Analytical Solution of the One-Dimensional Solute Advection-Dispersion Equation with Spatially Variable Retardation Factor using a Change of Variable and Integral Transform Technique

Praveen Kumar M.[1]
[1]Department of Mathematics,
KS School of Engineering & Management, Bangalore,
India

Dattatreya Hegde[3]
[3]Department of Mathematics,
Govt. First Grade College,
Sirsi, Karnataka
India.

Rekha J[2]
[2]Department of Mathematics,
Cambridge Institute of Technology,
Bangalore,
India

S. R. Sudheendra[4]
[4]Department of Mathematics,
T. John Institute of Technology,
Bangalore,
India

Abstract: **An analytical first order solution to the one-dimensional advection-dispersion equation with spatially variable retardation factor is derived using a generalized integral transform method to investigate the transport of sorbing but otherwise non-reacting solutes in hydraulic homogenous but geochemically heterogeneous porous formations. The solution is derived under conditions of steady-state flow and arbitrary initial and inlet boundary conditions. The results obtained by this solution agree well with the results obtained by numerically inverting Laplace transform-generated solutions previously published in the literature. The solution is developed for a third or flux type inlet boundary condition, which is applicable when considering resident solute concentrations and a semi-infinite porous medium. For mathematical simplicity it is hypothesized that the sorption processes are based on linear equilibrium isotherms and that the local chemical equilibrium assumption is valid. The result from several simulations, compared with predictions based on the classical advection-dispersion equation with constant coefficients, indicate that at early times, spatially variable retardation affects the transport behavior of sorbing solutes. The zeroth moments corresponding to constant and variable retardation are not necessarily equal. The center of mass appears to move more slowly, and solute spreading is enhanced in the variable retardation case. At late time, when the travel distance is much larger than the correlation scale of the retardation factor, the zeroth moment for the variable retardation case is identical to the case of invariant retardation. The analytical solution presented in this paper provides more flexibility with regard to the inlet conditions.**

INTRODUCTION

The impact of spatially variable hydraulic parameters on the transport and spreading of conservative, non-reacting solutes in natural subsurface has been the focus of many recent studies. Gelhar et. al. (1979), Sudheendra (2010, 2011). Aral et.al (1996) and others, have provided methodologies for improving the description and prediction of non-reacting solute transport in complex structured formations, compared with the prediction based on the classical advection-dispersion equation with constant coefficients. On the other hand, the transport of sorbing solutes in geochemically as well as hydraulically heterogeneous porous media has received little attention.

For the importance case of transport of sorbing solutes in geochemically homogeneous porous media, the effects of sorption are commonly accounted for by a dimensionless retardation factor, which may be defined as the ration of the average interstitial fluid velocity to the propagation velocity of the solute. Excluding the possibilities of mass transport limitations and solute transformation or decay, any observed fluctuations on the retardation factor are attributed solely to the variability of the distribution coefficient, which is an experimentally obtained measure of sorption or solute retention by the solid formation. Sorption processes can be complex and depend on many variables, including temperature, pressure, solution pH, and ionic strength, sorbent surface charge, sorbent sorptive capacity, and the presence of species that complete for sorption sites. Spatial or temporal fluctuations in any of these variables accordingly affect the distribution coefficient and, consequently, the movement of sorbing solutes in subsurface porous media. For example, the distribution coefficient of non-polar organic solutes (synthetic organic chemicals, major constituents of groundwater toxic pollutants) is correlated with the organic carbon content of the sorbent (Karckhoff (1984) and Sudheendra (2014)). Although such a correlation is not fully reliable for every solute-sorbent system (Curtis and Roberts, 1985), it can explain to some extent the variable retardation observed in field experiments (Roberts et.al 1986).

Garabedian (1987) & Sudheendra (2012) employed spectral methods to analyze reactive solute macro-dispersion under the assumption that the log-hydraulic conductivity is linearly related to both the porosity and the distribution coefficient. His result indicate that solute spreading is enhanced when there is negative correlation between the log-hydraulic conductivity and the distribution coefficient. The present work is focused on the transport of pollutants but otherwise non-reacting solutes under local equilibrium conditions in a one-dimensional unsaturated porous medium. Analytical solutions are employed to solve the one-dimensional advection-dispersion equation with uniform, steady fluid flow conditions and spatially variable retardation factor, for a semi-infinite medium and flux-type inlet boundary condition.

