires that

\[ \text{max}(T'(x)) < 1 \]

for the sample functions, where \(\text{max}(\cdot)\) is the maximum operator, and that

\[ C_v = \frac{\sigma_T}{T} < 1 \]

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 (6)-(7) into (5) and differentiating with respect to \( x \) one obtains the hydraulic gradient in the direction of the regional groundwater flow:

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

(9)

Applying Leibnitz rule for differentiation under integrals and solving,

\[
\frac{\partial h}{\partial x} = h_0' - \frac{h_0'}{T} \int_0^x \frac{\partial T'(\xi)}{\partial \xi} d\xi.
\]

(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 (10),

\[
u_x(x) = \frac{-h_0'}{nh_0} \left( \frac{1}{T'} - \int_0^x \frac{\partial T'(\xi)}{\partial \xi} d\xi - \frac{1}{T_0} \int_0^x T'(x) \frac{\partial T'(\xi)}{\partial \xi} d\xi \right)
\]

(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 (11) we obtain the mean pore velocity, \( \overline{u}_x \).
\[ \overline{u_x} = E(u_x(x)) = -\frac{h_0'}{nh_0}\left(\frac{\sigma^2_T}{T} - \frac{\sigma^2_T}{T}(1 - e^{-\rho x})\right). \]  

(12)

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

\[ \overline{u_x} = -\frac{h_0'T}{nh_0}. \]  

(13)

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

\[ u_x'(x) = u_x - \overline{u_x} = -\frac{h_0'}{nh_0}\left(T' - \int_0^x \frac{\partial T'(\xi)}{\partial \xi} d\xi\right). \]  

(14)

The right 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 (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

Finally, set \( x_1 = x_2 = x \) to obtain the variance of the pore
This equation indicates that the variance of the pore velocity increases with distance. For large values of $\rho$ the increase is linear with distance, whereas for small values of $\rho$ the increase is nonlinear with distance. (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)

$$\frac{\partial C}{\partial t} + \frac{\partial (u_x C)}{\partial x} + \frac{\partial (u_y C)}{\partial y} = 0, \quad (17)$$
where $C$ represents solute concentration (mg/l); $t$ 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 as before.

From the observation that the dispersion parameters are functions of distance, and after the results in section 2, particularly (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 is 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:

$$u_x(x) = \bar{u}_x + u'_p + u'_x,$$

where $u'_p$ 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. In conformity with existing field observations, we have further assumed that the large scale mechanism of transverse dispersion is negligible. Thus the $y$ (transverse) component of the pore velocity is defined as $u_y = u'_y$, where $u'_y$ represents the random component in the $y$ direction of the pore scale velocity. For an infinite aquifer and an instantaneous point source (a spill) at the origin, (17) becomes

$$\frac{\partial C}{\partial t} + \frac{\partial (\bar{u}_x C)}{\partial x} + \frac{\partial (u'_p C)}{\partial y} + \frac{\partial (u'_x C)}{\partial y} = 0, \quad -\infty < x < \infty, -\infty < y < \infty, 0 < t.$$  \hspace{1cm} (18)

subject to
\[ C(\pm \infty, y, t) = C(x, \pm \infty, t) = 0, \quad C(x, y, 0) = C_i \delta(x) \delta(y), \quad (19) \]

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

Adopting the Fickian approximation at the small scale,
\[ u'_x C = -D_x \frac{\partial C}{\partial x} \quad \text{and} \quad u'_y C = -D_y \frac{\partial C}{\partial y}, \]
where \( D_x \) and \( D_y \) are the dispersion coefficients \((m^2/\text{month})\) 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
\[ C(x, y, t) = C_i X(x, t) Y(y, t), \quad (20) \]

where \( X(x, t) \) satisfies
\[
\frac{\partial X}{\partial t} + u'_x \frac{\partial X}{\partial x} = D_x \frac{\partial^2 X}{\partial x^2} - \frac{\partial (u'_x) X}{\partial x}, \quad X(\pm \infty,t) = 0, X(x,0) = \delta(x), -\infty < x < \infty, 0 < t, \quad (21)
\]

and \( Y(y, t) \) satisfies
\[
\frac{\partial Y}{\partial t} - D_y \frac{\partial^2 Y}{\partial y^2} = 0, \quad Y(\pm \infty,t) = 0, Y(y,0) = \delta(y), -\infty < y < \infty, 0 < t. \quad (22)
\]

