MIGRATION OF CHLOROFORM IN AQUIFERS

By Sergio E. Serrano

ABSTRACT: This paper attempts to contribute to the fluid dynamics knowledge on the migration of chloroform, and other related volatile organic constituents, in ground-water systems, and to complement the existing qualitative information with the development and analysis of quantitative models. Two exploratory models are developed and tested as to their ability to reproduce the limited historical information on the evolution of the contaminant concentration in the unsaturated and saturated zones of the alluvial aquifer in Louisville, Kentucky. The model's development and an uncertainty analysis originating from measurement errors, model assumptions, nonpoint source distribution, and computational approximations, are conducted using recent contributions to the theory of stochastic partial differential equations.

INTRODUCTION

Chloroform (CHCl₃) is a chemical constituent that 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 their enormous production in the United States has generated a large portion of the contemporary ground-water pollution problems. It has been known for some time 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 that require regulatory action, largely nonsorbing and therefore quite mobile in ground-water systems, and rather volatile. CHCs have a distinct migratory pattern in porous media, and until relatively recently they were not recognized as a serious threat to ground-water systems, nor was there available experimental information to aid 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, this paper attempts to contribute to the fluid dynamics knowledge on the migration of CHCs in ground-water systems, and to complement the existing qualitative information with the analysis of two exploratory quantitative models for a case study. The writer 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 paper are based on different experimental observations of Schwille's study. Related studies of transport of other organic constituents in the unsaturated zone include Jury et al. (1983), Baehr (1987), Weeks et al. (1982), Metcalfe and Farquhar (1987), and Mendoza and Frind (1990).

The selected case study was chloroform contamination in the Louisville aquifer in Kentucky. On July 2, 1975, well 22 at the Louisville works of E. Assoc. Prof., Dept. of Civ. Engrg., Univ. of Kentucky, Lexington, KY 40506-0046.

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167
I. DuPont de Nemours and Company began producing water that initially contained 25 mg/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 m$^3$ 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 (USGS) began an investigation aimed at determining the source of contamination and the areal extent of ground water 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 USGS team to concentrate the investigation on 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 USGS concentration field in mg/kg of bulk soil at 127.4 m altitude (11 m 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 in November 1978. The second
FIG. 2. Concentration of Chloroform in Soil Samples from 127.4-m Altitude [after Davis and Matthews (1983)]

source of information, the only one available from the saturated zone, is the monthly report on daily chloroform concentration in mg/l at DuPont well 22 reported by the company to the USGS from 1975–1986, and available through the USGS 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 follows: (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 nonpoint 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 DuPont well 22.

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 ground water at the water table. Infiltration events periodically transported dissolved chloroform to the saturated zone (Schwille 1988).
FIG. 3. Concentration of Chloroform in Soil Samples from 121.6-m Altitude [after Davis and Matthews (1983)]

Second, 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 from a nonpoint source. In this respect, the model 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 ground-water flow velocity. It was assumed that the dominant transport mechanisms are horizontal advection due to the high regional ground-water 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 three-dimensional model is not possible since only one well, well 22, produced data for verification. It was found that the fluctuation in the ground-water-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. 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 was important to obtain an objective measure of the uncertainty associated with the predictability of the model, that is, 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 writer on the theory of stochastic partial differential equations (Serrano 1988a,b, 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.

**MODELING CHLOROFORM EVOLUTION IN UNSATURATED ZONE**

A general equation describing chloroform migration in the unsaturated zone can be treated as an evolution equation of the form

\[ \frac{\partial C}{\partial t} - AC = g \quad t \geq 0 \]  

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

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

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

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

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

The boundary and initial conditions imposed on (1) are

\[ 171 \]
\[ C(\pm \infty, y, z, t) = C(x, \pm \infty, z, t) = C(x, y, 0, t) = 0 \]
\[ C(x, y, z, 0) = 0 \]  \hspace{1cm} (4a)
\[ C(x, y, z, t) = 0 \]  \hspace{1cm} (4b)

With the vertical axis coinciding with the average net infiltration of water, the following assumptions are behind (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. These assumptions agree with results on similar organic volatile constituents (Metcalf 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 USGS (Davis and Matthews 1983). These are a measure of chloroform concentration in all combined phases, although they are interpreted to represent mainly gaseous concentration (Schwille 1988).

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 \(-v \leq z < 0\). This implies that the presence of a water table at \( z = a \) should not affect the concentration at points \((x, y, z < a)\) and that (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, (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 compared with the time scale of observation of about 99 months, that an assumption of an instantaneous source function is justified.