The main objective of the study is to provide mathematical model for better understanding of transport of pollutant through unsaturated porous media. A mathematical model is an important tool and can play a crucial role in understanding the mechanism of groundwater pollution problems. It is a simplified description of physical reality expressed in mathematical terms. Mathematical models that attempt to simulate atmospheric processes involved in groundwater pollution are based, in general, on the equation of mass conservation for individual pollutant species. Such models relate in one equation the effects of all the physical aspects and dynamic processes that influence the mass balance on groundwater which include transport, diffusion, removal of pollutants and loss or transformation through chemical reactions.

MATHEMATICAL MODEL

The Advection-Dispersion equation along with initial condition and boundary conditions can be written as

$$\frac{\partial C}{\partial t}+\frac{(1-n)}{n}\frac{\partial S}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-w\frac{\partial C}{\partial z}-\lambda C$$

The equilibrium isotherm between solution and adsorbed phase is given by $\frac{\partial S}{\partial t}=K_d\frac{\partial C}{\partial t}$, K_d is the distribution coefficient.

$$\frac{\partial C}{\partial t}+\frac{(1-n)}{n}K_d\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-w\frac{\partial C}{\partial z}-\lambda C$$

$$\left[1+\frac{(1-n)}{n}K_d\right]\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-w\frac{\partial C}{\partial z}-\lambda C$$

$$R\frac{\partial C}{\partial t}=D\frac{\partial^2 C}{\partial z^2}-w\frac{\partial C}{\partial z}-\lambda C$$

Let us take D_1 = D/R, w_1 = w/R, $\lambda_1=\lambda/R$. Initially, saturated flow of fluid of concentration, $C = 0$, takes place in the porous media.

$$\frac{\partial C}{\partial t}=D_1\frac{\partial^2 C}{\partial z^2}-w_1\frac{\partial C}{\partial z}-\lambda_1 C \qquad (1)$$

Thus, the appropriate boundary conditions for the given model

$$\left.\begin{array}{ll} C(z,0)=0 & z\ge 0\\ C(0,t)=C_0e^{-\gamma t} & t\ge 0\\ C(\infty,t)=0 & t\ge 0\end{array}\right\}. \qquad (2)$$

The problem then is to characterize the concentration as a function of z and *t*, where the input condition is assumed at the origin and a second type or flux type homogeneous condition is assumed. C_0 is initial concentration. To reduce equation (3) to a more familiar form, we take

$$C(z,\ t)=\Gamma(z,\ t)\,Exp\left[\frac{w_1 z}{2D_1}-\frac{w_1^2 t}{4D_1}-\lambda_1 t\right] \quad (3)$$

Substituting equation (3) into equation (1) gives

$$\frac{\partial \Gamma}{\partial t}=D_1\frac{\partial^2 \Gamma}{\partial z^2} \qquad (4)$$

The initial and boundary conditions (2) transform to

$$\left.\begin{array}{ll} \Gamma(0,\ t)=C_0\ Exp\left[\frac{w_1^2 t}{4D_1}+(\lambda_1-\gamma)t\right] & t\ge 0\\ \Gamma(z,\ 0)=0 & z\ge 0\\ \Gamma(\infty,\ t)=0 & t\ge 0\end{array}\right\} (5)$$

Equation (4) may be solved for a time dependent influx of the fluid at *z = 0*. The solution of equation (4) may be obtained readily by use of Duhamel's theorem (Carslaw and Jaeger, 1947).

If $C=F(x,\ y,\ z,\ t)$ is the solution of the diffusion equation for semi-infinite media in which the initial concentration is zero and its surface is maintained at concentration unity, then the solution of the problem in which the surface is maintained at temperature $\phi(t)$ is

$$C=\int_0^t \phi(\tau)\frac{\partial}{\partial t}F(x,y,z,t-\tau)\,d\tau$$

This theorem is used principally for heat conduction problems, but the above has been specialized to fit this specific case of interest. Consider now the problem in which initial concentration is zero and the boundary is maintained at concentration unity. The boundary conditions are

$$\left.\begin{array}{ll} \Gamma(0,t)=0 & t\ge 0\\ \Gamma(z,0)=1 & z\ge 0\\ \Gamma(\infty,t)=0 & t\ge 0\end{array}\right\}$$

The Laplace transform of equation (4) is

$$L\left[\frac{\partial \Gamma}{\partial t}\right]=D_1\frac{\partial^2 \Gamma}{\partial z^2}$$

Hence, it is reduced to an ordinary differential equation

$$\frac{\partial^2\overline{\Gamma}}{\partial z^2} = \frac{p}{D_1}\overline{\Gamma} \qquad (6)$$

The solution of the equation is $\overline{\Gamma} = Ae^{-qz} + Be^{qz}$

where, $q = \pm\sqrt{\frac{p}{D_1}}$.