(22) is simply a dispersion (heat flow) equation with constant dispersion coefficient. Its solution is (Serrano, 1992b),

The solution to (21) may be expressed as the Neumann series
\[ Y(y, t) = \frac{e^{-\frac{y^2}{4D_x t}}}{\sqrt{4\pi D_x t}}. \] (23)

(Serrano, 1992a) \( X = X_0 + X_1 + X_2 + \ldots \), where the first term, \( X_0 \), satisfies
\[
\frac{\partial X_0}{\partial t} + u_x \frac{\partial X_0}{\partial x} = D_x \frac{\partial^2 X_0}{\partial x^2}, \quad X_0(\pm \infty, t) = 0, X_0(x, 0) = \delta(x), -\infty < x < \infty, 0 < t,
\] (24)

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, 1992)
\[
X_0(x, t) = \frac{e^{-\frac{(x-x_0)^2}{4D_x t}}}{\sqrt{4\pi D_x t}}.
\] (25)

Any subsequent term, \( X_i \), in the Neumann expansion of (21) satisfies
\[
\frac{\partial X_i}{\partial t} + u_x \frac{\partial X_i}{\partial x} = -\frac{\partial(u_x X_{i-1})}{\partial x}, \quad X_i(\pm \infty, t) = 0, X_i(x, 0) = 0, -\infty < x < \infty, 0 < t, \ i \geq 1
\] (26)
The Green's function of this differential equation, $G(x, t; x', t')$, satisfies

$$\frac{\partial G}{\partial t} + u_x \frac{\partial G}{\partial x} = 0, \quad G(\pm \infty, t, x', t') = 0, \quad G(x, 0; x', t') = \delta(x), \quad -\infty < x < \infty, \quad 0 < t. \quad (27)$$

Defining the Laplace transform of $G$ as $\hat{G} = \int_0^\infty e^{-st} G dt$, (27) reduces to

$$\frac{d\hat{G}}{dx} + \frac{s}{u_x} \hat{G} = \frac{\delta(x)}{u_x}. \quad (28)$$

Solving this equation and Laplace inverting, one obtains

$$G(x, t; x', t') = \delta(0) - \left( t - t' - \frac{x - x'}{u_x} \right). \quad (29)$$

which represents the pure translation effect of continuity.

Now the solution of (26) may be expressed in terms of the Green's function as

$$X_i(x, t) = -\int_0^\infty \int G(x, t; x', t') \frac{\partial}{\partial x'}(u'_{i-1}(x', t')) dx' dt'. \quad (30)$$

Using (24), (29) and (30), and solving the internal spatial integral,
the second term in the series solution of (21) is

\[ X_1(x, t) = -\int_0^t \frac{\partial}{\partial x}(u'_x(x - \bar{u}_{x,t} + \bar{u}_{x,t}')X_0(x - \bar{u}_{x,t})dt'. \] (31)

Similarly, using (29), (30) and (31), the third term in the solution of (21) is

\[ X_2(x, t) = \int_0^t a_x(x-u_{x,t}) \frac{\partial X_0(x-u_{x,t})}{\partial x} \int_0^{t'} u'_x(x-u_{x,t}+u_{x,t}') u'_x(x-u_{x,t}+u_{x,t})dt' \] (32)

\[ - x_0(x-u_{x,t}) \int_0^{t'} u'_x(x-u_{x,t}+u_{x,t}') \frac{\partial u'_x(x-u_{x,t}+u_{x,t})}{\partial x} dt'. \]

