# An Analytical Solution of Transport of Pollutants in Unsaturated Porous Media with and Without Adsorption

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***Abstract:*** **Most of the investigators use the coordinate transformation (z - *ut*) in order to solve the equation for dispersion of a moving fluid in porous media. Further, the boundary conditions $C = 0$ at z = $\infty$ and $C = C_0$ at z = $-\infty$ for $t > 0$ are used, which results in a symmetrical concentration distribution. In this paper, the effect of adsorption has been studied for one-dimensional transport of pollutants through the unsaturated porous media. In this study, the advection-dispersion equation has been solved analytically to evaluate the transport of pollutants which takes into account of dissipation coefficient and porosity by considering input concentrations of pollutants that vary with time and depth. The solution has been obtained using Laplace transform, moving coordinates and Duhamel's theorem is used to get the solution in terms of complementary error function.**

***Key words:*** ***Advection, dispersion, adsorption, Integral transforms, Fick's law, Moving coordinates, Duhamel's theorem***

## 1. INTRODUCTION:

In recent years considerable interest and attention have been directed to dispersion phenomena in flow through porous media. Scheidegger (1954), deJong (1958), and Day (1956) have presented statistical means to establish the concentration distribution and the dispersion coefficient. Advection–diffusion equation describes the solute transport due to combined effect of diffusion and convection in a medium. It is a partial differential equation of parabolic type, derived on the principle of conservation of mass using Fick's law. Due to the growing surface and subsurface hydro environment degradation and the air pollution, the advection–diffusion equation has drawn significant attention of hydrologists, civil engineers and mathematical modelers. Its analytical/numerical solutions along with an initial condition and two boundary conditions help to understand the contaminant or pollutant concentration distribution behavior through an open medium like air, rivers, lakes and porous medium like aquifer, on the basis of which remedial processes to reduce or eliminate the damages may be enforced. It has wide applications in other disciplines too, like soil physics, petroleum engineering, chemical engineering and biosciences.

In the initial works while obtaining the analytical solutions of dispersion problems in ideal conditions, the basic approach was to reduce the advection–diffusion equation into a diffusion equation by eliminating the convective term(s). It was done either by introducing moving co-ordinates (Ogata and Banks 1961; Harleman and Rumer 1963; Bear 1972; Guvanasen and Volker 1983; Aral and Liao 1996; Marshal *et al* 1996) or by introducing another dependent variable (Banks and Ali 1964 Ogata 1970; Lai and Jurinak 1971; Marino 1974 and Al-Niami and Rushton 1977). Then Laplace transformation technique has been used to get desired solutions.

Some of the one-dimensional solutions have been given (Tracy 1995) by transforming the non-linear advection–diffusion equation into a linear one for specific forms of the moisture content *vs.* pressure head and relative hydraulic conductivity *vs.* pressure head curves which allow both two-dimensional and three-dimensional solutions to be derived. A method has been given to solve the transport equations for a kinetically adsorbing solute in a porous medium with spatially varying velocity field and dispersion coefficients (Van Kooten 1996, Sudheendra et.al. 2014).

Later it has been shown that some large subsurface formations exhibit variable dispersivity properties, either as a function of time or as a function of distance (Matheron and deMarsily 1980; Sposito *et al*

1986; Gelhar *et al* 1992). Analytical solutions were developed for describing the transport of dissolved substances in heterogeneous semi infinite porous media with a distance dependent dispersion of exponential nature along the uniform flow (Yates 1990, 1992). The temporal moment solution for one dimensional advective-dispersive solute transport with linear equilibrium sorption and first order degradation for time pulse sources has been applied to analyze soil column experimental data (Pang *et al* 2003, Sudheendra et.al. 2014). An analytical approach was developed for non-equilibrium transport of reactive solutes in the unsaturated zone during an infiltration–redistribution cycle (Severino and Indelman 2004).

The solute is transported by advection and obeys linear kinetics. Analytical solutions were presented for solute transport in rivers including the effects of transient storage and first order decay (Smedt 2006, Sudheendra 2011, 2012). Pore flow velocity was assumed to be a non-divergence, free, unsteady and non-stationary random function of space and time for ground water contaminant transport in a heterogeneous media (Sirin 2006). A two-dimensional semi-analytical solution was presented to analyze stream–aquifer interactions in a coastal aquifer where groundwater level responds to tidal effects (Kim *et al* 2007).

