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FATE AND TRANSPORT OF POLLUTANTS IN GROUNDWATER SYSTEMS

Purpose: To learn two basic models for predicting the fate and transport of pollutants in groundwater systems

BACKGROUND

In this exercise 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

Instantaneous Pollutant Input

Before we show the mathematical development of the governing equation for an instantaneous input, we present a conceptual approach that shows how each part of the equation relates to a physical model of an aquifer (illustrated below). First, we should note that a groundwater system is one of the most complicated environmental systems to model.

Unlike in river and lake systems modeled in Fate, pollution entering the aquifer is not mixed immediately but mixes with the groundwater as it is transported downgradient (the equivalent of downstream in a river). We handle this in the model by introducing a dispersion term, D_x . Since we are modeling only in the longitudinal (x) direction, we have only one dispersion term. If we were using a three-dimensional model, we would also need terms in the y and z directions. In addition to dispersion, most pollutants in groundwater systems react (adsorb and desorb) with the soils and minerals of the aquifer. To account for these reactions, we add a retardation term (R) calculated from the adsorption coefficient (K , described in the mathematical section below). We must also correct the volume term to account for solid particles. This is accounted for in the R term by multiplying by the bulk density (which gives an estimate of the water volume, also described in the mathematical section). We also account for chemical and biological degradation using a first-order reaction constant, k .

In the equation governing instantaneous fate and transport, we use v for the average water velocity, t for time, M for the added mass of pollutant, and x for distance from the point of introduction (usually, a groundwater well for landfill). Using this approach, we can estimate the concentration of pollutant downgradient from the point of introduction. One assumption of the model is that the pollution is added over the entire height of the porous aquifer material. In Figure 26-1, the spread of pollution downgradient is illustrated by shaded areas transitioning to larger and larger rectangles (from left to right). The increase in the size of the pollution plume is a result of mixing with the groundwater, which also dilutes the pollution and decreases the pollutant concentration. The change in shape is also a result of the adsorption/desorption phenomena and the fact that dispersion (mixing) in the x direction is the greatest. Next, we develop the model for step inputs of pollution.

Step Pollutant Input

The governing equation shown in Figure 26-2 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

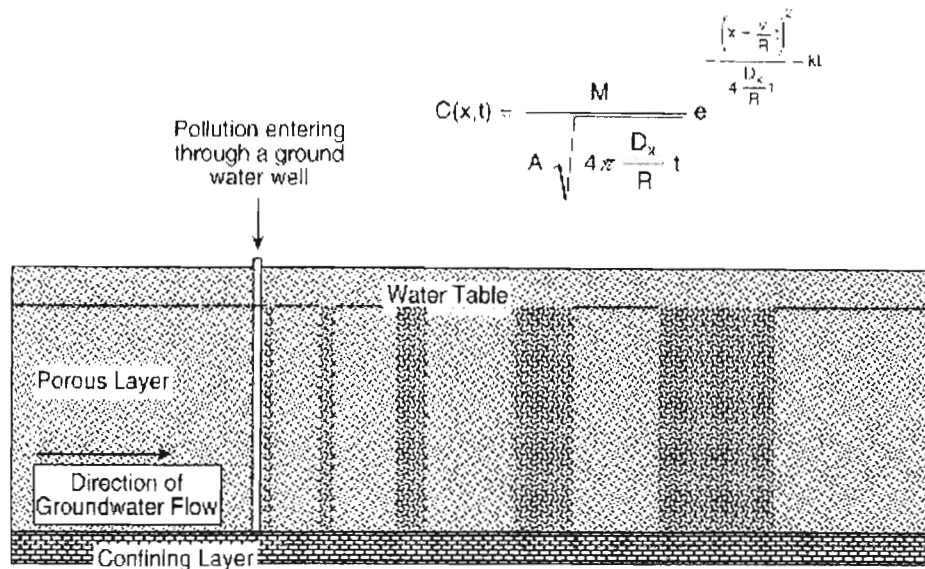


Figure 26-1. Instantaneous (pulse) input of pollution to an aquifer.

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 a 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.