The boundary condition as $z \to \infty$ requires that $B = 0$ and boundary condition at $z = 0$ requires that $A = \frac{1}{p}$ thus the particular solution of the Laplace transformed equation is

$$\overline{\Gamma} = \frac{1}{p}e^{-qz}$$

The inversion of the above function is given in any table of Laplace transforms. The result is

$$\Gamma = 1 - erf\left(\frac{z}{2\sqrt{D_1 t}}\right) = \frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{Dt}}}^{\infty} e^{-\eta^2} d\eta$$

Using Duhamel's theorem, the solution of the problem with initial concentration zero and the time dependent surface condition at $z = 0$ is

$$\Gamma = \int_0^t \phi(\tau) \frac{\partial}{\partial t}\left[\frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{D(t-\tau)}}}^{\infty} e^{-\eta^2} d\eta\right] d\tau$$

Since $e^{-\eta^2}$ is a continuous function, it is possible to differentiate under the integral, which gives

$$\frac{2}{\sqrt{\pi}}\frac{\partial}{\partial t} \int_{\frac{z}{2\sqrt{D_1(t-\tau)}}}^{\infty} e^{-\eta^2} d\eta = \frac{z}{2\sqrt{\pi D_1}(t-\tau)^{3/2}} Exp\left[\frac{-z^2}{4D_1(t-\tau)}\right]$$

The solution to the problem is

$$\Gamma = \frac{z}{2\sqrt{\pi D_1}} \int_0^t \phi(\tau)\, Exp\left[\frac{-z^2}{4D_1(t-\tau)}\right] \frac{d\tau}{(t-\tau)^{3/2}} \qquad (7)$$

Putting $\mu = \frac{z}{2\sqrt{D_1(t-\tau)}}$ then the equation (7) can be written as

$$\Gamma = \frac{2}{\sqrt{\pi}} \int_{\frac{z}{2\sqrt{D_1 t}}}^{\infty} \phi\left(t - \frac{z^2}{4D_1\mu^2}\right) e^{-\mu^2} d\mu \qquad (8)$$

Since $\phi(t) = C_0\ Exp\left(\frac{w_1^2 t}{4D_1} + (\lambda_1 - \gamma)t\right)$ the particular solution of the problem be written as

$$\Gamma(z,t) = \frac{2C_0}{\sqrt{\pi}} Exp\left(\frac{w_1^2 t}{4D_1} + (\lambda_1 - \gamma)t\right)$$

$$\left\{\int_0^{\infty} Exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu - \int_0^{\alpha} Exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu\right\} \qquad (9)$$

where, $\alpha = \frac{z}{2\sqrt{D_1 t}}$ and

$$\varepsilon = \sqrt{\left(\frac{w_1^2}{4D_1} + \lambda_1 - \gamma\right)}\left(\frac{z}{2\sqrt{D_1}}\right).$$

Evaluation of the integral solution

The integration of the first term of equation (9) gives

$$\int_0^{\infty} Exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu = \frac{\sqrt{\pi}}{2} e^{-2\varepsilon} \qquad (10)$$

For convenience the second integral may be expressed on terms of error function (Horenstein, 1945), because this function is well tabulated.

Noting that

$$-\mu^2 - \frac{\varepsilon^2}{\mu^2} = -\left(\mu + \frac{\varepsilon}{\mu}\right)^2 + 2\varepsilon = -\left(\mu - \frac{\varepsilon}{\mu}\right)^2 - 2\varepsilon .$$

The second integral of equation (9) may be written as

$$I = \int_0^{\alpha} Exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right) d\mu = \frac{1}{2}\left\{e^{2\varepsilon}\int_0^{\alpha} Exp\left[-\left(\mu + \frac{\varepsilon}{\mu}\right)^2\right] d\mu + e^{-2\varepsilon}\int_0^{\alpha} Exp\left[-\left(\mu - \frac{\varepsilon}{\mu}\right)^2\right] d\mu\right\} \qquad (11)$$

