11.1 Introduction

Groundwater contamination follows nearly everything else in this book because you need most of what precedes it to understand the many interwoven processes involved. The fate of subsurface contamination depends on the local geology, groundwater flow patterns, pore-scale processes, and molecular-scale...
Groundwater Contamination

processes. Contamination might spread rapidly within a high-conductivity sand lens, or it might diffuse at a snail’s pace through a low-conductivity clay. Some contaminants adsorb onto the surface of aquifer solids, moving very little from their source, while others migrate freely with the flowing pore water, sometimes ending up many kilometers from their source. Chemical reactions along the way can cause a contaminant to disappear, or worse, appear from apparently nowhere.

When we speak of groundwater contamination, we mean solutes dissolved in the water that can render it unfit for our use or unfit for an ecosystem that the water enters. Most natural waters contain at least some amount of dissolved substances that we think of as contaminants. Each glass of water we drink contains some lead and arsenic, for example. But in most cases, these substances are present at very low concentrations that pose no risk for us. For a contaminant to be a true problem, it must be present at a concentration that poses some significant risk to human health or an ecosystem.

The most common contaminants and their important properties are introduced first. Then the processes that affect their movement in the subsurface are discussed, followed by a few case studies. Modeling methods and field methods are then introduced briefly. The chapter ends with an overview of tactics for remediating groundwater contamination.

11.2 Contamination Sources

Sources of groundwater contamination come in a great variety of sizes and shapes. It may be a leaking underground pipeline or tank, a wastewater lagoon, a septic system leaching field, a spill into a drain at a factory, or leaking barrels of waste chemicals. These examples are all relatively small and would be classified as point sources. On the other hand, nonpoint sources are larger, broadly distributed sources. Examples of nonpoint sources include polluted precipitation, pesticides applied to a cropland, and runoff from roadways and parking lots.

Sometimes contamination is introduced to the subsurface as an aqueous solution such as septic system effluent or landfill leachate. This is not always the case, though. The source of contamination can be a spilled separate liquid phase like gasoline or dry-cleaning solvent. These liquids, usually organic, are known by the acronym NAPL, for nonaqueous-phase liquid. NAPLs can persist in the subsurface and slowly dissolve into the water, acting as a continuous point source for years. Organic contamination and NAPLs are such a
large portion of groundwater contamination problems that they are discussed separately in subsequent sections.

### 11.2 Contamination Sources

#### 11.2.1 Leaking Storage Tanks

Tanks are widely used to store fuels and chemicals, and many of these have leaked over the years. Underground tanks have caused the most contamination, because they can leak slowly for a long time without being discovered. The U.S. Environmental Protection Agency estimated that by 1996 there had been 318,000 releases from underground storage tanks reported at the federal, state, and local levels in the U.S. (EPA, 1996). The most common tank sources are gas tanks at filling stations, and fuel and solvent storage tanks at industrial facilities. What leaks out of these are organic NAPLs.

Most tanks installed before the 1970s were bare steel tanks that tended to corrode. Many of these tanks and their associated piping eventually sprang leaks when corrosion went too far. Most of us have seen gas stations, temporarily closed, with gaping excavations made for removal of the old tanks and installation of the new.

Newer tank systems are most commonly made of fiberglass-reinforced plastic, coated and cathodically protected steel, or composites of these two materials. Cathodic protection greatly slows the rate of galvanic corrosion of buried steel tanks and piping. Hundreds of thousands of these new types of tanks have been in service in the U.S. for up to 30 years, with very few failures reported (EPA, 1988). New tanks sometimes have double wall layers with leak-detection devices between the walls. As of 1998, underground storage tanks in the U.S. have to meet certain requirements regarding leak detection, spill and overfill protection, and corrosion protection.

#### 11.2.2 Septic Systems

Septic systems for subsurface disposal of human wastewater are the rule in more rural areas not served by sewers and sewage treatment systems. Most septic systems serve a single household, but some larger systems serve a cluster of homes and/or offices.

A typical septic system starts in the series of drainpipes in a home’s plumbing system. These all connect and drain to one pipe that runs outside to a buried septic tank, where solids settle and are trapped. The tank needs to be pumped out periodically to remove accumulated solids. From the tank, wastewater flows to a leaching field, usually a network of porous distribution pipes set in a porous material in the unsaturated zone (Figure 11.1).
Wastewater contains dissolved organic compounds that fuel redox reactions in microbes that live in the system. Redox reactions in the tank are usually anaerobic, including fermentation, methane generation, and sulfate reduction (Wilhelm et al., 1994). The water leaving the tank has high concentrations of organic compounds, CO$_2$, and ammonium (NH$_4^+$).

In the leaching field, oxygen is available and aerobic respiration and nitrification are the key processes (Table 10.13). The concentrations of organic compounds and NH$_4^+$ decrease, CO$_2$ is evolved, and the nitrate (NO$_3^-$) concentration increases. It is typical for effluent leaving the unsaturated zone of a properly functioning leaching field to have nitrate concentrations in the range of 20 to 70 mg/L (NO$_3^-$–N: mass of nitrogen in nitrate per volume), which exceeds the U.S. drinking water maximum contaminant level (MCL) of 10 mg/L (NO$_3^-$–N). In most septic systems, nitrate is a groundwater contaminant of concern. Some septic system designs include another anaerobic zone beyond the aerobic zone in the leaching field, where denitrification (Table 10.13) reduces nitrate concentrations in the effluent (Robertson and Cherry, 1995; Robertson et al., 2000).

It has recently come to light that wastewater effluent from commercial and household disposal systems can also contain a range of chemical compounds found in medications, food, personal care products, and household products (Kolpin et al., 2002; Standley et al., 2008). Chemicals in medications and food pass through humans and persist in the system effluent. For example, caffeine has been used as an indicator of septic system contamination (Seiler et al., 1999). Hormones are particularly troubling chemicals that persist long enough to migrate through the disposal system to groundwaters and surface waters, where they can harm aquatic life. In Cape Cod, Massachusetts, where over 85% of homes have septic systems, several ponds in the sand and gravel aquifer contained estrogenic hormones at concentrations approaching those known to induce physiological responses in fish (Standley et al., 2008).
11.2 Contamination Sources

Septic systems fail when the leaching field doesn’t have enough access to oxygen to fully degrade the organic carbon with aerobic respiration. This can happen when the system is placed too close to the water table, in soils that are too fine grained, or in old systems that become clogged with a biological mat that remains saturated.

11.2.3 Landfills

The term landfill covers a broad range of facilities that harbor a range of different potential contaminants. Depending on the landfill, its contents may include municipal solid wastes (MSW), construction debris, or industrial wastes like incinerator ash and paper mill sludge. MSW landfills are the most common variety, handling household refuse.

Not many decades ago, we knew landfills as dumps, and they were nothing more than unlined pits filled with refuse. Dumps were usually placed on property of low value like an abandoned gravel pit or a swampy parcel. Unfortunately these were often places where water could move rapidly from the refuse to groundwater or surface water.

Infiltrating water moves down through the refuse, picking up dissolved constituents on its way. Leachate is water that percolates out of the base of the refuse. It usually has a high dissolved solids content, and it may also pick up dissolved organic contaminants, depending on what is in the refuse. Older dumps, numbering in the tens of thousands in the U.S., have generated many leachate plumes. In more permeable settings, these plumes have reached kilometers in length.

Modern landfills have low-permeability caps to limit infiltration, and liner and leachate collection systems to intercept and treat what leachate is generated (Figure 11.2). The low-permeability layers in the cap and/or liner may be

Figure 11.2  Vertical cross-section through a modern double-lined landfill liner system. The upper sand layer and drainpipe are the primary leachate collection system. Leachate collects in the pipes, which drain to a treatment plant. The lower leachate collection layer and the membrane are redundant systems, which would only be needed in case of a leak in the primary (upper) liner. The corrugated shape of the liner system base helps leachate drain effectively.
made of remoulded clay or synthetic liner membranes. Synthetic membranes are now made of plastics with welded seams or of low-permeability clay interwoven with a synthetic fabric (geosynthetic clay liners). A modern landfill is operated one small, uncapped cell at a time, to minimize the area of refuse that is exposed to infiltration. This strategy minimizes the amount of leachate generated.