A more direct method is presented here for solving the differential equation governing the process of dispersion. It is assumed that the porous medium is homogeneous and isotropic and that no mass transfer occurs between the solid and liquid phases. It is assumed also that the solute transport, across any fixed plane, due to microscopic velocity variations in the flow tubes, may be quantitatively expressed as the product of a dispersion coefficient and the concentration gradient. The flow in the medium is assumed to be unidirectional and the average velocity is taken to be constant throughout the length of the flow field. In this paper, the solutions are obtained for two solute dispersion problems in a longitudinal finite length, respectively. In the first problem time dependent solute dispersion of increasing or decreasing nature along a uniform flow through a homogeneous domain is studied. The input condition is of uniform and varying nature, respectively.

## 2. MATHEMATICAL FORMULATION AND MODEL

We consider one-dimensional unsteady flow through the semi-infinite unsaturated porous media in the x-z plane in the presence of a toxic material. The uniform flow is in the z-direction. The medium is assumed to be isotropic and homogeneous so that all physical quantities are assumed to be constant. Initially the concentration of the contaminant in the media is assumed to be zero and a constant source of concentration of strength $C_0$ exists at the surface. The velocity of the groundwater is assumed to be constant. With these assumptions the basic equation governing the flow is

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

where $C$ is the constituent concentration in the soil solution, $t$ is the time in minutes, $D$ is the hydrodynamic dispersion coefficient, $z$ is the depth, $u$ is the average pore-water velocity and $\frac{1-n}{n}K_d C$ is the adsorption term.

Initially saturated flow of fluid of concentration, C = 0, takes place in the medium. At t = 0, the concentration of the plane source is instantaneously changed to $C = C_0$. Then the initial and boundary conditions (Fig. 1) for a semi-infinite column and for a step input are

$$\left.\begin{aligned} C(z,\ 0) &= 0\ ; \quad z \ge 0 \\ C(0,\ t) &= C_0\ ; \quad t \ge 0 \\ C(\infty,\ t) &= 0\ ; \quad t \ge 0 \end{aligned}\right\} \qquad (2)$$

The problem then is to characterize the concentration as a function of x and t.

To reduce equation (1) to a more familiar form, let

$$C(z,\ t) = \Gamma(z,\ t)\exp\left[\frac{wz}{2D} - \frac{w^2 t}{4D} - \frac{(1-n)}{n}K_d t\right] \qquad (3)$$

Substitution of equation (3) reduces equation (1) to Fick's law of diffusion equation

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

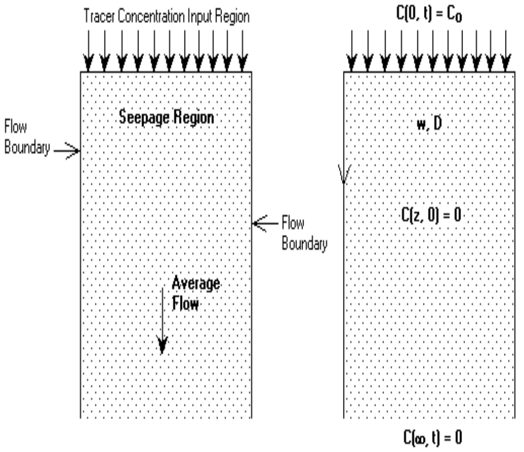


**Figure 1 : Physical Layout of the Model**

The above initial and boundary conditions (2) transform to

$$\left.\begin{aligned}\Gamma(0,\ t)&=C_0\ \exp\left(\frac{w^2t}{4D}+\frac{(1-n)}{n}K_d t\right); && t\geq 0\\ \Gamma(z,\ 0)&=0\,; && z\geq 0\\ \Gamma(\infty,\ t)&=0\,; && t\geq 0\end{aligned}\right\}\quad (5)$$

It is thus required that equation (4) be solved for a time dependent influx of fluid at z = 0. The solution of equation (4) can be obtained by using Duhamel's theorem [Carslaw and Jeager, 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 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

$$\left.\begin{aligned}\Gamma(0,\ t)&=1\,; && t\geq 0\\ \Gamma\ (z,\ 0)&=0\,; && z\geq 0\\ \Gamma(\infty,\ t)&=0\,; && t\geq 0\end{aligned}\right\}.$$

This problem can be solved by the application of the Laplace transform. The concentration Γ which is function of t and whatever space coordinates, say z, t, occur in the problem. We write

$$\overline{\Gamma}(z,\ p)=\int_0^\infty e^{-pt}\ \Gamma(z,\ t)\,dt$$

Hence, if equation (4) is multiplied by $e^{-pt}$ and integrated term by term it is reduced to an ordinary differential equation

$$\frac{d^2\overline{\Gamma}}{dz^2}=\frac{p}{D}\,\overline{\Gamma}\qquad (6)$$

The solution of the equation (6) can be written as

$$\overline{\Gamma}=A\,e^{-qz}+B\,e^{qz}$$

where $q=\sqrt{\dfrac{p}{D}}$.