The solution to (1) is given by the convolution integral [see Serrano (1988a, b)]

$$C(x, y, z, t) = \int_0^t J(x, y, z, t - \tau)g(\tau)d\tau \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (5)$$

where $J$ = the strongly continuous semigroup associated with the operator $A$ in (2) and is given by Serrano (1988a, b)

$$J(x, y, z, t - \tau)g(\tau) = \frac{1}{8\pi^2 D_1 D_2 (t - \tau)^3} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp \left\{ -\frac{(x - x')^2}{4D_1(t - \tau)} -\frac{(y - y')^2}{4D_1(t - \tau)} -\frac{(z - u(t - \tau) - z')^2}{4D_2(t - \tau)} \right\} g(x', y', z', \tau) \, dz' \, dy' \, dx' \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (6)$$

where $x'$, $y'$, and $z'$ are dummy integration variables in the $x$-, $y$-, and $z$-directions, respectively.

Substituting (3) and (6) into (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

$$C(x, y, z, t) = \frac{C_0}{8\pi^2 D_1 D_2 \rho^{3/2}} \int_{-h}^{h} \int_{-h}^{h} \int_{-\infty}^{\infty} \exp \left\{ -\frac{(x - x')^2}{4D_1(t - \tau)} -\frac{(y - y')^2}{4D_1(t - \tau)} -\frac{(z - u(t - \tau) - z')^2}{4D_2(t - \tau)} \right\} dz' \, dy' \, dx' \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (7)$$

Solving the spatial integrals the general solution of (1) is

$$C(x, y, z, t) = \frac{C_0}{8} \left\{ \text{erf} \left[ \frac{x + h}{(4D_1 t)^{1/2}} \right] - \text{erf} \left[ \frac{x - h}{(4D_1 t)^{1/2}} \right] \right\} \cdot \left\{ \text{erf} \left[ \frac{y + h}{(4D_1 t)^{1/2}} \right] - \text{erf} \left[ \frac{y - h}{(4D_1 t)^{1/2}} \right] \right\} \cdot \left\{ 2\text{erf} \left[ \frac{z - ut}{(4D_2 t)^{1/2}} \right] - \text{erf} \left[ \frac{z - ut + v}{(4D_2 t)^{1/2}} \right] - \text{erf} \left[ \frac{z - ut - v}{(4D_2 t)^{1/2}} \right] \right\} \quad \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots (8)$$

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

The parameters of model (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 an altitude of 121.6 m, which corresponds to a depth of $z = 17$ m) from October–November 1978. These values were such that the
The simulated shape of the concentration plume would approximately follow that generated by the observed samples. The parameter values are as follows: The horizontal and vertical dispersion coefficients are $D_1 = 4.0 \text{ m}^2/\text{month}$ and $D_2 = 0.115 \text{ m}^2/\text{month}$, respectively; the deep percolation velocity, which is related to the average vertical infiltration rate of water, is $u = 0.0982 \text{ m/month}$; an estimated soil volume covered by the spill during the first few hours gives the value of $h = 8.0 \text{ m}$ and the value of $v = 1.05 \text{ m}$, which would amount a net volume of about $40 \text{ m}^3$ of chloroform, which is twice as much the amount reported originally, as pointed out 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 $1,602 \text{ kg/m}^3$, a chloroform density of $1,490 \text{ kg/m}^3$, and an assumed porosity of $0.3$, giving a value of $C_0 = 218,200 \text{ mg}$ 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, (8) was used to observe the plume evolution in the unsaturated zone, to reconstruct the history of contamination, and finally to compute the source pollution entering the saturated zone. 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. To obtain a better fit, a substantially higher number of soil samples would be required. In a later section, 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 ($t = 10 \text{ months}$ after the spill reported in August 1970), October 1974 ($t = 50 \text{ months}$), and November 1978 ($t = 99 \text{ months}$, the time of the USGS investigation). Note, the general

**FIG. 4. Simulated Chloroform Concentration (mg/kg) in Unsaturated Zone (127.4-m Altitude) on October 1978**

![Diagram showing simulated chloroform concentration in the unsaturated zone on October 1978.](image-url)
FIG. 5. Simulated Chloroform Concentration (mg/kg) in Unsaturated Zone (121.6-m Altitude) on October 1978

FIG. 6. Model-Reconstructed Chloroform Concentration in Unsaturated Zone (mg/kg) on June 1971 (t = 10 Months), October 1974 (t = 50 Months), and November 1978 (t = 99 Months)
plume evolution resembles that of reported laboratory experimentation, as discussed earlier.

It was concluded that this 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 (8) as a forcing function for the saturated zone model.

