

So, how does one obtain estimates of dispersion for a polluted site? There is not one absolute answer to this. Unfortunately, you cannot usually perform the extensive characterization experiments at the polluted site, due to cost and fear of increasing the environmental damage from the contamination by pumping pollutants off site. But when possible (when sufficient accuracy is needed to warrant the expense), dispersion and water velocity estimates can be obtained through experimentation at a site with geology similar to that of the polluted area (generally near the polluted site). As a worst-case scenario, one could use data from Figure 8.21 or similar plots, but fate and transport prediction must use the complete range of dispersion values present in the plot at each distance from the point source. One of the best, and perhaps most common, ways of estimating site-specific dispersion coefficients is to perform explanatory modeling on the contaminated site based on historical input source data and results from an extensive groundwater monitoring program. Then the estimated dispersion coefficients, water velocities, and  $K$  values can be used to perform future fate and transport modeling.

## 8.7 MATHEMATICAL MODELS

*Instantaneous (Pulse) Pollutant Input.* If we assume the spill contaminates the entire thickness of the aquifer, as shown in Figure 8.22, an equation can be obtained using Laplace transformation to predict the pollutant concentration as a function of time or distance from the point source:

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

### Instantaneous Pollutant Input

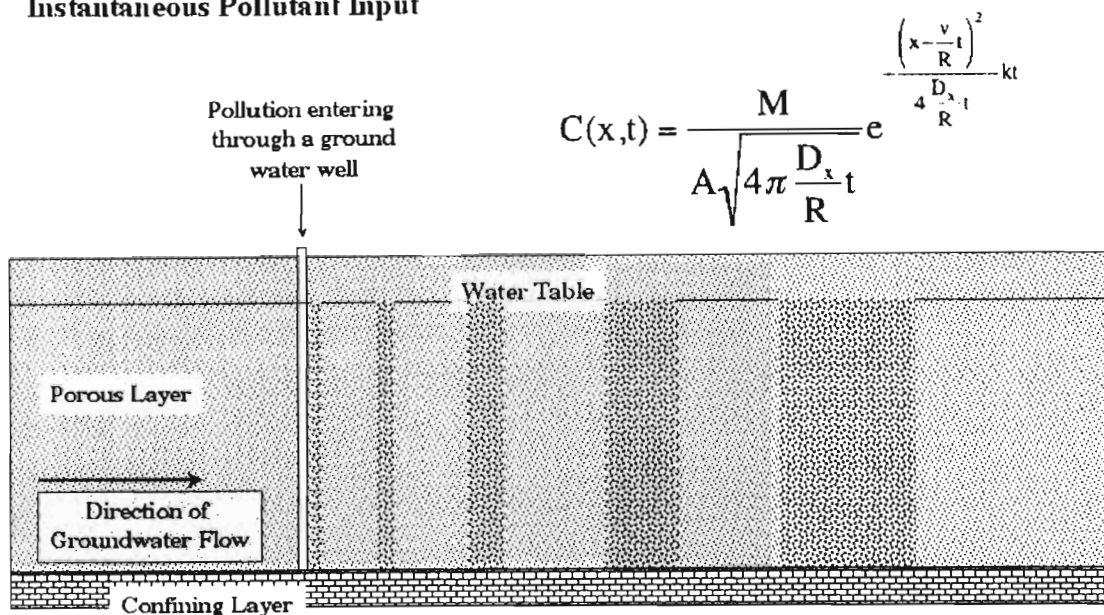


Figure 8.22. An illustration of an instantaneous (pulse) input of pollution to an aquifer.

where  $x$  is distance from the source (m),  $t$  is time (days),  $M$  is the mass of contaminant added to the aquifer (mg),  $A$  is the cross-sectional void volume contaminated by the pollution ( $\text{m}^2$ ),  $D_x$  is the dispersion coefficient ( $\text{m}^2/\text{day}$ ),  $R$  is the retardation factor (unitless),  $v$  is velocity ( $\text{m}/\text{day}$ ), and  $k$  is the first-order reaction rate ( $1/\text{day}$ ). First, note the use of the dispersion coefficient (dispersivity) instead of the dispersion. Unfortunately, dispersion coefficients must be used, since we need a way of estimating dispersion as water moves away from the point source. We noted the dangers of this approach in the previous section, but all of the fate and transport equations used today rely on this approach, even if there little to no experimental basis for its use. This coefficient defined by

$$D_x = D \times v$$

where  $D_x$  is the called the dispersivity or dispersion coefficient,  $D$  is the dispersion, and  $v$  is the water velocity. 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 (distance) over which they are measured because the degree of heterogeneity within the aquifer generally increases with scale.