### 11.2.4 Others

There are too many potential contamination sources to list them all, but some of the other more common ones are listed below with a brief summary about each.

- **Injection wells.** Some kinds of liquid wastes are disposed of in injection wells. These operate like a pumping well in reverse, forcing fluids out of the well screen into the surrounding formation. The wells should be designed toinject into a formation that is isolated from any useful aquifers or surface water ecosystems. The types of wastes most commonly injected are brines and other waters recovered from oil fields, fluids from solution mining, and treated wastewaters.

- **Pesticides, herbicides, and fertilizers.** Modern farming includes several practices that can lead to groundwater contamination: pesticide, herbicide, and fertilizer application, irrigation, and animal waste storage. Pesticides and herbicides are usually organic compounds that are sprayed on fields in an aqueous solution. Many of these compounds biodegrade rapidly, but some are persistent and contaminate groundwaters over broad areas. Fertilizer application can result in high nitrate and phosphate concentrations in groundwater, and high nutrient loads in surface runoff.

- **Animal wastes.** Concentrated animal feed lots for cattle, pigs, and other meat animals generate large amounts of animal wastes that can contaminate recharge to underlying groundwater. Common contaminants in these settings include nitrate, veterinary pharmaceuticals (antibiotics, among others), and steroid hormones, (Bartelt-Hunt et al., 2011).

- **Irrigation.** When crops are irrigated, most of the applied water infiltrates, is transpired, or evaporates. Evaporation and transpiration of irrigated water leave the remaining water with higher solute concentrations. Especially in drier climates and where the water used for irrigation has high dissolved solids to begin with, irrigation can lead to the accumulation of
salts and other contaminants in the soils and in local surface waters. Some fertilizers are salts, and dissolution of them adds dissolved solids in soil moisture and runoff. Selenium is commonly concentrated to high levels in irrigation runoff in arid parts of the western United States with selenium-rich marine sedimentary rock. In a review of western U.S. surface water quality in irrigated regions, Seiler et al. (2003) found that selenium concentrations exceeded the U.S. Environmental Protection Agency standard for aquatic life in 40% of sampled waters. Selenium concentrations fluctuated greatly, with low levels during wet periods and high levels during dry periods with more irrigation.

- **Mining activities.** Mines are located where nature has concentrated elements in rocks with unusual chemistry. Water that percolates through the mine workings and through the tailings often has unusual chemistry as well. Sulfide mines, where most copper, lead, and zinc come from, yield very acidic leachate because of iron and sulfide oxidation reactions (Table 10.13). The acidic leachate, in turn, can mobilize various metals from surface complexes (Figure 10.12). Leachate from uranium mines can contain hazardous levels of radioisotopes.

- **Road salting.** In places that have ice and snow in winter, roads are deiced by spreading salt or sand–salt mixtures. The salts are dissolved into melting ice and ultimately increase the sodium and chloride concentrations of infiltration near the roadways.

### 11.3 Organic Contaminants

A large portion of all groundwater contamination problems involve organic contaminants. We use vast quantities of hydrocarbon fuels, solvents, and other organic liquids and it should come as no surprise that they are frequently spilled into the subsurface. Some releases were intentional, many of them perfectly legal because there used to be little or no regulation of waste disposal. Between the 1950s and the 1980s, environmental awareness and regulation increased dramatically, so now most releases are accidental or illegal. Until the last several decades, few people were aware that spilled organic liquids could move deep into the subsurface, dissolve into groundwater, and then migrate great distances. Organic contamination can migrate as a separate liquid phase, in the aqueous phase, and in the gas phase. Typical patterns of migration are discussed in the following section.
11.3.1 Overview of Migration Patterns

Most organic contaminants begin their trip to the subsurface as some form of organic liquid (NAPL). These liquids are immiscible with water, like oil and water in salad dressing. This doesn’t mean that no mixing occurs, just that there is limited mixing. The molecules in the organic liquid dissolve into the water, usually at relatively low aqueous concentrations.

When an organic liquid is spilled, it tends to migrate downward in the unsaturated zone, usually following some irregular path of least resistance. Depending on how much NAPL is spilled, it may migrate only a short distance from the spill, or it may migrate far and deep (Figure 11.3). As NAPL migrates, it leaves behind a trail of small, immobile blobs of NAPL that are trapped in the bigger pore spaces. For NAPL to be mobile, there must be enough of it in a pore space to build pressure sufficient to push into other pores. The larger the spill, the farther the NAPL can migrate before it all becomes immobile. Immobile NAPL usually occupies a small percent of the pore space, sharing it with water and, in the unsaturated zone, air.

If enough NAPL is spilled so that it penetrates down to the top of the saturated zone, its fate then hinges on its density. If it is less dense than water, it tends to float and pool at the top of the saturated zone as shown on the right-hand side of Figure 11.3. When it is more dense than water, it can plunge down into the saturated zone as shown in Figures 11.4 and 11.5. An organic liquid that is less dense than water is an LNAPL (light nonaqueous-phase liquid) and a denser liquid is a DNAPL (dense nonaqueous-phase liquid).

The Hyde Park chemical landfill site in Niagara Falls, New York, is an example of deep DNAPL migration. An estimated 80,000 tons of liquid and solid
chemical wastes were disposed at the site between 1953 and 1975 (Cohen and Mercer, 1993). The site is underlain by a fractured dolomite and it lies about 600 m east of the Niagara River gorge, downstream from Niagara Falls. DNAPLs at this site are known to have migrated to depths of at least 30 m into the fractures of the dolomite, and at least 450 m horizontally from the source areas (Cohen et al., 1987).
Groundwater Contamination

Water that percolates through NAPL-infested pores, whether in the unsaturated or saturated zones, will gain dissolved constituents from the NAPL. These zones of aqueous contamination are shown in Figures 11.3 and 11.4. NAPL will continue to dissolve into the passing water until the NAPL disappears entirely. For many sizable spills, there is enough NAPL to last for decades or centuries without dissolving away.

In addition to the mass transfers between NAPL and water, there can be mass transfer to the gas phase, in the pores of the unsaturated zone. Organic molecules evaporate directly from the NAPL phase and from the aqueous phase. These vapors can migrate under air pressure and density gradients in the unsaturated zone. Moving vapors can spread contamination to unsaturated zone pore waters along their path of flow.

Fortunately, there are a few mechanisms that naturally attenuate many organic groundwater contaminants. Some organic contaminant molecules such as polychlorinated biphenyls (PCBs) adsorb strongly onto aquifer solids, which limits the extent of solute migration. Organic contaminant molecules often turn out to be food for microbes that inhabit shallow groundwater environments. Biochemical redox reactions within these organisms can reduce or eliminate the mass of dissolved contaminant. Without natural microbial degradation, gasoline contamination plumes would be far more extensive and damaging than they actually are.

11.3.2 Structure and Occurrence of Common Contaminants

As discussed briefly in the previous chapter, organic molecules are compounds with a backbone of carbon atoms that are covalently bonded to themselves and to other elements, usually hydrogen, oxygen, nitrogen, sulfur, and the halogens (fluorine, chlorine, bromine, and iodine). Most organic molecules originate, at least in part, in living tissues. Some man-made molecules are classified as organic because they are synthesized from natural organic molecules and their structure is similar to a natural molecule.

A huge number of different organic molecules have become groundwater contaminants at one site or another. The U.S. Environmental Protection Agency currently has drinking water standards for 54 different organic compounds, and there are dozens more that can be significant pollutants in groundwaters.

We will focus on just a short list of compounds that includes some of the most common organic contaminants, and use these to illustrate important
properties and processes. The origin and uses of these compounds is summarized as follows, based on listings by Verschueren (1996) and Montgomery (2000).