Since the method of reducing integral to a tabulated function is the same for both integrals in the right side of equation (11), only the first term is considered. Let $a = \varepsilon/\mu$ and the integral may be expressed as

$$I_1 = e^{2\varepsilon}\int_0^{\alpha} Exp\left[-\left(\mu + \frac{\varepsilon}{\mu}\right)^2\right] d\mu$$

$$= -e^{2\varepsilon}\int_{\varepsilon/\alpha}^{\infty}\left(1 - \frac{\varepsilon}{a^2}\right) Exp\left[-\left(\frac{\varepsilon}{a} + a\right)^2\right] da + e^{2\varepsilon}\int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a} + a\right)^2\right] da \qquad (12)$$

Further, let, $\beta = \left(\frac{\varepsilon}{a} + a\right)$

in the $\beta = \frac{\varepsilon}{a} + a$ first term of the above equation, then

$$I_1 = -e^{2\varepsilon} \int_{\alpha+\frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta + e^{2\varepsilon} \int_{\frac{\varepsilon}{\alpha}}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a}+a\right)^2\right] da . \tag{13}$$

Similar evaluation of the second integral of equation (11) gives

$$I_2 = e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a}-a\right)^2\right] da - e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a}-a\right)^2\right] da$$

Again substituting $-\beta = \frac{\varepsilon}{a} - a$ into the first term, the result is

$$I_2 = e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta - e^{-2\varepsilon} \int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a}-a\right)^2\right] da .$$

Noting that

$$\int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(a+\frac{\varepsilon}{a}\right)^2 + 2\varepsilon\right] da = \int_{\varepsilon/\alpha}^{\infty} Exp\left[-\left(\frac{\varepsilon}{a}-a\right)^2 - 2\varepsilon\right] da$$

Substitution into equation (11) gives

$$I = \frac{1}{2}\left(e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta - e^{2\varepsilon} \int_{\alpha+\frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta\right) . \tag{14}$$

Thus, equation (9) may be expressed as

$$\frac{C}{C_0} = \frac{1}{2} Exp\left[\frac{w_1 z}{2D_1} - \gamma t\right] \left\{ Exp\left[\frac{\sqrt{w_1^2 + 4D_1(\lambda_1-\gamma)}}{2D_1} z\right] \right.$$

$$\Gamma(z,t) = \frac{2C_0}{\sqrt{\pi}} Exp\left(\frac{w_1^2 t}{4D_1} + (\lambda_1-\gamma)t\right) \left\{ \frac{\sqrt{\pi}}{2} e^{-2\varepsilon} - \frac{1}{2}\left[e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta - e^{2\varepsilon} \int_{\alpha+\frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta \right] \right\} \tag{15}$$

However, by definition,

$$e^{2\varepsilon} \int_{\alpha+\frac{\varepsilon}{\alpha}}^{\infty} e^{-\beta^2} d\beta = \frac{\sqrt{\pi}}{2} e^{2\varepsilon}\, erfc\left(\alpha + \frac{\varepsilon}{\alpha}\right)$$

also,

$$e^{-2\varepsilon} \int_{\frac{\varepsilon}{\alpha}-\alpha}^{\infty} e^{-\beta^2} d\beta = \frac{\sqrt{\pi}}{2} e^{-2\varepsilon}\left(1 + erf\left(\alpha - \frac{\varepsilon}{\alpha}\right)\right).$$

Writing equation (15) in terms of error functions, we get

$$\Gamma(z,t) = \frac{C_0}{2} Exp\left(\frac{w_1^2 t}{4D_1} + (\lambda_1-\gamma)t\right). \left[e^{2\varepsilon} erfc\left(\alpha+\frac{\varepsilon}{\alpha}\right) + e^{-2\varepsilon} erfc\left(\alpha-\frac{\varepsilon}{\alpha}\right)\right] \tag{16}$$

Thus, Substitution into equation (3) the solution is

$$\frac{C}{C_0} = \frac{1}{2} Exp\left[\frac{w_1 z}{2D_1} - \gamma t\right] \left[e^{-2\varepsilon} erfc\left(\alpha-\frac{\varepsilon}{\alpha}\right) + e^{2\varepsilon} erfc\left(\alpha+\frac{\varepsilon}{\alpha}\right)\right]$$

Re-substituting for ε and α gives

$$erfc\left[\frac{z + \sqrt{w_1^2 + 4D_1(\lambda_1-\gamma)}}{2\sqrt{D_1 t}} t\right] + \left[Exp\left[-\frac{\sqrt{w_1^2 + 4D_1(\lambda_1-\gamma)}}{2D_1} z\right] erfc\left[\frac{z - \sqrt{w_1^2 + 4D_1(\lambda_1-\gamma)}}{2\sqrt{D_1 t}} t\right]\right] \Bigg\} \tag{17}$$

where boundaries are symmetrical the solution of the problem is given by the first term the equation (17). The second term is equation (17) is thus due to the asymmetric boundary imposed in the more general problem. However, it should be noted also that if a point a great distance away from the source is considered, then it is possible to approximate the boundary condition by $C(-\infty, t) = C_0$, which leads to a symmetrical solution.