**Example Problem.** A  $100\text{-m}^3$  tanker containing a  $100\text{-mg}/\text{m}^3$  solution of 2,4-dinitrotoluene crashes and empties its entire contents above an aquifer. The cross-sectional area of the spill is  $50\text{ m}^2$ . The aquifer has a porosity of 30%, a bulk density of  $1.6\text{ g}/\text{cm}^3$ , a velocity of  $10\text{ m}/\text{yr}$ , and a dispersion coefficient ( $D_x$ ) of  $10\text{ m}^2/\text{yr}$ . The distribution coefficient of 2,4-dinitrotoluene for this aquifer material has been measured to be  $2.5\text{ mL}/\text{g}$ . 2,4-dinitrotoluene biodegrades through a first-order reaction at a rate of  $0.693\text{ yr}^{-1}$ . Calculate the concentration 10 m down-gradient from the lagoon 10 years after the input.

#### Solution

1. Calculate the retardation factor from the distribution coefficient.

$$\begin{aligned} R &= 1 + \frac{\rho_b K_d}{n} \\ &= 1 + \frac{\left(1.6 \frac{\text{g}}{\text{cm}^3}\right) \left(2.5 \frac{\text{mL}}{\text{g}}\right)}{0.3} = 14.33 \end{aligned}$$

2. Correct the cross-sectional area of the spill site to the void volume (rather than the total volume).

$$\text{Cross-sectional area} \times \text{Porosity} = 50\text{ m}^2 \times 0.3 = 15\text{ m}^2$$

3. Calculate the total mass of dinitrotoluene spilled.

$$\begin{aligned} &\text{Volume spilled} \times \text{Concentration of solution} \\ &= (100\text{ m}^3) \left(1000 \frac{\text{mg}}{\text{m}^3}\right) = 100,000\text{ mg or }100\text{ g} \end{aligned}$$

4. If necessary, calculate the first order degradation rate from the half-life.

$$-\frac{\ln 0.5}{t_{1/2}} = k = \frac{-0.693}{0.09625(\text{yr})} = 0.693 \text{ yr}^{-1}$$

5. Arrange data into proper units

Groundwater velocity,  $v = 10 \text{ m/yr}$

Retardation factor,  $R = 14.33$

Mass of contaminant,  $M = 100,000 \text{ mg}$

Dispersion coefficient,  $D_x = 10 \text{ m}^2/\text{yr}$

Reaction rate constant,  $k = 0.693 \text{ yr}^{-1}$

Cross-sectional area,  $A = 15 \text{ m}^2$

6. Input data into the Fate<sup>®</sup> program or governing equation and obtain/draw a graph.

7. Calculate the concentration 10 m down-gradient from the lagoon 10 years after the input.

$$\begin{aligned}
 C(x, t) &= \frac{M}{A \times \sqrt{4\pi \frac{D_x}{R} t}} \times e^{\frac{\left(\left(x - \frac{v}{R}\right) \times t\right)^2}{4 \frac{D_x}{R} t} - kt} \\
 &= \frac{100,000 \text{ mg}}{15 \text{ m}^2 \sqrt{4\pi \left(\frac{10 \frac{\text{m}^2}{\text{yr}}}{14.33}\right) \times 10 \text{ yr}}} \times e^{\frac{\left(10 \text{ m} - \left(\frac{10 \frac{\text{m}}{\text{yr}}}{14.33}\right) 10 \text{ yr}\right)^2}{4 \times \left(\frac{10 \frac{\text{m}^2}{\text{yr}}}{14.33}\right) \times 10 \text{ yr}} - \left(0.693 \frac{1}{\text{yr}}\right) 10 \text{ yr}} \\
 &= 1971 \text{ mg/m}^3 \text{ or } 1.971 \mu\text{g/L 2,4-dinitrotoluene.}
 \end{aligned}$$

*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 basic advective-dispersive groundwater equation may be solved using Laplace transformations to yield (see Figure 8.23)