- Benzene, ethylbenzene, toluene, xylenes: Occur naturally in petroleum. Constituents of petroleum-based fuels like gasoline and jet fuel.
- Benzo(a)pyrene: Occurs naturally in petroleum and coal. Constituent of gasoline, motor oil, creosote, and coal tar.
- Polychlorinated biphenyls (PCBs): Man-made. Insulating liquids in electrical capacitors and transformers; in lubricating and cutting oils; and in pesticides, adhesives, plastics, inks, paints, and sealants.
- 1,2-Dichloroethane (1,2-DCA), 1,1,1-trichloroethane (1,1,1-TCA), trichloroethylene (TCE), tetrachloroethylene (PCE): Man-made. Solvents for paints, dyes, food extractions, and dry cleaning; metal degreasing; and intermediate compounds in the synthesis of other chlorinated organic compounds.
- Methyl tert-butyl ether: Man-made. Added to gasoline as an oxygenate to boost octane, enhance combustion, and limit organic compounds in exhaust gases.

The carbon framework of most organic molecules consists of six-carbon rings (aromatic compounds) or straight/branched chains (aliphatic compounds). Figure 11.6 shows the structure of the aromatic compounds within our list, and Figure 11.7 shows the structure of the aliphatic compounds. In the following discussion of these structures, some basic organic chemistry nomenclature is introduced. The interested reader can find plenty more on this topic in an organic chemistry textbook (Solomons, 1992; Wade, 1999).

Functional groups are specific structures in the carbon framework or attached to the carbon framework that tend to govern how the molecule reacts chemically. For example, the CH$_3$ in toluene and xylenes is a methyl group, CH$_2$CH$_3$ in ethylbenzene is an ethyl group, and –O– in MTBE is an ether group. Where a functional group is bonded to a simple structure, the name of the functional group becomes a prefix to the chemical name. Ethylbenzene is a benzene ring with an ethyl group. The more conventional chemical name for toluene is methylbenzene because it is a benzene ring with a methyl group.

Aromatic molecules are all some variation on the same theme: six-carbon benzene rings with one or more functional groups attached. Benzo(a)pyrene is
Figure 11.6  Structure of some common aromatic contaminants. Each ring structure has a carbon atom at each of its six corners. The covalent bonding is evenly distributed between the carbons in a ring and each carbon is capable of one additional bond outside of the ring.

Figure 11.7  Structure of some common aliphatic contaminants, plus ethane, ethylene, and methane. Each line represents a shared electron pair in a covalent bond.
one of many compounds known as polycyclic aromatic hydrocarbons (PAHs), which contain multiple rings bonded together.

PCBs have two C$_6$H$_5$ rings (phenyl groups) bound by a single bond. Any one PCB liquid contains a variety of biphenyl molecules that are chlorinated to varying degrees. These mixtures are classified based on the average chlorine content. PCB-1248 (Arochlor-1248) is so named because it has 12 carbons and about 48% of its mass is chlorine. In PCB-1248, about 2% of the molecules are C$_{12}$H$_8$Cl$_2$, about 18% are C$_{12}$H$_7$Cl$_3$, about 40% are C$_{12}$H$_6$Cl$_4$, about 36% are C$_{12}$H$_5$Cl$_5$, and about 4% are C$_{12}$H$_4$Cl$_6$ (Verschueren, 1996). Other PCBs such as PCB-1242 or PCB-1254 have different percentages of these compounds and different average chlorine contents.

There are three different isomers of xylene (Figure 11.6). Isomers have the same chemical formula as each other, but different structure. The only difference between the xylene isomers is the relative position of the two methyl groups. In $o$-xylene, the two methyls are on adjacent carbons, in $m$-xylene they are two carbons apart, and in $p$-xylene they are three carbons apart. The more conventional chemical names for the xylene isomers are given in parentheses in Figure 11.6. The numbers in the conventional names indicate which carbons the two methyl groups are bonded to.

The chlorinated ethane compounds 1,1,1-TCA and 1,2-DCA are structurally similar to ethane, as shown in Figure 11.7. 1,1,1-Trichloroethane (1,1,1-TCA) has three chlorine atoms where ethane has hydrogens and 1,2-dichloroethane (1,2-DCA) has two chlorine atoms where ethane has hydrogens. In 1,1,1-TCA all three chlorines are associated with one of the carbons. In 1,2-DCA one chlorine is associated with one carbon and the other chlorine is associated with the other carbon.

The chlorinated ethylene compounds trichloroethylene (TCE) and tetrachloroethylene (perchloroethylene or PCE) are structurally similar to ethylene (ethene). In TCE, there are three chlorines and one hydrogen, and in PCE there are four chlorines and no hydrogens. Numbers are not needed (for example, 1,1,2-TCE) because there is just one isomer, one unique way to arrange the chlorines in both TCE and PCE.

Most organic liquids are mixtures of many different molecules, but some are nearly pure. Solvents like TCE and PCE are nearly pure when new but after use they become contaminated with molecules from the oils, greases, or whatever the solvent is used to dissolve. Hydrocarbon fuels are always mixtures of great numbers of organic molecules.

Crude oil (petroleum) is distilled to produce various hydrocarbon products. During distillation, the hundreds of different kinds of organic molecules
in petroleum are separated into fractions according to their boiling points (Table 11.1). A given petroleum-based fuel consists of the molecules that boil off in a certain range of temperatures. Smaller molecules with fewer carbon atoms tend to boil at lower temperatures, in general. Of the fractions listed in Table 11.1, the largest of U.S. oil refinery outputs in 1995 were gasoline (44%), kerosene (31%), gas plus petroleum ether (9%), and residual fuel oil (5%) (American Petroleum Institute, 2000).

Unleaded gasoline contains dozens of different organic compounds, most of which make up less than a few percent of the liquid. The most toxic and persistent groundwater contaminants in gasoline and other light petroleum fuels are benzene, toluene, ethylbenzene, and xylenes, known collectively by the acronym BTEX. Methyl tert-butyl ether (MTBE) was added to many gasolines in the 1980s and 1990s to increase octane and reduce air pollution from automobiles. MTBE turns out to be a widespread groundwater pollutant because it is so soluble and persistent in water.

### 11.3.3 Properties of Common Contaminants

The chemical properties of our suite of common contaminants are listed in Table 11.2. Most of these properties were defined in the previous chapter, but NAPL solubility, maximum contaminant level (MCL), and vapor pressure were not, so they will be defined presently.

The **solubility** of an NAPL is the equilibrium aqueous concentration of the substance in water that is in contact with the NAPL. Solubility is a function of temperature, usually with higher solubility at higher temperatures. Other than MTBE and DCM, these molecules have fairly low solubilities, in
11.3 Organic Contaminants