3. RESULTS & DISCUSSIONS:

This study presents analytical solutions for one-dimensional advection–dispersion equations in unsaturated porous medium in finite domain. The transform method coupled with the generalized integral transform technique is used to obtain the analytical solutions. Solutions are obtained for both first- and third-type inlet boundary conditions. The developed analytical solutions for finite domain are compared with solutions for the semi-infinite domain to clarify how the exit boundary influences the one-dimensional transport in a porous medium system.

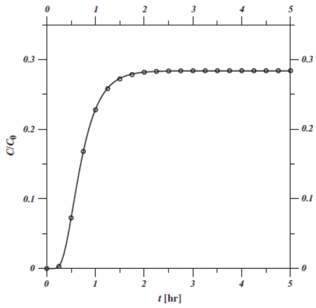

Fig. 2: Break-through-curve for C/C_0 v/s time for z=10m, R=1.0, λ=0.5 & γ = 0

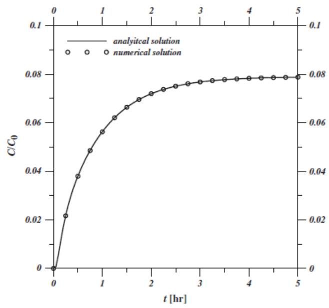

Fig. 3: Break-through-curve for C/C_0 v/s time for z=10m, R=1.0, λ=0.5 & γ = 0.25

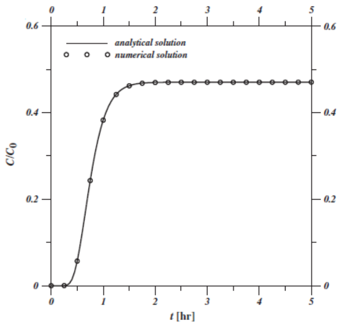

Fig. 4: Break-through-curve for C/C_0 v/s time for z=10m, R=1.0, λ=0.5 & γ = 0.5

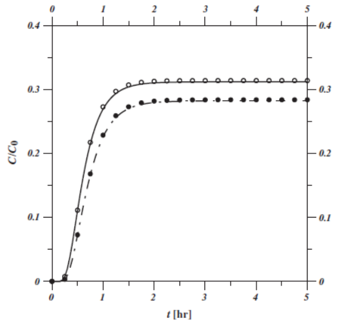

Fig. 5: Break-through-curve for C/C_0 v/s time for z=10m, R=1.0, λ=0.5, γ = 0.75 & 1.0

The main limitations of the analytical methods are that the applicability is for relatively simple problems. The geometry of the problem should be regular. The properties of the soil in the region considered must be homogeneous in the sub region. The analytical method is somewhat more flexible than the standard form of other methods for one-dimensional transport model. Figures 1 to 4 represents the concentration profiles verses time in the adsorbing media for depth z = 10m and Retardation factor R=1. It is seen that for a fixed velocity w, dispersion coefficient D and distribution coefficient K_d, C/C_0 decreases with depth as porosity n decreases due to the distributive coefficient K_d and if time increases the concentration decreases for different time and decay chain.

Accordingly, the analytical solutions derived for the finite domain will thus be particularly useful for analyzing the one-dimensional transport in unsaturated porous medium with a large dispersion coefficient whereas the analytical solution for semi-infinite domain is recommended to be applied for a medium system with a small dispersion coefficient. Moreover, the developed solution is especially useful for validating numerical model simulated solution because realistic problems generally have a finite domain.

From this paper, we conclude that the mathematical solutions have been developed for predicting the possible concentration of a given dissolved substance in steady unidirectional seepage flows through semi-infinite, homogeneous, and isotropic porous media subject to source concentration that vary exponentially with time for spatially variable retardation factor using a change of variable and integral transform technique. The expressions take into account the contaminants as well as mass transfer from the liquid to the solid phase due to adsorption. For simultaneous dispersion and adsorption of a solute, the dispersion system is considered to be adsorbing at a rate proportional to its concentration.

ISSN: 2278-0181
ICESMART-2015 Conference Proceedings

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