## Step Pollutant Input

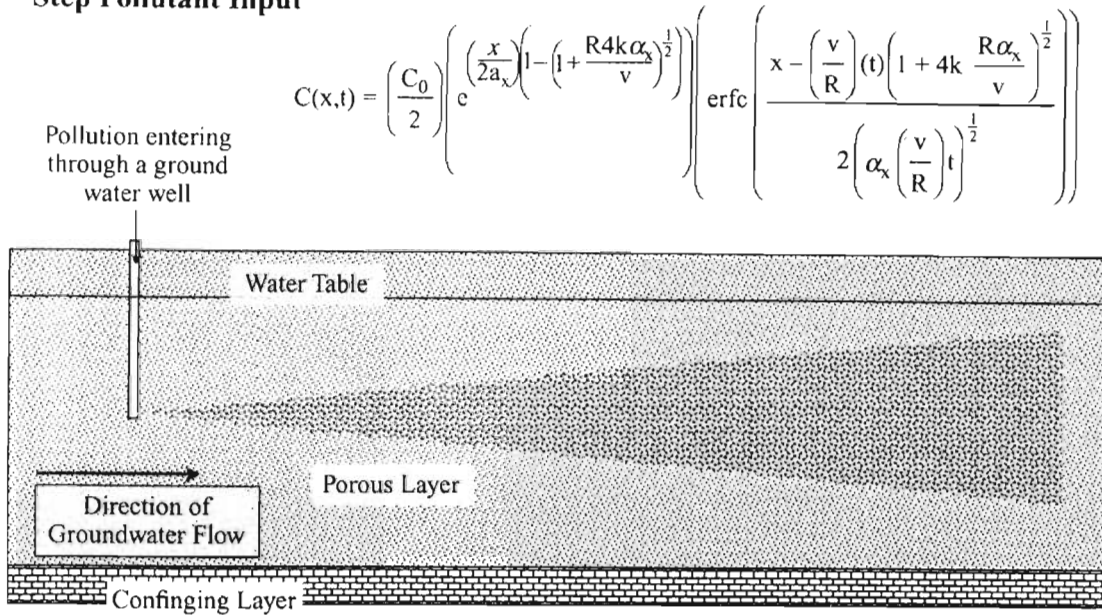


Figure 8.23. An illustration of a step (continuous) input of pollution to an aquifer.

$$C(x,t) = \left( \frac{C_0}{2} \right) e^{\left( \frac{x}{2D_x} \left( 1 - \left( 1 + \frac{R4kD_x}{v} \right)^{\frac{1}{2}} \right) \right)} \left( \operatorname{erfc} \left( \frac{x - \left( \frac{v}{R} \right) (t) \left( 1 + 4k \frac{RD_x}{v} \right)^{\frac{1}{2}}}{2 \left( D_x \left( \frac{v}{R} \right) t \right)^{\frac{1}{2}}} \right) + e^{\left( \frac{x}{D_x} \right)} \operatorname{erfc} \left( \frac{x + \left( \frac{v}{R} \right) (t) \left( 1 + 4k \frac{RD_x}{v} \right)^{\frac{1}{2}}}{2 \left( D_x \left( \frac{v}{R} \right) t \right)^{\frac{1}{2}}} \right) \right)$$

where  $C_0$  is the initial concentration of the contaminant,  $x$  is distance from the source,  $D_x$  is longitudinal dispersivity (dispersion coefficient),  $k$  is the first-order reaction rate,  $v$  is velocity,  $t$  is time, and  $\operatorname{erfc}$  is the complementary error function.

The final term in the above equation,

$$e^{\left( \frac{x}{D_x} \right)} \operatorname{erfc} \left( \frac{x + \left( \frac{v}{R} \right) (t) \left( 1 + 4k \frac{RD_x}{v} \right)^{\frac{1}{2}}}{2 \left( D_x \left( \frac{v}{R} \right) t \right)^{\frac{1}{2}}} \right)$$

is generally considered insignificant and is ignored. This term is ignored in Fate<sup>®</sup>.

Again, note that the dispersion coefficient, not dispersion, is used in these equations.

The complementary error function (erfc in the equation given above) is the area between the midpoint of the normal curve and the value that you are taking the error function of. The basic purpose of the complementary error function is to calculate the area under the bell-shaped curve representing pollutant concentrations through time or with distance downstream following a pulse input of pollutant.