<table>
<thead>
<tr>
<th>Substance</th>
<th>Formula</th>
<th>Density (g/cm³)</th>
<th>Solub. (mg/L)</th>
<th>MCL (mg/L)</th>
<th>Log(Kₗₒw)</th>
<th>Kᵥ</th>
<th>Vapor Pr. (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>C₆H₆</td>
<td>0.88</td>
<td>1750</td>
<td>0.005</td>
<td>2.1</td>
<td>0.18</td>
<td>76</td>
</tr>
<tr>
<td>Toluene</td>
<td>C₇H₈</td>
<td>0.87</td>
<td>520</td>
<td>1.0</td>
<td>2.7</td>
<td>0.15</td>
<td>28</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>C₈H₁₀</td>
<td>0.87</td>
<td>180</td>
<td>0.7</td>
<td>3.1</td>
<td>0.15</td>
<td>9</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>C₈H₁₀</td>
<td>0.88</td>
<td>175</td>
<td>*</td>
<td>3.1</td>
<td>0.20</td>
<td>6</td>
</tr>
<tr>
<td>m-Xylene</td>
<td>C₈H₁₀</td>
<td>0.86</td>
<td>160</td>
<td>*</td>
<td>3.2</td>
<td>0.14</td>
<td>8</td>
</tr>
<tr>
<td>p-Xylene</td>
<td>C₈H₁₀</td>
<td>0.86</td>
<td>190</td>
<td>*</td>
<td>3.2</td>
<td>0.14</td>
<td>9</td>
</tr>
<tr>
<td>MTBE</td>
<td>C₅H₁₀₂O</td>
<td>0.74</td>
<td>45,000</td>
<td>**</td>
<td>1.2</td>
<td>1.7</td>
<td>350</td>
</tr>
<tr>
<td>Benzo(a)pyrene</td>
<td>C₂₀H₁₂O</td>
<td>1.35</td>
<td>0.003</td>
<td>0.0002</td>
<td>6.0</td>
<td>2900</td>
<td>5 × 10⁻⁹</td>
</tr>
<tr>
<td>PCB-1248</td>
<td>C₁₂H₁₀₉Clₙ</td>
<td>1.41</td>
<td>0.055</td>
<td>0.0005</td>
<td>6.1</td>
<td>0.25</td>
<td>4 × 10⁻⁴</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>C₂H₄Cl₂</td>
<td>1.25</td>
<td>8400</td>
<td>0.005</td>
<td>1.5</td>
<td>0.91</td>
<td>85</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>C₂H₃Cl₃</td>
<td>1.35</td>
<td>1300</td>
<td>0.2</td>
<td>2.5</td>
<td>0.060</td>
<td>120</td>
</tr>
<tr>
<td>TCE</td>
<td>C₂HCl₃</td>
<td>1.46</td>
<td>1100</td>
<td>0.005</td>
<td>2.4</td>
<td>0.11</td>
<td>70</td>
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<tr>
<td>PCE</td>
<td>C₂Cl₄</td>
<td>1.62</td>
<td>150</td>
<td>0.005</td>
<td>2.4</td>
<td>0.060</td>
<td>19</td>
</tr>
<tr>
<td>DCM</td>
<td>CH₂Cl₂</td>
<td>1.33</td>
<td>14,000</td>
<td>0.005</td>
<td>1.3</td>
<td>0.40</td>
<td>440</td>
</tr>
</tbody>
</table>

Properties are representative average values for 20 to 25°C.

Density of the NAPL, except for benzo(a)pyrene, which is solid.

Solub. = aqueous solubility.

MCL = maximum contaminant level permissible in U.S. public water supplies.

Kₗₒw = octanol–water partition coefficient (dimensionless; see Eq. 10.80).

Kᵥ = Henry's law constant (dimensionless; see Eq. 10.31).

* MCL is 10 mg/L for total of all three xylene isomers.

** No MCL is yet defined. Health advisory based on taste and odor is 0.02 to 0.04 mg/L.

PCBs are a mixture of chlorinated biphenyls with formula as shown.

PCB-1248 contains 48% chlorine by weight, and n = 2 to 6.

Sources for properties: EPA (1994b); Montgomery (2000); Verschueren (1996).

Source for MCLs: EPA (2000).

The hundreds or thousands of parts per million. Recall that water is a polar solvent and organic molecules tend to be nonpolar. The solubility of larger organic molecules is generally lower than the solubility of smaller molecules. Some functional groups such as ether in MTBE are more polar and cause higher solubilities.

When an NAPL is a mixture rather than purely one chemical, each compound in the NAPL will dissolve into water at lower concentrations than their pure solubilities. For example, the equilibrium concentrations of gasoline constituents are substantially below their individual pure solubilities, as shown in Table 11.3. The large ranges in this table are mostly due to the large range of gasoline compositions. If both the NAPL mixture and the water solution have ideal behavior, the equilibrium aqueous concentration of an NAPL constituent will be given by

$$c_{aq} = XS \quad (11.1)$$
Table 11.3 Equilibrium Aqueous Concentrations of BTEX Gasoline Constituents

<table>
<thead>
<tr>
<th>Compound</th>
<th>Weight % of Gasoline*</th>
<th>Equilibrium Aqueous Concentration with Gasoline NAPL (mg/L)</th>
<th>Solubility of Pure NAPL (mg/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>0.7–3.8</td>
<td>12.3–130</td>
<td>1780</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.7–2.8</td>
<td>1.3–5.7</td>
<td>180</td>
</tr>
<tr>
<td>Toluene</td>
<td>4.5–21.0</td>
<td>23–185</td>
<td>520</td>
</tr>
<tr>
<td>m-, p-Xylenes</td>
<td>3.7–14.5</td>
<td>2.6–22.9</td>
<td>160, 190</td>
</tr>
<tr>
<td>o-Xylene</td>
<td>1.1–3.7</td>
<td>2.6–9.7</td>
<td>175</td>
</tr>
</tbody>
</table>

*Range from 31 gasoline samples.

where $c_{aq}$ is the constituent’s aqueous-phase equilibrium concentration, $X$ is the mole fraction of the constituent in the NAPL mixture (moles of constituent/moles of all molecules in mixture), and $S$ is the pure NAPL solubility of the constituent. This relation is known as Raoult’s law. It generally holds for organic mixtures where the molecules in the mixture have similar properties. Cline et al. (1991) found that Raoult’s law was reasonably accurate for gasoline constituents.

**Example 11.1** Assume that MTBE makes up 9% by weight of a gasoline that is spilled into the subsurface. Estimate the equilibrium concentration of MTBE in groundwater that contacts the gasoline. Assume that the average molecular weight of all gasoline constituents is 102 g/mol.

We will use Eq. 11.1, but first we must convert the weight percent of MTBE to its mole fraction in the gasoline. The weight percent of MTBE is the mass of MTBE/mass of gasoline. The mole fraction, $X$ in Eq. 11.1, is the moles of MTBE/mole of gasoline molecules. To convert to mole fraction, we need the molecular weight of MTBE. The chemical formula of MTBE is $C_5H_{12}O$, so its molecular weight is

$$MW = (12.01 \times 5) + (1.01 \times 12) + (16.00 \times 1) = 88.17 \text{ g/mol}$$

The mole fraction of MTBE is

$$X = \left( \frac{0.09 \text{ g MTBE}}{\text{g gasoline}} \right) \left( \frac{102 \text{ g/mol gasoline}}{88.17 \text{ g/mol MTBE}} \right) = 0.104 \text{ mol MTBE/mol gasoline}$$
Now, using Eq. 1.1 we find the aqueous concentration of MTBE in water in equilibrium with this gasoline:

\[
c_{aq} = \left( \frac{0.104 \text{ mol MTBE}}{\text{mol gasoline}} \right) (45,000 \text{ mg/L})
\]

\[
= 4700 \text{ mg/L}
\]

The chemistry of a spilled NAPL mixture will change with time, as some constituents dissolve from it more rapidly than others. Because the solubility of MTBE is about 25–250 times higher than the solubility of BTEX compounds, gasoline with MTBE will lose its MTBE to dissolution much more rapidly than it loses the BTEX compounds. So with time, the remaining gasoline NAPL will be depleted of MTBE and enriched in the less soluble compounds.

Maximum contaminant levels (MCLs) are regulations on public drinking water supplies set by the U.S. Environmental Protection Agency to protect human health. A contaminant tends to be troublesome if it doesn’t easily break down and its solubility exceeds its MCL by many orders of magnitude. Most of the chemicals listed in Table 1.2 fit this description.

The vapor pressure is the equilibrium pressure of the gas phase of a substance in contact with the pure liquid or solid state of the substance. Chemicals with a high vapor pressure tend to evaporate (volatilize). Generally, liquids have higher vapor pressures than solids; note the low vapor pressure of the solid benzo(a)pyrene compared to the other liquid chemicals. Smaller, lighter molecules tend to have higher vapor pressure than larger molecules; note the high vapor pressure of the smaller chlorinated ethanes and ethenes compared to the low vapor pressure of PCB-1248. VOC is an often-used acronym for volatile organic compounds.

The vapor pressure of a constituent of an NAPL mixture is less than the vapor pressure of the same chemical as a pure NAPL. In an ideal solution, the vapor pressure of a chemical above a mixture is directly proportional to its mole fraction of the mixture, another consequence of Raoult’s law:

\[
v_p^{\text{mix}} = X v_p^{\text{pure}}
\]

where \( v_p^{\text{mix}} \) is the equilibrium vapor pressure above an NAPL mixture, \( X \) is the mole fraction of the constituent, and \( v_p^{\text{pure}} \) is the constituent’s pure NAPL vapor pressure, as reported in Table 11.2.
**Example 11.2** Thirty-five percent of an NAPL’s molecules are 1,1,1-TCA. Calculate the vapor pressure and concentration of 1,1,1-TCA in air that is in equilibrium with this NAPL. Give your results in mm Hg, atm, and ppm.