The boundary condition as z → ∞ requires that B = 0 and boundary condition at z = 0 requires that $A={}^{1}\!/_{p}$, thus the particular solution of the Laplace transform equation is

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

The inversion of the above function is given in a table of Laplace transforms (Carslaw and Jaeger, 1947). The result is

$$\Gamma=1-erf\left(\frac{x}{2\sqrt{Dt}}\right)=\frac{2}{\sqrt{\pi}}\int_{\frac{z}{2\sqrt{Dt}}}^{\infty}e^{-\eta^2}\,d\eta.\qquad (7)$$

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

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

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

$$\frac{2}{\sqrt{\pi}}\frac{\partial}{\partial t}\int_{\frac{z}{2\sqrt{D(t-\tau)}}}^{\infty}e^{-\eta^2}\,d\eta\ =\frac{z}{2\sqrt{\pi D}(t-\tau)^{3/2}}\,e^{-z^2/4D(t-\tau)}$$

The solution of the problems is

$$\Gamma=\frac{z}{\pi\sqrt{D}}\int_0^t\phi(t)\,e^{-z^2/4D(t-\tau)}\frac{d\tau}{(t-\tau)^{3/2}}$$

Letting

$$\mu=\frac{z}{2\sqrt{D(t-\tau)}}$$

the solution can be written as

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

Since $\phi(t)=C_0\exp\left(\dfrac{w^2t}{4D}+\dfrac{(1-n)}{n}K_d t\right)$ the particular solution of the problem can be written as

$$\Gamma(z,\ t)=\frac{2C_0}{\sqrt{\pi}}e^{\left(\frac{w^2}{4D}+\frac{(1-n)}{n}K_d\right)t}$$

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

(9)

where $\varepsilon = \sqrt{\left(\frac{w^2}{4D} + \frac{(1-n)}{n}K_d\right)}\frac{z}{2\sqrt{D}}$ and $\alpha = \frac{z}{2\sqrt{Dt}}$.

### 3. Evaluation of the integral solution

The integration of the first term of equation (9) gives (Pierce, 1956)

$$\int_0^\infty e^{-\mu^2 - \frac{\varepsilon^2}{\mu^2}} d\frac{(1-n)}{n}K_d C = \frac{\sqrt{\pi}}{2}e^{-2\varepsilon}$$

For convenience the second integral can be expressed in 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) can be written as

$$I = \int_0^\alpha \exp\left(-\mu^2 - \frac{\varepsilon^2}{\mu^2}\right)d\mu$$

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

(10)

Since the method of reducing integral to a tabulated function is the same for both integrals in the right side of equation (10), only the first term is considered. Let $a = \frac{\varepsilon}{\mu}$ and adding and subtracting, we get

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

The integral can be expressed as

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

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

Further, let

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

in the first term of the above equation, then

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

Similar evaluation of the second integral of equation (10) 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

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

Substitute this into equation (10) gives

$$I = e^{-2\varepsilon}\int_{\frac{\varepsilon}{\alpha}-\alpha}^\infty e^{-\beta^2}d\beta - e^{2\varepsilon}\int_{\frac{\varepsilon}{\alpha}+\alpha}^\infty e^{-\beta^2}d\beta.$$

Thus, equation (9) can be expressed as

$$\Gamma(z,t) = \frac{2C_0}{\sqrt{\pi}}e^{\left(\frac{w^2}{4D} + \frac{(1-n)}{n}K_d\right)t}.$$

$$\left\{\frac{\sqrt{\pi}}{2}e^{-2\varepsilon} - \frac{1}{2}\left[e^{-2\varepsilon}\int_{\frac{\varepsilon}{\alpha}-\alpha}^\infty e^{-\beta^2}d\beta - e^{2\varepsilon}\int_{\frac{\varepsilon}{\alpha}+\alpha}^\infty e^{-\beta^2}d\beta\right]\right\} \quad (11)$$

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 (11) in terms of the error functions, we get

$$\Gamma(z,t) = \frac{C_0}{2} e^{\left(\frac{w^2}{4D}+\frac{(1-n)}{n}K_d\right)t}\left[e^{2\varepsilon} erfc\left(\alpha+\frac{\varepsilon}{\alpha}\right) + e^{-2\varepsilon} erfc\left(\alpha-\frac{\varepsilon}{\alpha}\right)\right]$$

Substitute the value of $\Gamma(z,t)$ in equation (3) the solution reduces to

$$\frac{C}{C_0} = \frac{1}{2}\exp\left[\frac{wz}{2D}\right]\left[e^{2\varepsilon} erfc\left(\alpha+\frac{\varepsilon}{\alpha}\right) + e^{-2\varepsilon} erfc\left(\alpha-\frac{\varepsilon}{\alpha}\right)\right]. \quad (12)$$