**Example Problem.** A waste lagoon containing 100 mg/L benzene is contaminating the underlying aquifer. The aquifer has a porosity of 30%, a bulk density of 1.6 g/cm<sup>3</sup>, a velocity of 10 m/yr, and a dispersivity of 10 m<sup>2</sup>/day. The distribution coefficient of benzene for this aquifer material has been measured to be 5 mL/g. Benzene biodegrades through a first order reaction at a rate of 0.025 yr<sup>-1</sup>. Calculate the concentration 10 m down-gradient from the lagoon 10 years after the input.

*Solution*

1. Calculate the retardation factor from the distribution coefficient.

$$R = 1 + \frac{\rho_b K_d}{n}$$

$$= 1 + \frac{\left(1.6 \frac{\text{g}}{\text{cm}^3}\right) \left(5 \frac{\text{mL}}{\text{g}}\right)}{0.3} = 27.67$$

2. If necessary, calculate the dispersivity from the dispersion coefficient and the velocity.

This step is not necessary here.

3. If necessary, calculate the first order degradation rate from the half-life.

$$-\frac{\ln 0.5}{t_{1/2}} = k = -\frac{-0.693}{27.72(\text{yr})} = 0.025 \text{ yr}^{-1}$$

4. Convert data into proper units:

$$C_0 = 100 \text{ mg/L}$$

$$v = 10 \text{ m/yr}$$

$$D_x = 10 \text{ m}$$

$$R = 27.67$$

$$k = 0.025 \text{ yr}^{-1}$$

5. Input data into the Fate<sup>®</sup> program or governing equation and obtain/draw a graph.
6. Calculate the concentration 10 m down-gradient from the lagoon 10 years after the input.

$$C(x, t) = \left( \frac{100 \frac{\mu\text{g}}{\text{L}}}{2} \right) e^{\left( \left( \frac{10 \text{ m}}{2(10 \text{ m})} \right) \left( 1 - \left( \frac{(27.27)(4) \left( 0.025 \frac{1}{\text{yr}} \right) (10 \text{ m})}{10 \text{ m}} \right)^{\frac{1}{2}} \right) \right)} \left( \text{erfc} \frac{10 \text{ m} - \left( \frac{10 \frac{\text{m}}{\text{yr}}}{27.67} \right) (10 \text{ yr}) \left( 1 + (4) \left( 0.025 \frac{1}{\text{yr}} \right) \left( \frac{(27.67)(10 \text{ m})}{10 \frac{\text{m}}{\text{yr}}} \right) \right)^{\frac{1}{2}}}{2 \left( (10 \text{ m}) \left( \frac{10 \frac{\text{m}}{\text{yr}}}{27.67} \right) (10 \text{ yr}) \right)^{\frac{1}{2}}} \right)$$

$$= 0.78 \mu\text{g/L benzene}$$

## 8.8 SENSITIVITY ANALYSIS

While chemical factors, such as sorption and degradation, can determine the down-gradient pollutant concentration, the most difficult parameter to estimate is hydrodynamic dispersion. Sensitivity analysis should include a variety of values for distribution and partition coefficients and chemical, biological, and nuclear degradation rates. In terms of dispersion estimates, Figure 8.21 should be used for your initial estimate and should be combined with water velocity to obtain estimates of dispersion coefficients. Note that your sensitivity analysis should use large ranges of dispersion coefficients, in some cases from two to four orders of magnitude.

## 8.9 LIMITATIONS OF OUR MODELS

In this chapter, we presented the classic one-dimensional general transport equation in order to keep the mathematics simple and concentrate on the important processes. It should be noted that professional modelers use two- and three-dimensional models and also use numerical methods of analysis, which allow for variations in aquifer conditions such as water velocity, sorption phenomena, degradation rates, and, most importantly, dispersion. Obtaining an accurate estimate of dispersion or the dispersion coefficient is the major limiting factor in groundwater modeling.

## 8.10 REMEDIATION

Contaminated groundwater systems are one of the most difficult environmental media to remediate, due to their location below the land surface (out of direct obser-

vation), the large volumes of soil and water involved, and the slow water velocities inherent in these aquifers. Many technologies and approaches have been developed specifically for groundwater remediation with mixed and site-specific successes and failures. There are numerous books on groundwater remediation; given the expansive research in this area, we will only briefly summarize some of the common approaches to this problem. In general, we will begin with the least expensive and complicated and progress to the more expensive.