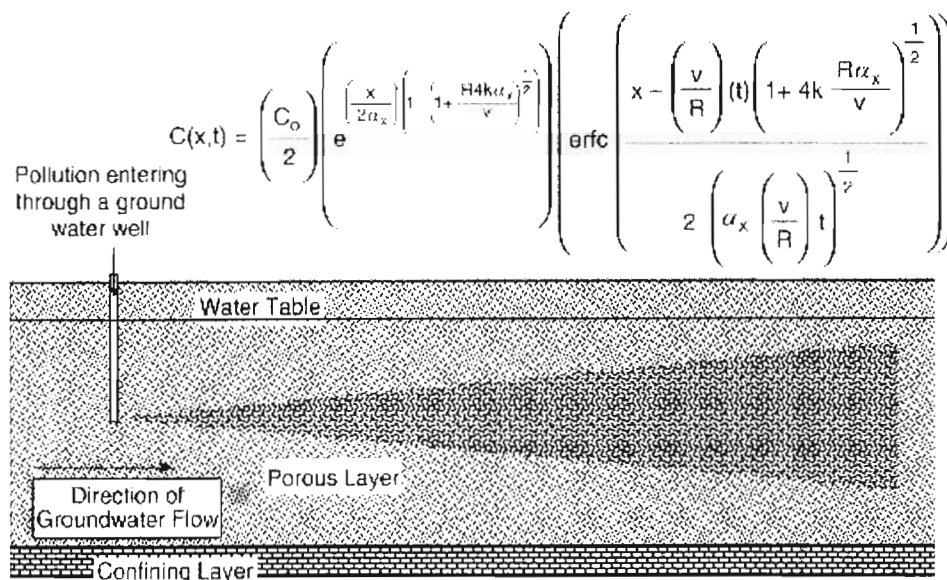


Figure 26-2. Step (continuous) input of pollution to an aquifer.

consider how the estimated pollutant concentration would change if we were using a three-dimensional model. Next, we develop the mathematical approach to groundwater modeling.

Mathematical Approach to a Lake System

Although groundwater is actually a three-dimensional system, we use a one-dimensional model in Fate to simplify the mathematics. The primary consequence of ignoring transport in the y and z directions is an underestimation of 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 is the concentration, v_x the velocity in the x direction, t the time, and x the 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 is the diffusion coefficient (cm^2/s).

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 is the first-order rate constant (s^{-1}) 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 equation

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - kC \quad (26-1)$$

Equation (26-1) 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*, the attachment of a compound to a surface, is frequently modeled using a distribution coefficient, K_d :

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

where S is the concentration adsorbed (mg/g) and, C is the 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 is 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^* is 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

$$\frac{\partial C_v}{\partial t} = \frac{\rho_b K_d}{n} \frac{\partial C}{\partial t} \quad (26-2)$$

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

We can incorporate relationship (26-2) into the advective-dispersive equation to yield

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b K_d}{n} \frac{\partial C}{\partial t} - kC \quad (26-3)$$

Equation (26-2) can be rearranged to yield

$$\frac{\partial C}{\partial t} \left(1 + \frac{\rho_b K_d}{n} \right) = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - kC$$

or

$$R \frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - kC \quad (26-4)$$

The term $1 + \rho_b K_d/n$ 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 is the contaminant velocity and v is 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).

Instantaneous Pollutant Input

If we assume that the spill contaminates the entire thickness of the aquifer, equation (26-4) can be integrated to yield

$$C(x, t) = \frac{M}{A\sqrt{4\pi(D_x/R)t}} \exp\left\{-\frac{[x - (v/R)t]^2}{A(D_x/R)t} - kt\right\}$$

where x = distance from the source

t = time

M = mass of contaminant added to the aquifer

A = cross-sectional void volume contaminated by the pollution

D_x = dispersion coefficient

R = retardation factor

v = velocity

k = first-order reaction rate

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

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

where C_0 = initial concentration of the contaminant

x = distance from the source

α_x = longitudinal dispersivity

k = first-order reaction rate

v = velocity

t = time

erfc = complementary error function

The final term in equation (26-5),

$$e^{x/\alpha_x} \operatorname{erfc} \left\{ \frac{x + (v/R)t[1 + 4k(R\alpha_x/v)]^{1/2}}{2[\alpha_x(v/R)t]^{1/2}} \right\}$$

is generally considered insignificant and is ignored; the term is also ignored in Fate.

Finally, we 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 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 for which you are taking the error function. The *complementary error function*, the error function subtracted from 1, accounts for the spreading of the plume.

REFERENCES

- Fetter C. W., *Applied Hydrogeology*, Charles E. Merrill, Toronto, 1980.
 Fetter C. W., *Contaminant Hydrogeology*, Macmillan, New York, 1993.