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

Instantaneous Pollutant Input: Before we show the mathematical development of the governing equation for an instantaneous input, we will 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 immediately mixed 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 in only the longitudinal (x) direction, we only have one dispersion term. If we were using a three-dimensional model, we would also need terms in the y and z direction. 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 the Figure 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 will develop the model for step inputs of pollution.
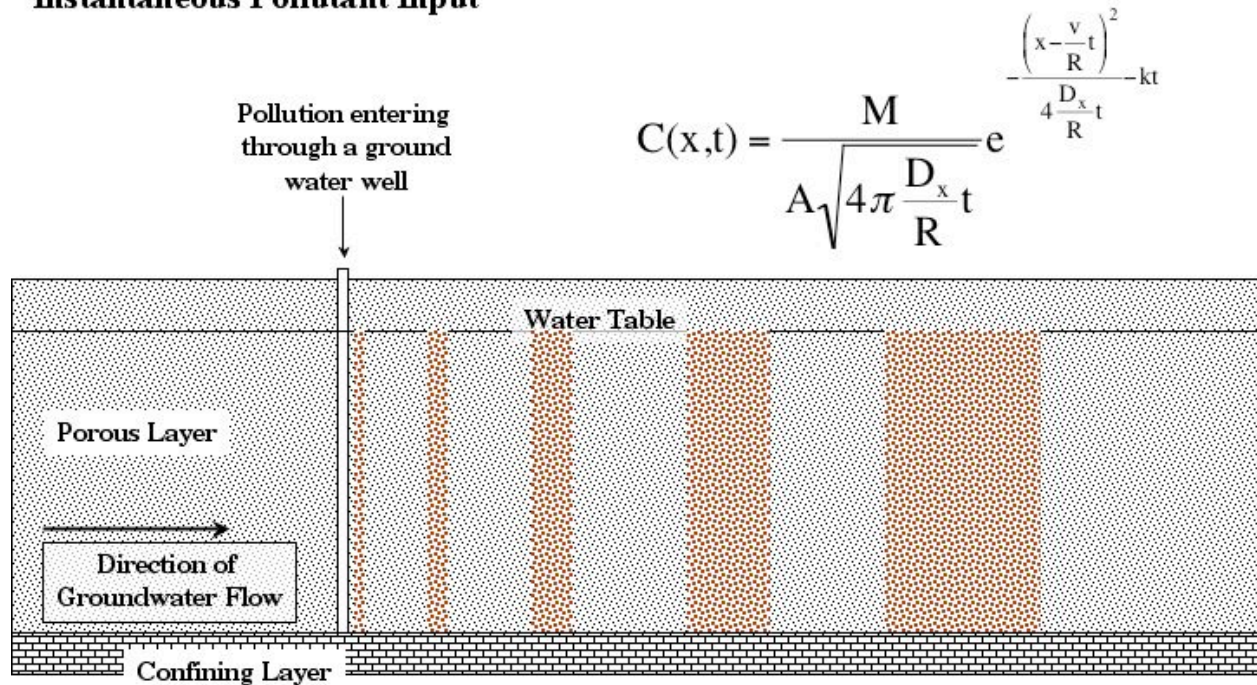
Instantaneous Pollutant Input

Pollution entering
through a ground
water well

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

Water Table

Porous Layer

Direction of
Groundwater Flow

Confining Layer

Figure 1. Illustration of a step (continuous) 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.

<u>Advection</u> 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/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,

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

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

$$\frac{\partial C}{\partial t} = -v_x \frac{\partial C}{\partial x} + D_x \frac{\partial^2 C}{\partial x^2} - \frac{\rho_b K_d}{n} \frac{\partial C}{\partial t} - kC. \qquad \text{Eqn 2.}$$

The previous equation can be rearranged to yield

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

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

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).

Instantaneous Pollutant Input: If we assume the spill contaminates the entire thickness of the aquifer, Equation 3 can be integrated to yield

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

where x = distance from the source,
t = time,
M = the mass of contaminant added to the aquifer,
A = the cross-sectional void volume contaminated by
the pollution
D_x = the dispersion coefficient,
R = the retardation factor,
v = velocity, and
k = the first-order reaction rate.

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.

Fetter, C.W. *Contaminant Hydrogeology*. Macmillan Publishing Company, New York, 1993.