A summary of suggested and common remediation actions are given in Figure 8.24 (EPA, 1988), and this list has been expanded upon since its original publication. These actions are divided into natural attenuation, containment, and active restoration. The first two categories, while similar, are two distinct approaches adopted by EPA. Both of these can be undertaken in a variety of cases and for a variety of reasons. For example, even when a risk assessment shows no immediate risk, governing bodies (EPA, local government, or the public) sometimes decide that some control of the site is necessary. Natural attenuation or containment may also be employed when there is no acceptable remediation plan at present and the site needs to be removed from possible human contact, or when remediation of the site using one of the acceptable technologies may create a worse problem than waiting for the development of a whole new remediation approach. Notice that all remediation plans involve long-term monitoring of the site.

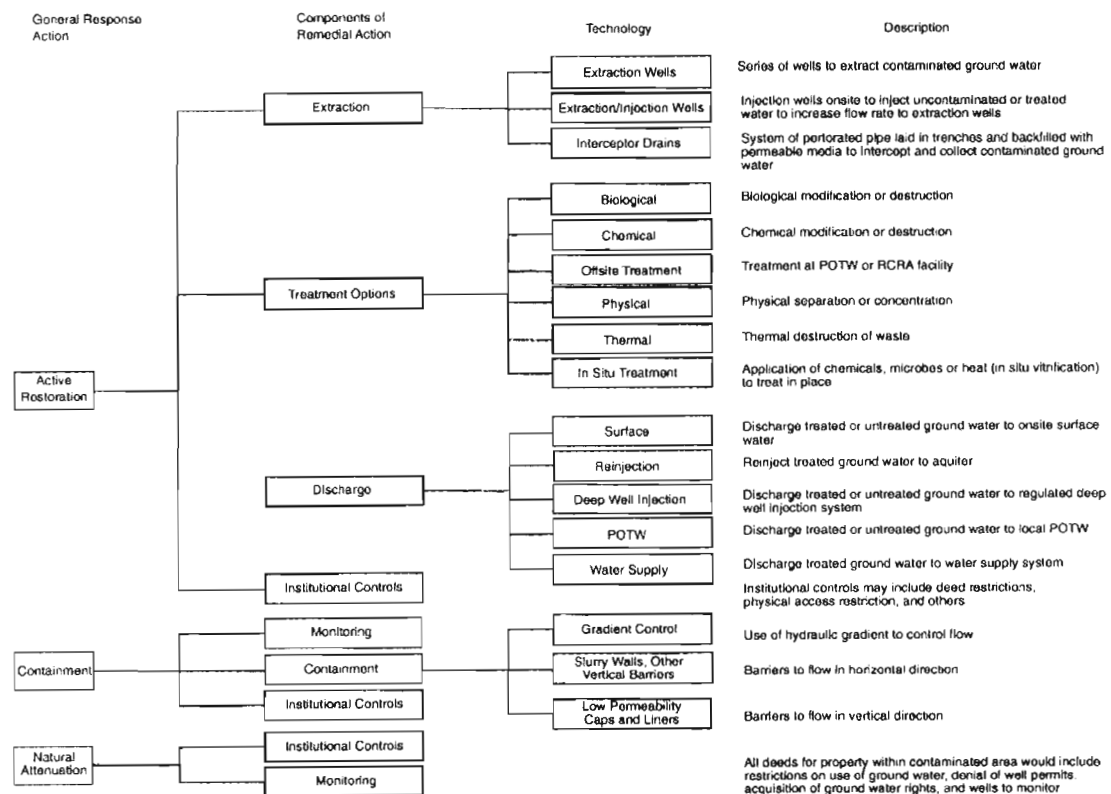


Figure 8.24. A summary of technologies used in groundwater remediation (EPA, 1988, p. 5-10).

Today, natural attenuation may be expanded to a form of active restoration, by employing the addition of nutrients to aid in the microbial removal of pollutants. These projects still take years to decades to complete, but operating costs are relatively inexpensive compared to other approaches such as removal and treatment of the soil. Institutional controls, a common listing in Figure 8.24, are basically easements placed on the land deed specifying and limiting how the land can be used or developed in the future.

In some cases, containment may be the only viable and affordable option. Containment does nothing to treat the site, but limits the further spread of pollution and is intended to protect local citizens from exposure to the toxins while a more permanent solution can be designed. Containment uses ways to limit or stop water and therefore pollutant migration from the site boundaries. This can be accomplished by controlling the gradient (placing water pumping and extraction wells around the contaminated area), surrounding the underground site with walls of impermeable media (grout and clay), and capping the site to prevent water from entering from the ground surface and spreading the pollution to new areas.