Resubstituting the value of ε and α gives

$$\frac{C}{C_0} = \frac{1}{2}\exp\left[\frac{wz}{2D}\right]\left[\exp\left[\left(\sqrt{\frac{w^2}{4D}+\frac{(1-n)}{n}K_d}\right)\frac{z}{\sqrt{D}}\right] \cdot erfc\left(\frac{z}{2\sqrt{Dt}} - \sqrt{\frac{w^2 t}{4D}+\frac{(1-n)}{n}K_d t}\right) + \exp\left[-\left(\sqrt{\frac{w^2}{4D}+\frac{(1-n)}{n}K_d}\right)\frac{z}{\sqrt{D}}\right]\right]. \cdot erfc\left(\frac{z}{2\sqrt{Dt}} - \sqrt{\frac{w^2 t}{4D}+\frac{(1-n)}{n}K_d t}\right) \quad (13)$$

where boundaries are symmetrical the solution of the problem is given by the first term of equation (13). The second term in equation (13) is thus due to the asymmetric boundary imposed in a general problem. However, it should be noted that if a point a great distance away from the source is considered, then it is possible to appropriate the boundary conditions by $C(-\infty, t) = C_0$, which leads to a symmetrical solution.

**4. Results & Discussions:**

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 distance along the media for different values of porosity n. 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 $K_d$, whereas concentration profile versus time for different values of depth z. For a fixed z it is seen that concentration increases in the beginning due to lesser effect of dispersion coefficient D and reaches a steady-state value for larger time.

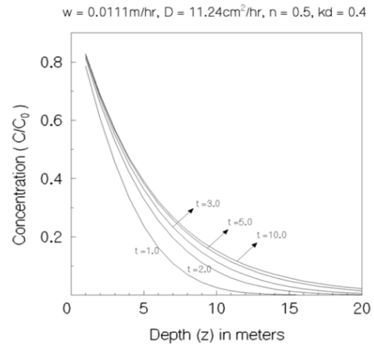


Fig. 1: Break-through-curve for $C/C_0$ v/s depth for n=0.5 and $K_d$=0.4

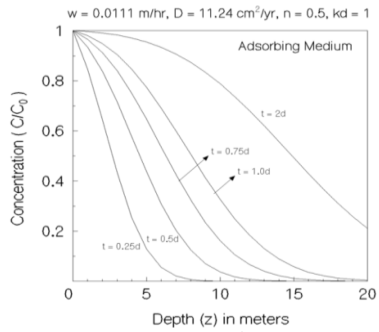


Fig. 2: Break-through-curve for $C/C_0$ v/s depth for n=0.5 and $K_d$=1.0

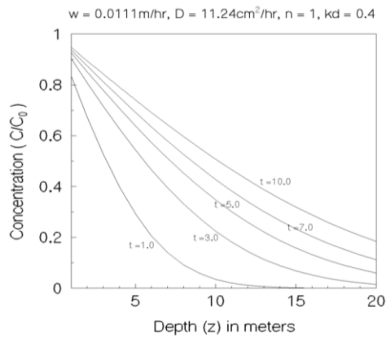


Fig. 3: Break-through-curve for $C/C_0$ v/s depth for n=1.0 and $K_d$=0.4

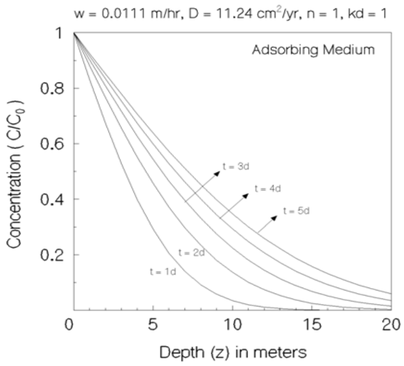

Fig. 4: Break-through-curve for $C/C_0$ v/s depth for n=1.0 and $K_d$=1.0

The figures represent $C/C_0$ verses time for different values of distribution coefficient $K_d$. It is seen that for a fixed $K_d$, concentration increases slowly up to t=10 days because of the less adsorption of pollutants on the solid surface and then reaches a constant value for larger time where the effect of distribution coefficient $K_d$ is small. We conclude that the integral transform method is a powerful method to derive analytical solutions for solute transport of a adsorption in homogeneous porous media and under different flow conditions. Steady-state concentration distributions and temporal moments can be directly derived from these solutions and transient concentration distribution is accessible via numerical inversion. The derived solutions are of great value for bench-marking numerical reactive transport codes.

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