

Pollutant Fate and Transport in Groundwater Systems

In this portion of Fate[©], we are concerned with instantaneous and step releases of a pollutant into a groundwater system. Instantaneous inputs to groundwater generally result from spills or short-term releases from pipes, tanks, or lagoons. Continuous (step) releases can occur from landfill, leaking storage tanks, and from groundwater wells.

Groundwater contaminant transport, as in contaminant transport in rivers, is controlled by the physical processes of advection and dispersion. However, the causes of dispersion in a groundwater system are somewhat different from those in a river. Dispersion in groundwater systems can be broken down into microscale and macroscale processes. Microscale variables include molecular diffusion, pore sizes, flow path lengths, velocity gradients within flow paths, and diverging flow paths. Macroscale dispersion is caused by large-scale variations within the aquifer. In general, dispersion is larger in a groundwater system than in a river because of the greater number of mechanisms causing dispersion in an aquifer.

Conceptual Development of Governing Fate and Transport Equation

Step Pollutant Input: The governing equation shown in the Figure 2 can seem intimidating. But groundwater modeling, especially that of step inputs, is very complicated. As described in the instantaneous groundwater model, there are many chemical and physical processes that we must account for in aquifer media. The same complex dynamics of dispersion, retardation, and degradation that were discussed for instantaneous inputs also apply to step inputs. In addition to these processes, in considering step inputs, we must account for spreading of the constantly emitted pollutant. This is completed using an mathematical error function, represented by erfc in the figure. As in the equation governing instantaneous fate and transport, we again use v for the average water velocity, t for time, C_0 for the initial concentration of pollutant, and x for distance from the point of introduction (usually a groundwater well or landfill). Using this approach, we can estimate the concentration of pollutant downgradient (as a function of distance or time) from the point of introduction. In the following figure, you will note that the pollutant plume is continuous and increases in height and diameter. You may also want to consider how the estimated pollutant concentration would change if we were using a three-dimensional model. Next, we will develop the mathematical approach to groundwater modeling.

Step Pollutant Input

$$C(x,t) = \left(\frac{C_0}{2} \right) \left(e^{\left(\frac{x}{2\alpha_x} \right) \left(1 - \left(1 + \frac{R4k\alpha_x}{v} \right)^{\frac{1}{2}} \right)} \right) \left(\operatorname{erfc} \left(\frac{x - \left(\frac{v}{R} \right) t \left(1 + 4k \frac{R\alpha_x}{v} \right)^{\frac{1}{2}}}{2 \left(\alpha_x \left(\frac{v}{R} \right) t \right)^{\frac{1}{2}}} \right) \right)$$

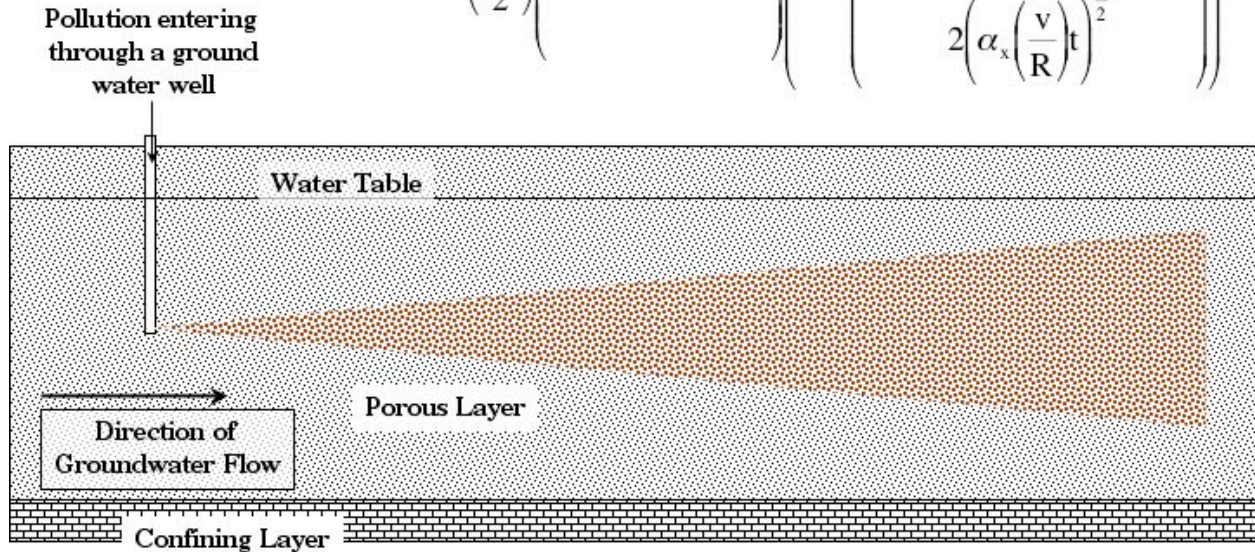


Figure 2. Step (pulse) input of pollution to an aquifer.

Mathematical Approach to a Lake System

Although groundwater is actually a three-dimensional system, we will use a one-dimensional model in Fate[®] in order to simplify the mathematics. The primary consequence of ignoring transport in the y and z directions is an underestimation the dilution of the contaminant by spreading in these directions. The fundamental processes involved are the same in one or three dimensions.

Advection in one dimension can be described as

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x},$$

where C = concentration,
 v_x = velocity in the x direction,
 t = time, and
 x = distance.