There are a seemingly endless number of active treatment technologies for polluted groundwater and soil sites. These are divided into extraction of polluted groundwater (termed “pump and treat”), direct treatment options that may involve the removal of the contaminated soil and water, and institutional controls that limit use of the water from the site. The first approach, pump and treat, was originally thought of as the cure-all of polluted groundwater. The concept is simple: Polluted groundwater is pumped out relatively slowly, treated at the ground surface, and then the “clean or cleaner” groundwater is pumped back into the polluted aquifer in order to displace more pollution. The water extraction and injection wells are placed so as to contain the polluted groundwater plume. By using partition and distribution coefficients, it is relatively easy to estimate how many aquifer volumes of groundwater must be removed and treated for the pollution to be effectively removed. However, after decades of use, this technology has proved ineffective in many, though not all, cases. Sites that were once thought to be remediated have been later found to still contain unsafe levels of pollutants in their water. This is due to the slow desorption of pollutants from the soils. After the pump and treat system has been shut off, the pollution re-occurs by desorbing from the polluted soil. Thus the pump and treat approach has been augmented with the addition of *in situ* biological and chemical treatment processes to increase pollutant degradation and/or removal.

There are many *ex situ* treatment technologies that can be used on the polluted groundwater after it has been brought to the surface. These are too numerous to even mention here but include physical, biological, and chemical treatment. After treatment, the water may be re-injected or disposed of in other manners depending on the local restrictions.

Polluted aquifers are one of the most difficult and costly sites to remediate. In fact, most of the Superfund effort has focused on remediating groundwater. Yet, there is much to be accomplished in the future given the difficult nature of these systems.



## SUGGESTED PAPERS FOR CLASS DISCUSSION

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Dunnivant, F. M., P. M. Jardine, D. L. Taylor, and J. F. McCarthy. Cotransport of cadmium and hexachlorobiphenyl by dissolved organic carbon through columns containing aquifer material. *Environ. Sci. Technol.* **26**(2), 360–368 (1992).

Dunnivant, F. M., M. E. Newman, C. W. Bishop, D. Burgess, J. R. Giles, B. D. Higgs, J. M. Hubbell, E. Neher, G. T. Norrell, M. C. Pfeifer, I. Porro, R. C. Starr, and A. H. Wylie. Water and radioactive tracer flow in a heterogeneous field-scale system. *Groundwater* **36**(6), 949–958 (1998).

### Concepts

1. Contrast the following pairs of terms:  
Saturated versus unsaturated media  
Porous versus fractured media  
Consolidated versus nonconsolidated media
2. Research the Safe Drinking Water Act (SDWA) on the Internet. Write a one-page summary of the act with respect to groundwater, priority pollutants, and maximum contaminant levels.
3. Describe three examples of step inputs and three examples of pulse inputs of pollutants to a groundwater system in your area.
4. Discuss the difficulties in installing a monitoring well with respect to obtaining a representative groundwater sample.
5. Describe the major ways of installing a groundwater monitoring well. List the advantages and disadvantages of each.
6. Describe each of the three ways of obtaining a  $K_d$  or  $K_p$  for a pollutant.
7. Select two pollutants from Table 2.6 and calculate  $K_p$  value for them using two of the predictive equations in this chapter. Compare the values between the two equations.
8. Explain the relationship between  $R$  and  $K$ .
9. Draw typical breakthrough curves (BTC) for pulse and step inputs of pollutant.
10. Use Figure 8.20 to explain the difficulties in estimating dispersion for an untested system.
11. Summarize the three ways of estimating/determining dispersion in a groundwater system.

### Exercises

1. A storage tank breaks during an earthquake event, spilling gasoline treated with MTBE into the surrounding soil (glacial till) and contaminating the groundwater. Create plots of (1) concentration of MTBE versus distance (0–22 m) 10 years after the spill and (2) concentration of MTBE versus time (0–15 years) 10 m from the spill, using the following parameters (check your answers with Fate<sup>®</sup>):

Void volume:  $11.5 \text{ m}^3$

Groundwater velocity:  $5 \text{ m/yr}$

Retardation factor: 8.457

Initial concentration of MTBE resulting from spill:  $35 \text{ mg/m}^3$

Half-life of MTBE: 1 year

Dispersion coefficient:  $10 \text{ m}^2/\text{yr}$

Bulk density:  $1.6 \text{ g/cm}^3$

$K_d$ :  $1.072 \text{ mL/g}$

Porosity: 0.23

Now, for your sensitivity analysis, prepare the previous plots using  $1 \text{ m}^2/\text{yr}$  as your dispersion coefficient.