Higher order elements in the series solution could be derived. However, the calculation of the expected value of such terms would require information on the moments of order greater than two, and as stated before, this information is usually not available in most applications. Therefore the solution to (21) is approximated as

\[ X(x, t) = X_0 + X_1 + X_2, \]

where the components \( X_0, X_1, X_2 \) are given by (25), (31) and (32) respectively. The solute concentration is then given by (20). On taking expectations on both sides of (20), the mean concentration is given by

\[ E(C(x, y, t)) = \bar{C}(x, y, t) = C_0 \bar{X}(x, t) Y(y, t), \] (33)

where \( Y(y, t) \) is given by (23), and
$\bar{X}(x, t) = E\{X(x, t)\} = X_0 + \bar{X}_1 + \bar{X}_2$, with $E\{X_i\} = \bar{X}_i, i = 1, 2$. Since $u'_x$ is a zero mean random process (see previous section), taking expectations on (31) yields $\bar{X}_1 = 0$. Taking expectations on (32) and using the pore velocity correlation function (15) derived in the previous section, with $x_1 = x - \bar{u}_x t + \bar{u}_x r$, $x_2 = x - \bar{u}_x t + \bar{u}_x t'$, one obtains after some manipulation

$$\bar{X}_2(x, t) = \left[ \frac{h_0^2 \sigma_T}{n h_0} \right] X_0 \left[ Z e^{-\rho(x - \bar{u}_x t)} (W - \rho^2) + W \left\{ -\frac{2 e^{-\rho \bar{u}_x t}}{\rho^2 \bar{u}_x^2} + \frac{\rho \bar{u}_x t^3}{3} \right\} + \frac{t^2 (\rho (x - \bar{u}_x t) + 1)}{\rho \bar{u}_x} + \frac{2}{\rho^2 \bar{u}_x^2} \right]$$

(34)

where

$$W = \left( \frac{x - \bar{u}_x t}{2 D_x t} \right)^2 - \frac{1}{2 D_x t'}. $$

$$Z = \frac{1}{\rho \bar{u}_x} \left( \frac{1}{\rho \bar{u}_x} - e^{-\rho \bar{u}_x t} \right) \left( t + \frac{1}{\rho \bar{u}_x} \right).$$

Numerical tests on the form of $X(x, t)$ indicated that the mean $x$ component of the concentration spatial distribution is a Gaussian distribution with a time dependent first moment with respect to the origin (the center of mass of the plume, $\mu = \bar{u}_x t$), and a time dependent second moment with respect to the mean (the plume variance, $\sigma_x^2$). This longitudinal plume variance is given by
\[ \sigma_x^2(t) = \int (x - \mu)^2 \bar{X}(x, t) dx. \] Substituting in this expression for \( \bar{X} \) [(25) and (34)], integrating term by term and using the moments properties of Gaussian distributions,

\[ \sigma_x^2(t) = 2D_x t + \left( \frac{h_0' \sigma_x}{nh_0} \right)^2 \left[ \frac{2}{3} \rho \mu \bar{x}^3 + 2t^2 - \frac{4t}{\rho \mu_x} + \frac{4}{\rho^2 \mu_x^2} - \frac{4e^{-\rho \mu_x t}}{\rho^2 \mu_x^2} \right. \]

\[ \left. + 2Z e^{\rho^2 D_x t} \left( 1 + 2\rho^2 D_x t \right) \right] \quad (35) \]

The above development is based on a Neumann expansion of (21) and an expectation of each of the terms in the series. It is easy to show (Serrano, 1992a) that the uniform convergence of the series requires that \( \frac{\text{max}(R_{ww})t}{2} < 1 \). From (15), this occurs at \( x_1 = x_2 = x \), that is \( \text{max}(R_{ww}) = \sigma_u^2 \) and from (16)

\[ \text{max}(\sigma_u^2) = 2\rho x_m \left( \frac{h_0' \sigma_T}{nh_0} \right)^2, \] where \( x_m \) is the maximum distance in the simulations. Therefore the above solution is strictly valid for \( t < t_m \), where \( t_m \) is the maximum simulation time given by

\[ t_m = \frac{1}{2\rho x_m \left( \frac{h_0' \sigma_T}{nh_0} \right)^2}. \] In practical applications when the desired simulation time, \( t \), exceeds the maximum time, one would think that the simulations might be done step wise: The mean concentration distribution at time \( 2t_m \) would have as initial condition
the mean concentration at time $t_m$. This of course does not mean that we need to calculate $n$ concentration distributions, if $n = \frac{t}{t_m}$, since we may use the shifting properties of Gaussian distributions. Thus it is easy to show that $\bar{X}(x, t) = \bar{X}(x, nt_m)$ results from the evaluation of $\bar{X}$ once with a mean equal to $\bar{u}_x$ and with a variance equal to $n\sigma_x^2(t_m)$.