First, according to Eq. 11.2, the vapor pressure of 1,1,1-TCA for the mixture is

\[ \nu_{\text{mix}} = 0.35 \times 120 \text{ mm Hg} \]
\[ = 42 \text{ mm Hg} \]

Convert this vapor pressure to atmospheres using the correct conversion factor:

\[ \frac{42 \text{ mm Hg}}{\frac{1 \text{ atm}}{760 \text{ mm Hg}}} = 0.055 \text{ atm} \]

This means that 5.5% of the molecules in the gas are 1,1,1-TCA. This is equivalent to 55,000 molecules per million (ppm).

As discussed in the previous chapter, \( K_{ow} \) is the octanol–water partition coefficient (see Eq. 10.80 and the accompanying discussion). Compounds with high \( K_{ow} \) tend to adsorb strongly to organic matter in the aquifer solids. Strong partitioning to organic phases tends to be associated with low aqueous solubility, a trend that shows in the data of Table 11.2.

The Henry’s law constant \( (K_H) \) describes the partitioning of a substance between the aqueous and gas states (see Eqs. 10.30 and 10.31). Vapor pressure, solubility, and Henry’s law describe the three possible equilibrium partitioning relations for a system containing NAPL, water, and gas phases, as illustrated in Figure 11.8. The three constants are related as follows when proper unit conversions are made to resolve disparate units:

\[ \text{solubility} = K_H \times \text{vapor pressure} \quad (11.3) \]

### 11.4 Nonaqueous-Phase Liquids

Since most organic contaminants have NAPLs as their source, an important aspect of contamination problems is the movement of NAPLs in the subsurface. NAPL migration in the subsurface is quite different than water movement, and it is governed by some new phenomena that merit investigation. These
11.4 Nonaqueous-Phase Liquids

Figure 11.8 Schematic illustrating the equilibrium relations between vapor, NAPL, and aqueous phases.

Table 11.4 Density, Viscosity, and Interfacial Tension of Common NAPLs and Water at 20°C

<table>
<thead>
<tr>
<th>Liquid</th>
<th>Density, $\rho$ (g/cm$^3$)</th>
<th>Viscosity, $\mu$ (N·sec/m$^2$)</th>
<th>Interfacial Tension, $\sigma$ (dynes/cm)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNAPLs:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Unleaded gasoline</td>
<td>0.75–0.85</td>
<td>$&lt; 8 \times 10^{-4}$</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Leaded gasoline</td>
<td>0.73</td>
<td>$5 \times 10^{-4}$</td>
<td>20</td>
<td>1</td>
</tr>
<tr>
<td>Jet fuel (A/A1)</td>
<td>0.82</td>
<td>$2 \times 10^{-3}$</td>
<td>37</td>
<td>1</td>
</tr>
<tr>
<td>Home heating oil</td>
<td>0.86</td>
<td>$1.7 \times 10^{-3}$</td>
<td>27</td>
<td>1</td>
</tr>
<tr>
<td>Kerosene</td>
<td>0.81</td>
<td>$1 \times 10^{-3}$</td>
<td>23–32</td>
<td>1</td>
</tr>
<tr>
<td>Arabian medium crude oil</td>
<td>0.88</td>
<td>$2.3 \times 10^{-2}$</td>
<td>23</td>
<td>1</td>
</tr>
<tr>
<td>DNAPLs:</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>1.33</td>
<td>$4.4 \times 10^{-4}$</td>
<td>28</td>
<td>2</td>
</tr>
<tr>
<td>1,2-DCA</td>
<td>1.26</td>
<td>$8.4 \times 10^{-4}$</td>
<td>30</td>
<td>2</td>
</tr>
<tr>
<td>1,1,1-TCA</td>
<td>1.35</td>
<td>$8.4 \times 10^{-4}$</td>
<td>45</td>
<td>2</td>
</tr>
<tr>
<td>TCE</td>
<td>1.46</td>
<td>$5.7 \times 10^{-4}$</td>
<td>35</td>
<td>2</td>
</tr>
<tr>
<td>PCE</td>
<td>1.63</td>
<td>$9.0 \times 10^{-4}$</td>
<td>44</td>
<td>2</td>
</tr>
<tr>
<td>Water:</td>
<td>1.00</td>
<td>$1.0 \times 10^{-3}$</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Interfacial tension is for NAPL/water interfaces.
(1) Environmental Technology Center (2000).
(2) $\rho, \mu$: Schwille (1988); $\sigma$: Cohen and Mercer (1993).

...concepts also apply to multiphase flow of petroleum, which is a naturally occurring NAPL. Three books that go beyond the introduction given here are Pankow and Cherry (1996), Cohen and Mercer (1993), and Corey (1994).

Key physical properties of some common NAPLs are listed in Table 11.4. Whether the density is greater or less than that of water determines whether
the NAPL will float and accumulate at the top of the saturated zone or be able to plunge deep into the saturated zone. LNAPLs are “floaters” and DNAPLs are “sinkers.” Most hydrocarbon fuels are LNAPLs and most chlorinated hydrocarbons are DNAPLs. The greater the density of the NAPL compared to the air or water that surrounds it, the greater its tendency to drive deeper into the subsurface. The lower the viscosity or interfacial tension of an NAPL, the more mobile it tends to be in the subsurface (more on these properties later).

### 11.4.1 Saturation, and Wetting and Nonwetting Fluids

When NAPL is present in the unsaturated zone, there are three phases that can occupy the pores: air, water, and NAPL. In the saturated zone, two phases can be present: water and NAPL. Saturation is a parameter for describing the relative abundance of each phase. The saturation $S_i$ is the fraction of the pore space that phase $i$ occupies:

$$ S_i = \frac{V_i}{V_v} $$

(11.4)

where $V_i$ is the volume of phase $i$ and $V_v$ is the volume of voids in the material. The sum of the saturations of all phases present equals one. For example, in the unsaturated zone with air, water, and NAPL, the corresponding saturations total one: $S_a + S_w + S_n = 1$. In the saturated zone with only water and NAPL, $S_w + S_n = 1$.

When multiple immiscible fluids are present in the pores, the fluid with the strongest molecular attraction for the solid surfaces will coat the surfaces, while the other fluids occupy the central parts of pores, away from the solid surfaces. The fluid that wets the solid surfaces is called the wetting fluid and the other(s) are called the nonwetting fluid(s). In most situations, both in the unsaturated and saturated zones, water will be the wetting fluid, while air and/or NAPL are nonwetting fluids. If the unsaturated zone is completely devoid of water, NAPL is the wetting fluid and air is the nonwetting fluid. Figure 11.9 shows some example distributions of phases in both the saturated and unsaturated zone pores.

At low NAPL saturations, NAPL exists as isolated blobs that are immobile. These blobs occupy the largest pores and approach spherical shapes. At higher NAPL saturations, the blobs merge into ganglia that are irregular and continuous blobs that connect through multiple pores. The ganglia, if large enough, are mobile and allow NAPL to push into new pore spaces.
11.4.2 Interfacial Tension and Capillary Pressure

Figure 11.10 shows an interface where NAPL and water contact each other. Molecules in the NAPL have a greater attraction for themselves than they do for water molecules, and water molecules are more attracted to themselves than to NAPL molecules. One fluid typically has greater self-attraction than the other. Molecules near the interface are drawn away from the interface towards the interior of the fluid by these molecular forces.

Interfacial tension is a property that measures the amount of imbalance in molecular attractions at an interface between two fluids. It has dimensions of energy/area, or equivalently, force/length. For most common NAPLs and water,
the interfacial tension is in the range 20–50 dynes/cm (Table 11.4). Interfacial tension is so named because the interface looks as if there is some elastic membrane in tension stretched across the interface. The interface tends to contract around the nonwetting fluid, minimizing the surface area of the interface.