MODELING OF CHLOROFORM EVOLUTION IN SATURATED ZONE

The migration of chloroform in the saturated zone in this case should be interpreted as the contaminant evolution due to a nonpoint source of chloroform entering the water table. The spatial distribution and timing of the source coming from the unsaturated zone is described by (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 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 ground-water flow is

\[
\frac{\partial C_i}{\partial t} - D \frac{\partial^2 C_i}{\partial x_1^2} + \bar{u} \frac{\partial C_i}{\partial x_1} = g_i(x_1, t), \quad C_i(-\infty, t) = C_i(\infty, t) = C_i(x_1, 0) = 0
\]

(9)

where \(C_i(x_1, t)\) represents chloroform concentration in the saturated zone (mg/l); \(x_1 = \) distance from the new origin, now at DuPont well 22 (m), in a direction parallel to the regional ground-water flow (see Fig. 7); \(D = \) the saturated aquifer dispersion coefficient (m\(^2\)/month); \(\bar{u} = \) the average magnitude of the regional ground-water pore velocity (m/month); and \(g_i(x_1, t) = \) the chloroform source reaching the water table from the unsaturated zone. A new coordinate system was chosen to minimize the mathematical complexity of the governing differential equation. Fig. 7 illustrates the new coordinate system adopted for modeling in the saturated zone and its relationship to that of the unsaturated zone. Note that the new origin is at DuPont well 22, which is at \(x = X = -17.0\) m, and \(y = Y = 54.0\) m. The orientation of the axis \(x_1\) tilts at an angle \(\theta = 22.4^\circ\) with respect to \(x\), and its direction is parallel to the average regional ground-water flow direction, \(\bar{u}\).

The average direction of the ground-water velocity was estimated based on water table maps of the Louisville alluvium (Davis and Matthews 1983). The source function in (9), \(g_i(x_1, t)\), is given by (8) with \(x = X - x_1 \cos(\theta), \quad y = Y + x_1 \sin(\theta)\) and \(z\) the current depth of the water table with respect to the ground surface. The source concentration values are given in milligrams of chloroform per kilograms of dry soil sample, and must be transformed to milligrams 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 1,602 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 (8) 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 DuPont well 22. Following a procedure similar to that used previously [see Serrano (1988 a, b)], the solution to this equation is

$$C(x_1, t_1) = \int_{0}^{t_1} J(x_1, t_1 - \tau)g_1(\tau)\,d\tau \quad \text{......................... (10)}$$

where $t_1$ = 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; $J$ = the semigroup operator associated with the spatial partial differential operator of (9), which by analogy with (6) is given as

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

Eq. (10) was solved on a monthly basis by using a 24-point Gauss-Legendre quadrature for the double integral. 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 afterward. 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 $u$. Following a new parameter estimation procedure described herein, the optimal values were found to be $D = 0.9 \text{ m}^2/\text{month}$ and $u = 0.9 \text{ m/month}$. Fig. 8 illustrates the observed mean monthly chloroform concentration at well 22 (as supplied by the USGS open file system) compared with the simulated (reconstructed) concentration. Generally, the agreement between observed and simulated concentration is good, particularly in 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 ground-water 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 concentrations during the initial stages.

After this development, I would like to improve the prediction capability of the model by including a term that will account for the random differences between the observed and simulated values of concentration. These random differences are originated, as stated, 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 $\bar{u}$.

Rewriting the solution (10) in a form that includes the uncertainty term, one obtains

$$C_1(x_1, t_1, \omega) = \int_0^{t_1} J(x_1, t_1 - \tau)g_1(\tau)d\tau + f(t_1, \omega) \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots (12)$$

where the function $f(t_1, \omega) = a$ 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 (10). This provides a mathematical criterion for the optimal estimation of the parameters $D$ and $\bar{u}$. The estimation problem is simply to find the numerical value of the parameters such that the expected value of the concentration follows (10). In other words, find the values of $D$ and $\bar{u}$ such that the following equation holds:

![FIG. 9. Serial Correlation Coefficient of Uncertainty Term](image-url)
The residual $\hat{C}_t(0, t_1) - C_t(0, t_1)$ is a sample realization of the random process $f(t, \omega)$. The last modeling task is the investigation of the statistical properties of this process. We know it is a zero-mean process, that is $E\{f(t_i)\} = 0$. 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 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

$$r_f(k) = e^{-\rho|k|} \quad \text{.................................................. (14)}$$

with parameter $\rho = 0.5$. This implies a two-point autocorrelation function given by

$$E\{f(t_1)f(t_1 + k)\} = \sigma_f e^{-\rho|k|} \quad \text{.................................................. (15)}$$
where $\sigma_f = \text{the variance parameter of } f$. With the assumption of stationarity, one obtains $\delta_f = S_f = 4.80 \text{ mg/l}$, where $S_f = \text{the sample standard deviation of } f$. Fig. 10 illustrates the sample function of the uncertainty term $f$ plus and minus one standard deviation, as estimated from the preceding.

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.

**SUMMARY AND CONCLUSIONS**

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 ground-water 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. This paper attempted to contribute to the fluid dynamics knowledge on the migration of chloroform in ground-water 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 saturated zones 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 nonpoint source. It was found that the dominant transport process in the saturated zone was advection along the average regional horizontal ground-water 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.

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APPENDIX. REFERENCES