In summary, The mean concentration distribution is given by

$$\bar{C}(x, y, t) = C_i \bar{C}_x(x, t) \bar{C}_y(y, t),$$  \hspace{1cm} (36)$$

$$\bar{C}_x(x, t) = \frac{e^{-\frac{(x-\bar{u}_x)^2}{2n\sigma_x^2(t_m)}}}{\sqrt{2\pi n\sigma_x^2(t_m)}},$$  \hspace{1cm} (37)$$

$$\bar{C}_y(y, t) = Y(y, t) = \frac{e^{-\frac{y^2}{4D_y t}}}{\sqrt{4\pi D_y t}},$$  \hspace{1cm} (38)$$

$$n = \frac{t}{t_m}, \quad t_m = \frac{1}{\rho_x \left( \frac{h_0 \sigma_T}{nh_0} \right)^2},$$  \hspace{1cm} (39)$$

and $\sigma_x^2(t_m)$ is the plume variance (35) evaluated at $t = t_m$. 
Still remains to investigate the nature of large scale dispersion in the transverse sense, \( y \). There is some field evidence indicating that transverse dispersion is not as strongly dependent on scale as longitudinal dispersion and its departure from the classical convection dispersion equation is not as marked. However, an attempt was made to implement a similar development to that derived for the longitudinal direction, \( x \). It was assumed that the transverse random pore velocity, \( u'_y \), was defined by the same properties of its counterpart in the longitudinal direction (see section 2). However this generated unrealistically high levels of transverse dispersion. This suggests that in an aquifer with negligible mean pore transverse velocity such as the one under consideration, the random transverse pore velocity has a range of values substantially lower than those in the longitudinal direction. An explanation for this phenomenon comes from the regional hydrology: after all in the present example there is no net transverse hydraulic gradient. We believe that at this point an assumption establishing \( u'_y \) as governed by a factor of \( u'_x \), and the factor being a transverse dispersivity, is artificial and a physically based hypothesis should be built.

4. Verification with Existing Results

In this section we study a preliminary comparison between the dispersion model developed in the previous section, (35)-(39), with the two dimensional convection dispersion equation and the two dimensional Dagan’s model as applied to the Borden site experiment.

The classical deterministic convection dispersion equation with constant dispersion coefficients applied to the hypothetical aquifer is given by
The solution to this differential equation is

\[ C(x, y, t) = C(x, \pm \infty, t) = 0, \quad C(x, y, 0) = C, \delta(x) \delta(y). \]

The two dimensional version of the Dagan's model (Dagan, 1984, 1986) conceives a convection dispersion equation for the mean concentration with time dependent dispersion coefficients:

\[ \frac{\partial \bar{C}}{\partial t} - D_1(t) \frac{\partial^2 \bar{C}}{\partial x^2} + \bar{u}_x \frac{\partial \bar{C}}{\partial x} - D_2(t) \frac{\partial^2 \bar{C}}{\partial y^2} = 0, \quad -\infty < x < \infty, -\infty < y < \infty, 0 < t, \quad (42) \]

subject to the same boundary and initial conditions imposed on (40). The longitudinal \((x\) direction) dispersion coefficient is defined as

\[ D_1(t) = \frac{0.74 \bar{u}_x \sigma_y^2}{\rho} \left( 1 - \frac{1.5}{\tau} - \frac{3e^{-\tau}}{\tau^2} + \frac{3}{\tau^3}(1 - e^{-\tau}) \right) + D_x, \quad (43) \]

where \(\sigma_y^2\) is the variance of the log hydraulic conductivity; and \(\tau = \rho u_x t\).