The imbalance of molecular forces at the interface is compensated for by a discontinuity in pressure. The nonwetting fluid (NAPL in Figure 11.10) is on the inside of the interface curvature, and has higher pressure than the wetting fluid (water in Figure 11.10) \( P_w < P_n \). The difference in pressure across the interface is called the capillary pressure, \( P_c \):

\[
P_c = P_n - P_w
\]

where \( P_n \) is the pressure in the nonwetting fluid (typically NAPL) and \( P_w \) is the pressure in the wetting fluid (typically water). In the unsaturated zone with no NAPL, water is the wetting fluid, air is the nonwetting fluid, and the pore water pressure (gage pressure) equals \(-P_c\).

Where an interface is shaped like a spherical cap of radius \( r \), the capillary pressure is a simple function of interfacial tension \( \sigma \) and \( r \) (Corey, 1994):

\[
P_c = \frac{2\sigma}{r} \quad \text{(spherical interface)}
\]

Where the interface is shaped like a long cylinder of radius \( r \), then the capillary pressure is given by (Corey, 1994)

\[
P_c = \frac{\sigma}{r} \quad \text{(cylindrical interface)}
\]

Equation 11.6 is appropriate for roughly spherical pore openings like in granular media, and Eq. 11.7 is more applicable to fractures in rock. Although not all interfaces are shaped exactly like spheres or cylinders, capillary pressure is generally inversely proportional to the radius of curvature of the interface.

NAPL will invade a small pore only if the capillary pressure is high enough to bend the interface sharply enough to fit it through the entrance of the pore. An NAPL ganglion or blob that has high enough capillary pressures to be mobile will invade the largest pore it is surrounded by, but not the smaller ones. If the capillary pressure is not high enough to push the interface into any of the surrounding pores, the ganglion or blob is immobile. Within a single connected ganglion, the capillary pressure increases from top to bottom, so it is most likely that the interface will invade pores near the base of the ganglion. The taller the ganglion, the higher the capillary pressure and the more likely NAPL will move into new pores.
**Example 11.3** Calculate the capillary pressure at the base of a dichloromethane (DCM) DNAPL ganglion in the saturated zone, if the ganglion is 0.8 m high. Assume that the capillary pressure at the top of the ganglion is 1500 N/m$^2$, and that the pressure distributions in both the water and NAPL phases is hydrostatic.

With a hydrostatic pressure distribution in the water phase, the water pressure at the base of the ganglion, $P_{w(b)}$, can be written as

$$P_{w(b)} = P_{w(t)} + \rho_w gb$$

where $P_{w(t)}$ is the water pressure at the top of the ganglion, $\rho_w g$ is the unit weight of water, and $b$ is the height of the ganglion.

Likewise, the NAPL pressure at the base of the ganglion is

$$P_{n(b)} = P_{n(t)} + \rho_n gb$$

where $P_{n(t)}$ is the NAPL pressure at the top of the ganglion and $\rho_n g$ is the unit weight of NAPL.

The capillary pressure at the base of the ganglion is the difference between these two pressures:

$$P_{c(b)} = P_{n(b)} - P_{w(b)}$$

$$= P_{n(t)} - P_{w(t)} + (\rho_n - \rho_w)gb$$

$$= P_{c(t)} + (\rho_n - \rho_w)gb$$

$$= 1500 \text{ N/m}^2 + (1330 - 1000 \text{ kg/m}^3)(9.81 \text{ m/s}^2)(0.8 \text{ m})$$

$$= 4090 \text{ N/m}^2$$

**Figure 11.11** shows a dyed DNAPL (PCE) invading water-saturated pores in a medium consisting of uniform glass beads. In the upper photo, the PCE is thin and immobile; $P_c$ is not high enough to push the interface into any of the available pore openings. In the lower photo, more PCE has been added at the top, so now $P_c$ is high enough to push the interface into the pores below. As the ganglia grow taller vertically, $P_c$ at the base of the ganglia increases and the PCE has an even easier time invading new pores.

Heterogeneity plays a key role in the migration patterns of NAPL. It will always move into the largest pore spaces it contacts, so it will often migrate in unintuitive ways, following coarse lenses or wider fractures. **Figure 11.12** shows
the migration of dyed PCE through water-saturated glass beads, with a layer of finer beads under coarser beads. The downward-moving PCE accumulated at the top of the finer layer until its thickness and $P_c$ grew large enough to

Figure 11.11  PCE DNAPL (dark) resting on water-saturated glass beads. In the upper photo, the PCE is thin and immobile. In the lower photo, greater DNAPL thickness allows it to invade the pores below. Adapted from Schwille (1988) with permission of CRC Press.
invade the pores of the finer beads. Sometimes NAPL doesn’t get thick enough to invade a fine-grained lens as it did in Figure 11.12. Instead, NAPL just flows laterally across the top of the fine-grained lens, flowing down the dip of the lens, even if that may run counter to the local groundwater flow.

### 11.4.3 Capillary Pressure vs. Saturation and Residual Saturation

In a particular medium, the NAPL saturation $S_n$ increases with increased capillary pressure. Higher capillary pressure allows the NAPL–water interface to push into smaller pores, with NAPL displacing water in the process. The capillary-pressure–saturation relationship can be measured in a laboratory, resulting in curves that look much like a characteristic curve for water/air saturation, as discussed in Section 3.10.1. Figure 11.13 shows several such curves for different sand samples and PCE DNAPL. The tests that led to these curves were drainage tests: they started with water-saturated sand and then slowly introduced DNAPL at higher and higher capillary pressure, displacing water throughout the test.

Like the characteristic curves for water and air in the unsaturated zone, the capillary-pressure–saturation relationship is hysteretic, or history-dependent.

---

Figure 11.12  PCE DNAPL (dark) accumulating in a layer of coarse glass beads atop a layer of fine glass beads. The DNAPL is thick enough that it has begun invading the layer of finer beads. Adapted from Schwille (1988) with permission of CRC Press.
Figure 11.13  Capillary-pressure–saturation curves for sand samples from Canadian Forces Base Borden (CFB Borden), Ontario. The NAPL in this case is PCE. The hydraulic conductivity is listed for each sample. From Kueper, B. H. and E. O. Frind, 1991, Two-phase flow in heterogeneous porous media, 2. Model application, Water Resources Research, 27(6), 1059–1070. Copyright (1991) American Geophysical Union. Modified by permission of American Geophysical Union.

Figure 11.14 shows a typical cycle of saturation vs. capillary pressure for an NAPL spilled into the saturated zone. As NAPL saturation increases and water drains during NAPL invasion, it follows a drainage curve like the one labeled A in Figure 11.14. Eventually, the NAPL pulse moves through and NAPL saturations decrease as water reclaims some of the pore space taken up by NAPL (wetting curve B in Figure 11.14). The wetting curve is always displaced toward higher NAPL saturation compared to the drainage curve, at the same capillary pressure.

As the NAPL saturation decreases along the wetting curve, there is a transition from a thoroughly interconnected network of NAPL ganglia in the pore spaces to more isolated ganglia, and eventually to separate, unconnected blobs. The wetting curve stops at the point where the remaining NAPL blobs become immobile. The NAPL saturation at this point is called the residual NAPL saturation. Figure 11.15 shows residual NAPL saturation in an experiment with glass beads, water, and PCE. Residual NAPL saturations in the range of 0.01 to 0.15 have been reported for sands (Kueper et al., 1993; Schwille, 1988).

When NAPLs are spilled into the subsurface, they move downward in irregular paths, following a trail containing the largest available pores. If enough NAPL is spilled, it will accumulate at the top of the saturated zone (LNAPL) or on top of layers with small pores. These zones of accumulation will have
11.4 Nonaqueous-Phase Liquids

Figure 11.14  Capillary pressure $P_c$ vs. water saturation $S_w$ and NAPL saturation $S_n$. During drainage (curve A), NAPL displaces water. During wetting (curve B), water displaces NAPL. The displacement pressure $P_{c(d)}$ is the minimum capillary pressure needed for NAPL to begin invading the medium. The residual NAPL saturation $S_{n(r)}$ is the saturation at which the NAPL becomes immobile. The dashed wetting curve shows what would happen if wetting began after limited drainage. The final value of $S_{n(r)}$ depends on the saturation history.