2. A tanker car from a mining operation leaks and spills  $100 \text{ g HCN}$  over a sand aquifer with an area of  $20 \text{ m}^2$ . The EPA asks you to assess the damage and to determine the probable concentration of HCN in the ground water. The velocity of the groundwater is  $182.5 \text{ m/yr}$ , the dispersion coefficient is  $2 \text{ m}^2/\text{yr}$ , and the retardation factor is 1.050. The half-life of HCN under the conditions at the site is 1.00 year. The bulk density of the sand is  $1.5 \text{ g/cm}^3$  and the porosity is 0.3. The  $K_d$  for HCN is 0.01. Calculate the concentration of HCN 0.3, 0.9, and 2 years after the spill. Use Fate to create a graph of time versus concentration. Compare this scenario with one in which the pollutant travels more slowly ( $90 \text{ m/yr}$ ). In both cases measure  $10 \text{ m}$  away from the spill.
3. Arsenic in the ground contaminates an aquifer by a naturally occurring, continuous geological process. The sandy aquifer has a bulk density of  $1.08 \text{ g/cm}^3$  and a solid density of  $2.63 \text{ g/cm}^3$ . The distribution coefficient ( $K_d$ ) in this scenario is  $0.027 \text{ mL/g}$ . Consider that the initial concentration of arsenic at the source is  $21 \mu\text{g/L}$ , the longitudinal dispersion is  $0.1 \text{ m}$  per day, and the linear water velocity is  $100 \text{ m/yr}$ . Using this information, determine how far and how quickly arsenic must travel through this natural aquifer in order to be completely dispersed ( $>0.50 \mu\text{g/L}$ ). The data from this problem is organized in the table below.

*\*Note:* Arsenic does not have a rate constant as it is stable (does not degrade). However, you can use a very high value to graph this in Fate® (suggested value: 60,000).

Use Fate® to create a plot of the scenario and to check your results.

Bulk density:  $1.08 \text{ g/cm}^3$

Solids density:  $2.63 \text{ g/cm}^3$

$K_d$ :  $0.027 \text{ mL/g}$

Initial concentration:  $21 \mu\text{g/L}$

Dispersion:  $0.1 \text{ m/day}$

Water velocity:  $100 \text{ m/yr}$

4. Xylene is one of the major components of gasoline. It can be toxic if released into groundwater. Some of the harsher effects of xylene on the human body include brain hemorrhaging or death. One summer in 1979, before gas stations had started using double-layered underground storage tanks (USTs), a UST at a gas station began corroding. Gasoline had been spilling out of the UST for 10 years before any removal efforts were undertaken. Xylene has a half-life of 30 days. The ground beneath the UST is fairly porous: It has a bulk density of  $1.44 \text{ g/cm}^3$  and a solids density of  $2.94 \text{ g/cm}^3$ . The initial concentration of xylene was 370 ppm. Below the UST the groundwater moved at a velocity of 70 ft/yr and dispersed longitudinally  $5 \text{ m}^2/\text{yr}$ . The  $K_d$  of xylene is  $1.224 \text{ cm}^3/\text{g}$ . For this system, what was the concentration of xylene 20 m from the UST 1 year, 2 years, 5 years, and 10 years after the spill began?
5. You are a chemist who has been hired to analyze the step release of a DNAPL (1,1,1-trichloromethane) into a coarse sand aquifer with a porosity of 30%. The average linear groundwater velocity for this aquifer is 10 m/yr with a longitudinal dispersivity of  $19 \text{ m}^2/\text{yr}$ . The sand has a retardation factor of 42.6. The pollutant has a half-life of 56 days and is initially present at a concentration of 5.50 ppb. How much pollutant (what concentration) is present at distances of 5.0 m and 20.0 m from the release point at times of 3.0, 5.0, and 10.0 years after the accident?

### Spreadsheet Exercise

Create a spreadsheet that performs the same calculations as Fate<sup>®</sup> for a pulse input of pollutant to a groundwater system. Construct your spreadsheet so that it is interactive (so that you can change numeric values for parameters and the plot automatically updates itself).

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