The transverse \((y\) direction) dispersion coefficient is defined as
\[ D_2(t) = \frac{0.74 \rho \bar{u}_x \sigma_y^2}{2} \left( 1 - \frac{6}{\tau^2} + 2e^{-\tau}(1 + \frac{3}{\tau} + \frac{3}{\tau^2}) \right) + D_y \] (44)

The solution to (42) was derived by Barry and Sposito (1989) as

\[ \bar{C}(x, y, t) = e^{\frac{(x-\bar{u}_y t)^2}{4\Phi_1}} \cdot e^{\frac{y^2}{4\Phi_2}}, \] (45)

where \( \Phi_1(t) = \int_0^t D_x(t')dt' \), \( \Phi_2(t) = \int_0^t D_y(t')dt' \).

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:

\( \bar{u}_x = 2.73 \text{ m/month}, \sigma_x^2 = 0.24, \rho = 0.357 \text{ m}^{-1}, \) \( D_x = 0.03 \text{ m}^2/\text{month}, \)
\( D_y = 0.009 \text{ m}^2/\text{month}, \) \( h_0 = 6.0 \text{ m}, n = 0.33; \) the mean transmissivity is (Serrano, 1993) \( \bar{T} = 1112.4 \text{ m}^2/\text{month}; \) and \( \sigma_T = 579.34 \text{ m}^2/\text{month}. \)

By analogy of (36) with (45), one may conclude that the mean concentration in the proposed model satisfies a convection dispersion equation with time dependent dispersion coefficients, in agreement with the Dagan's model. However, an application of both models to the Borden aquifer reveals that important differences between the two models exist. After observing that \( \Phi_1(t) = \frac{\sigma_x^2}{2} \),
differentiating (35) with respect to \( t \), accounting for the restriction \( t < t_m \), one obtains an expression for an effective time dependent dispersion coefficient, \( \bar{D}(t) \). Fig. 1 illustrates a comparison between \( \bar{D} \) and \( D_1 \) as a function of time after the injection. The two models give the same value of effective dispersion coefficient only at around 35 months, which is near the asymptotic value in the Dagan’s model. For times less than 35 months, the proposed model gives values of dispersion less than the Dagan’s model. However, the present model does not exhibit an asymptotic value in the dispersion parameter; it will continue to grow with time.

In an investigation on the effect of recharge on contaminant dispersion, Serrano (1992b, and chapter II of this report) also concluded that, in the presence of recharge, the dispersion coefficient does not appear to have an asymptotic value, and its value would only be limited by the end of the recharge zone or the presence of a physical aquifer boundary.

A comparison between the proposed model (36)-(39) and the field analyses on the Borden aquifer reported by Barry et al. (1988) was favorable. The model appears to reproduce the main features of the measured plume: peak concentration magnitude, peak location, longitudinal contaminant range (spread). Presumably the model would perform better for large times (post-asymptotic time in the Dagan’s model). Fig. 2 illustrates a longitudinal breakthrough curve of the relative bromide concentration, \( C_i = 324 \text{ mg/l} \), versus distance 9 months after the injection. Fig. 3 illustrates the same curve obtained after applying the classical convection dispersion equation (41). This figure shows the well known features of the classical theory when applied to large scale conditions: Although the location of the peak concentration is the same, the peak magnitude is over-estimated, while the range of values is under-estimated.
5. Chapter Summary

A mathematical model designed to predict solute concentration at the field scale in heterogeneous aquifers was developed and tested. The results indicated the existence of two scales of dispersion: A small scale of the order of less than ten meters, 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 distance involved. Several new features are included in the model: The ability to consider large variability in the aquifer parameters, particularly large variances 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 knowledge of the mean and correlation structure is necessary (information more easily available in practical applications); the model 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 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, as applied to 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 coincided with that of the Dagan's model near the asymptotic value. However the present model gives a comparatively less dispersion for times less than this one, but continues to grow 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.

It remains to investigate the large scale behavior of the transverse dispersion. The difficulty lies in the physical determination of the transverse mean and correlation functions of the pore velocity process. In the hypothetical aquifer adopted for this study, the transverse hydraulic gradient, and thus the mean pore velocity are negligible.

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\[ C_{\text{bar}}(x,9) \]

\[ C_{\text{bar}}(x,0,9) \]
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$C_{\text{exact}}(x, 9)$