Figure 11.15  Residual saturation of PCE DNAPL in initially water-saturated glass beads. NAPL flowed in and then drained out from the pores. The NAPL now occupies only the largest pore openings as isolated blobs. Adapted from Schwille (1998) with permission of CRC Press.
relatively high NAPL saturations and the NAPL is capable of further movement (mobile NAPL in Figures 11.3 and 11.4).

Other than these zones of mobile NAPL, the trail followed by the NAPL will reduce to immobile residual NAPL saturation levels once the pulse of migrating NAPL has passed. Both the mobile and immobile NAPL zones serve as continuous sources, dissolving slowly into passing pore water (and pore gases in the unsaturated zone). Because most NAPLs have low solubility, the subsurface NAPL source can persist for a long time. For this reason, many early efforts to remediate subsurface organic contamination problems were far from successful.

11.4.4 Relative Permeability and Flow of Multiple Phases

The rates of water and NAPL flow when multiple phases are present are still governed by equations that look like Darcy’s law for variable density fluids (Eq. 3.40), but the equations are modified by a relative permeability factor \( \kappa \) that relates to saturation. Whether the fluid is water or NAPL, the specific discharge components of fluid \( i \) (discharge/area) are given by

\[
q_{xi} = -\frac{k_x \kappa_i}{\mu_i} \frac{\partial P_i}{\partial x} \\
q_{yi} = -\frac{k_y \kappa_i}{\mu_i} \frac{\partial P_i}{\partial y} \\
q_{zi} = -\frac{k_z \kappa_i}{\mu_i} \left( \frac{\partial P_i}{\partial z} + \rho_i g \right)
\]  

(11.8)

where \( k_x, k_y, \) and \( k_z \) are the components of intrinsic permeability, \( \mu_i \) is the fluid viscosity, \( P_i \) is the fluid pressure, \( \rho_i \) is the fluid density, and \( g \) is gravitational acceleration.

The relative permeability factor \( \kappa_i \) is one when fluid \( i \) completely saturates the medium (\( S_i = 1 \)), and it drops to zero at residual saturation when \( S_i = S_{i(r)} \) when the phase becomes immobile. The general nature of the relationship between \( \kappa \) and \( S \) is shown in Figure 11.16 for water–NAPL two-phase flow. It makes sense that permeability to a fluid increases as its saturation increases, because the fluid occupies more volume and is more interconnected.

The specific discharge of a fluid is inversely proportional to the fluid’s dynamic viscosity \( \mu \), as you would expect (Eq. 11.8). High-viscosity NAPLs like tars and crude oils flow very slowly compared to water and solvents.
11.5 Solute Transport Processes

The migration of NAPLs is one way that contaminants can move in the subsurface. The other is solute transport: the movement of dissolved substances in flowing groundwater. Several different physical and chemical processes team up to affect solute transport in interesting ways. Each process is discussed separately in the following sections.

11.5.1 Advection and Mechanical Dispersion

Advection is just a fancy word for the movement of mass entrained in the flow. Solute advection is the movement of dissolved substances because the water they are in is moving. The mass flux of a solute due to advection alone is simply

$$F_{ax} = q_x c$$  \hspace{1cm} (11.9)

where $F_{ax}$ is the advective flux of solute mass in the $x$ direction (mass/time/area normal to the $x$ direction), $q_x$ is specific discharge in the $x$ direction (volume/time/area), and $c$ is solute concentration (mass/volume). The average rate of solute migration equals the average linear velocity $\bar{v}$, as defined by Eq. 3.4. We will see in Section 11.5.3 that the apparent rate of solute advection differs from $\bar{v}$ when the solute reacts with the solid matrix it is flowing through.
Advection not only translates mass from one location to another, but it tends to spread or disperse the mass in the process. This occurs because the distribution of water velocity is not uniform. The actual distribution of groundwater velocity $v$ varies significantly both in space and in time. Velocity variations in space occur at scales ranging from the size of pores on up to the size of channel deposits in a floodplain.

Consider the pore scale first. Figure 11.17 shows water velocity distributions in a few pores of a granular medium. The flow is laminar, but there are still significant variations in velocity. The variations in velocity cause solutes in a discrete, compact plume to disperse in the direction of flow, as some solute speeds through pore throats and other solute lags at grain boundaries and in bigger pores. In perfectly steady and laminar groundwater flow, advection alone causes longitudinal spreading but no transverse spreading. In real groundwater solute transport, there are transient velocity variations and molecular diffusion, both of which contribute to transverse spreading (more on that shortly).

At a larger spatial scale, all geologic media are heterogeneous, which means that the average linear velocity field is irregular. Figure 11.18 shows the flow field for an analytic, two-dimensional model of flow through a field containing six lens-shaped heterogeneities. In the low-permeability lenses, gradients are high and $v$ is low. In high-permeability lenses, head gradients are low and $v$ is high. As with steady pore-scale advection, these spatial velocity variations cause a slug of solute to spread in the direction of flow, but not transverse to flow.

So far, we have only discussed spatial variations in velocity, which produce longitudinal dispersion of solute pulses in the direction of flow. Temporal variations in velocity are also important and can lead to transverse dispersion of solutes. When directions in the velocity field change with time, the direction of

---

**Figure 11.17** Velocity variations at the pore scale. The vector lengths are proportional to the water velocity $v$. The fastest flow is in the throats of constricted pores, and the slowest flow is near the mineral surfaces and in the larger pores.
11.5 Solute Transport Processes

Figure 11.18 An analytic model of two-dimensional steady flow with six heterogeneity domains (shaded) showing velocity variations at the heterogeneity scale. Going clockwise from the lower left heterogeneity, their $K$'s differ from the background $K$ by factors of 4.0, 0.5, 2.0, 3.0, 0.3, and 0.6. Head contours (dashed) show the inverse correlation of $K$ and gradient. Pathlines (blue) are traced downstream from left to right. Each pathline represents the same specified travel time from beginning to end. Longitudinal dispersion caused by heterogeneity is apparent in the staggered locations of the ends of the pathlines at the right side of the plot (circles).

Figure 11.19 Schematic two-dimensional section through a solute plume migrating and spreading with time. Blue arrows show the direction of $\vec{v}$ at each time, and the dashed line shows the path taken by the plume's center of mass. Solute concentration levels are shown by the degree of shading in the plumes; darker shades represent higher concentrations. The plume always disperses in the direction of flow. With a varying flow direction, this causes the plume to grow wider in addition to lengthening.

longitudinal spreading that occurs also changes with time. An elongate solute plume will spread laterally over time with respect to the average flow direction (Goode and Konikow, 1990; Rehfeldt and Gelhar, 1992). Figure 11.19 shows a time sequence of a plume dispersing with slightly variable flow directions. The plume is always spreading longitudinally, but the net effect of varying the flow direction is to increase spreading transverse to the average flow direction.

11.5.2 Molecular Diffusion

Molecular diffusion is mixing that occurs due to the random motion of molecules in a fluid. When a can of cat food is opened in the kitchen,
molecular diffusion spreads some of the molecules from the food through the air to the cat’s nose, where it detects that supper is being served. The same happens in water, although at a slower pace than in air.

The bumping and jostling of molecules in the liquid tends, over time, to spread solutes out so that solute concentrations become more evenly distributed in space. Diffusion moves solute mass from regions with high concentrations towards regions with low concentrations. Diffusion tends to smooth out sharp differences in concentration distributions with time, as shown in Figure 11.20.

Diffusive mass flux for solutes in a saturated porous medium is governed by a form of Fick’s first law, which for the $x$ direction is written as

$$F_{dx} = -nT^*_x D \frac{\partial c}{\partial x}$$

(11.10)

where $F_{dx}$ is the diffusive mass flux of solute in the $x$ direction (mass per time per area normal to the $x$ direction), $n$ is the porosity of the medium, $T^*_x$ is the tortuosity of the liquid phase in the $x$ direction, $D$ is a constant called the molecular diffusion coefficient, and $c$ is solute concentration. Similar expressions would apply in the $y$ and $z$ directions. The flux of solute in any direction is proportional to the gradient of concentration in that direction. The minus sign is in this equation because mass moves towards decreasing concentrations, in the direction opposite that of the concentration gradient.