Dispersion can be represented by Fick's Law in one dimension

$$\frac{\partial C}{\partial t} = D_x \frac{\partial^2 C}{\partial x^2},$$

where D_x = the diffusion coefficient (cm^2/sec).

Chemical processes such as the biological degradation of organic compounds or the decay of radioactive compounds may also be important to the fate of groundwater contaminants. First-order degradation may be expressed as

$$\frac{dC}{dt} = -kC,$$

where k = the first order rate constant ($1/\text{sec}$) for the specific process.

If we perform a mass balance over an elemental volume of an aquifer including the processes of advection, dispersion, and first-order chemical reaction, we obtain the following equation,

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - kC. \quad \text{Eqn 1}$$

Equation 1 is commonly referred to as the advective-dispersive equation. This is the same equation that governs step-inputs of a contaminant to groundwater.

The most common reaction of contaminants in groundwater is adsorption. Adsorption is the attachment of a compound to a surface and is frequently modeled using a distribution coefficient, K_d .

$$K_d = \frac{S}{C},$$

where S = concentration adsorbed (mg/g), and
 C = concentration in solution (mg/mL).

The distribution coefficient assumes that the reaction is reversible and at equilibrium.

The concentration of a contaminant adsorbed to the solid phase may be described as,

$$\frac{\partial S}{\partial t} = K_d \frac{\partial C}{\partial t},$$

where S = the contaminant mass on the solid phase.

To convert S into mass adsorbed per elemental volume of porous media, we need to introduce bulk density, ρ_b , so that

$$\frac{\partial C^*}{\partial t} = \rho_b K_d \frac{\partial C}{\partial t},$$

where C^* = the contaminant mass on the solid phase within an elemental volume.

To convert from mass per elemental volume to mass per void volume, we must incorporate porosity, n , as

$$\frac{\partial C_v}{\partial t} = \frac{\rho_b K_d}{n} \frac{\partial C}{\partial t},$$

where C_v = the of mass sorbed contaminant per void volume.

We can incorporate the above relationship into the advective-dispersive equation to yield

$$\frac{\partial C}{\partial t} = v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \left[\frac{\rho_b K_d}{n} \right] \frac{\partial C}{\partial t} \quad \text{Eqn 2.}$$

The previous equation can be rearranged to yield

$$\frac{\partial C}{\partial t} \left[1 + \frac{\rho_b K_d}{n} \right] = v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} \quad \text{Eqn 3.}, \text{ or}$$

$$R \frac{\partial C}{\partial t} = v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} \quad \text{Eqn 3.}$$

The term $1 + \frac{\rho_b K_d}{n}$ is called the retardation factor, R . The retardation factor represents the retardation of the solute relative to the average groundwater velocity (v), or

$$R = \frac{v}{v_c},$$

where v_c = the contaminant velocity, and
 v = the groundwater velocity.

When $v = v_c$, $R = 1$ and the contaminant is said to be conservative (i.e. it does not adsorb to the solid and has a K_d value of 0).

Step Pollutant Input: For the initial condition $C(x,0) = 0$, where the concentration equals zero everywhere, and the boundary condition $C(0,t) = C_0$, where the concentration at the source remains constant at the value of C_0 , the advective-dispersive equation may be solved using Laplace transformations to yield

$$C(x,t) = \frac{C_0}{2} e^{-\frac{kx}{v}} + \frac{C_0}{2} e^{-\frac{Rkx}{v}} + \frac{C_0}{2} e^{-\frac{4kR^2x^2}{v^2t}} + \frac{C_0}{2} \operatorname{erfc} \left[\frac{x + \frac{v}{R}t + \frac{4kR^2x^2}{v^2t}}{2\sqrt{\frac{v}{R}t}} \right] + \frac{C_0}{2} e^{-\frac{kx}{v}} \operatorname{erfc} \left[\frac{x + \frac{v}{R}t + \frac{4kR^2x^2}{v^2t}}{2\sqrt{\frac{v}{R}t}} \right]$$

where C_0 = the initial concentration of the contaminant,
 x = distance from the source,
 α_x = longitudinal dispersivity,
 k = the first-order reaction rate,
 v = velocity,
 t = time, and
 erfc = the complementary error function.

The final term in the above equation,

$$e^{-\frac{kx}{v}} \operatorname{erfc} \left[\frac{x + \frac{v}{R}t + \frac{4kR^2x^2}{v^2t}}{2\sqrt{\frac{v}{R}t}} \right]$$

is generally considered insignificant and is ignored. This term is ignored in Fate[©].

Finally, we will discuss two terms in the final fate and transport equations. Dispersion in groundwater, as in rivers, is a function of velocity, or

$$D = \alpha_x v,$$

where α_x is the called the dispersivity.

Because dispersivity is a function only of the aquifer matrix and not of velocity, it is used in many groundwater models in preference to the dispersion coefficient. Because of the many causes of dispersion, discussed previously, dispersivity is one of the most difficult parameters to measure accurately. Dispersivity values tend to increase with the scale over which they were measured because the degree of heterogeneity within the aquifer generally increases with the scale.

The error function is the area between the midpoint of the normal curve and the value you are taking the error function of. The complementary error function is the error function subtracted from one, and accounts for the spreading of the plume.

References:

Fetter, C.W. *Applied Hydrogeology*. Charles E. Merrill Publishing Company, Toronto, 1980.

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