For water in porous media, the rate of diffusion is slower than diffusion through water alone, because the water phase occupies only a fraction of the space in a network of tortuous, interconnected passageways. Tortuosity is dimensionless, always less than one, and is a measure of how tortuous the typical flow path is through the medium. It can be thought of as the net, straight-line length of a flow path divided by the average actual, tortuous flow path. de Marsily (1986) reports that typically $T^*$ ranges between 0.7 (sands)
11.5 Solute Transport Processes

Table 11.5 Molecular Diffusion Coefficients in Water

<table>
<thead>
<tr>
<th>Solute</th>
<th>$D$ (cm$^2$/sec)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Ions:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$H^+$</td>
<td>$9.3 \times 10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>$OH^-$</td>
<td>$5.3 \times 10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>$Na^+, K^+, F^-, Cl^-, HCO_3^-, SO_4^{2-}$</td>
<td>$1.1$ to $2.1 \times 10^{-5}$</td>
<td>1</td>
</tr>
<tr>
<td>$Ca^{2+}, Mg^{2+}, Fe^{2+}, Ra^{2+}, Fe^{3+}, Cr^{3+}, CO_3^{2-}$</td>
<td>$5.9$ to $9.6 \times 10^{-6}$</td>
<td>1</td>
</tr>
<tr>
<td><strong>VOCs:</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>DCM</td>
<td>$1.1 \times 10^{-6}$</td>
<td>2</td>
</tr>
<tr>
<td>1,1,1-TCA, PCE, TCE</td>
<td>$7.5$ to $8.3 \times 10^{-6}$</td>
<td>2</td>
</tr>
</tbody>
</table>

(1) Li and Gregory (1974).

and 0.1 (clays), with measured values as low as 0.01 in a highly compacted bentonite clay. Bear (1972) reports a range of $0.56 < T^* < 0.8$ for granular media.

Tortuosity varies with direction because the fabric of the porous medium varies with direction. This is especially true in sedimentary deposits and in fractured rock. Like hydraulic conductivity, $T^*$ in the most general sense is not isotropic, but is a tensor with nine components. If the coordinate axes line up with the principal directions of $T^*$ (the directions of greatest, least, and intermediate $T^*$), the tensor contains only three nonzero terms ($T_x^*$, $T_y^*$, and $T_z^*$). Tortuosity is not easily measured and is often assumed to be isotropic, described by a single parameter $T^*$.

The molecular diffusion coefficient $D$ has dimensions of [L$^2$/T]. It is a scalar property that depends on temperature and on the properties of the fluid and the solute. Higher temperatures mean faster molecular motions and larger $D$. Freeze and Cherry (1979) state that $D$ at 5°C is about half of $D$ at 25°C. Smaller molecules diffuse faster and have higher $D$ than larger molecules. Molecular diffusion coefficients are lower in more viscous fluids. For most contaminant solutes of interest, $D$ in water at 20°C is in the range of $10^{-6}$ to $10^{-5}$ cm$^2$/sec (Table 11.5). For VOCs, the air diffusion coefficient is usually about $10^4$ times larger than the water diffusion coefficient (Cohen and Mercer, 1993).

In water, the pace of molecular diffusion is quite slow, so that relatively sharp gradients in solute concentration can persist in contaminant plumes. Figure 11.21 shows that one-dimensional diffusion with typical values for $n$, $T^*$, and $D$ takes decades and more to disperse a solute pulse. Although diffusion is slow, it is an important process in very low conductivity materials like clays, where the advective flux (Eq. 11.9) may be even smaller than the diffusive flux.
Figure 11.21  One-dimensional spreading of a solute pulse due to diffusion only, based on the analytic solutions of Leij et al. (1991), as implemented in the software SOLUTRANS. At time \( t = 0 \), the pulse was a step of solute with \( c = 1 \) inside the 1 m wide zone and \( c = 0 \) outside the zone. With time, the solute pulse spreads out, the peak concentration declines, and the concentration gradients decrease. In this model, \( nT^*D = 2 \times 10^{-6} \text{ cm}^2/\text{sec} \), which is in the typical range for solutes in porous media.

Example 11.4 Consider a clay layer that will serve as a landfill liner. It is 1 m thick, and its conductivity is estimated at \( K = 10^{-7} \text{ cm/sec} \). Assume that the hydraulic gradient through the layer is 0.1, that the concentration of a solvent goes from \( c = 80 \text{ mg/L} \) at the top of the layer to \( c = 0 \text{ mg/L} \) at the bottom of the layer, and that \( n = 0.4 \), \( T^* = 0.1 \), and \( D = 8 \times 10^{-6} \text{ cm}^2/\text{sec} \). Estimate the magnitude of both the diffusive and the advective flux through the clay.

The diffusive flux is given by Eq. 11.10 as follows:

\[
F_{dx} = -nT^*D \frac{\partial c}{\partial x}
\]

\[
= -(0.4)(0.1)(8 \times 10^{-6} \text{ cm}^2/\text{sec}) \left( \frac{80 \text{ mg}/1000 \text{ cm}^3}{100 \text{ cm}} \right)
\]

\[
= -2.6 \times 10^{-10} \text{ mg/cm}^2 \cdot \text{sec}
\]

Assuming an average concentration of 40 mg/L, the advective flux based on Eq. 11.9 is

\[
F_{ax} = q_x c
\]

\[
= -K \frac{\partial h}{\partial x} c
\]
\[ \begin{align*}
&= -(10^{-7} \text{ cm/sec})(0.1)(40 \text{ mg/L})\left(\frac{L}{1000 \text{ cm}^3}\right) \\
&= -4 \times 10^{-10} \frac{\text{mg}}{\text{cm}^2 \cdot \text{sec}}
\end{align*} \]

In this case, the two fluxes are of similar magnitude. In more conductive materials like silts or sands, the advective flux is usually several orders of magnitude larger than the diffusive flux.

The slow process of diffusion does not move large amounts of solute mass great distances, but it does smooth out small, localized concentration gradients. Irregular sources combined with mechanical dispersion due to velocity variations causes many small-scale concentration variations that are then smoothed to some extent by molecular diffusion.

### 11.5.3 Sorption

Solute sorption processes were discussed in the previous chapter. These processes cause interesting effects on overall patterns of solute migration. If a solute does not sorb at all to the aquifer solids as it flows, the average rate of solute transport can be estimated directly from the average linear velocity \( v \).

When a solute does sorb significantly, its migration is slower than \( v \). An analogy may help explain why. Consider a conveyor belt with a pile of oranges on it, as illustrated in Figure 11.22. If someone rapidly removes oranges from the leading edge of the pile and simultaneously adds them to the trailing edge of the pile, the pile itself will migrate at a rate that is slower than the speed of the conveyor. The migration of sorbing solutes is similar. In the leading edge of a plume, solute concentrations are increasing with time, which will be accompanied by rising sorbed concentrations (Eq. 10.74, for example). In the leading edge, solute mass is being transferred from the aqueous phase

![Figure 11.22](image-url)
to the sorbed phase. The opposite is true at the trailing edge of a pulse; solute concentrations are falling, and mass is being transferred from sorption sites back into solution.

The migration of a pulse or front of sorbing solute is slower than the average linear velocity \( \bar{v} \). If linear equilibrium sorption can be assumed, and if the sorption is linear (Eq. 10.74), the average rate of solute front migration \( \bar{v}_s \) is linearly related to \( \bar{v} \):

\[
\bar{v}_s = \frac{\bar{v}}{R} \quad \text{(linear equilibrium sorption)}
\]

where \( R \) is a constant called the retardation factor. For example, if the solute migrates half as fast as the average linear velocity, \( R = 2 \). The rate \( \bar{v}_s \) is the rate that a moving pulse or a moving solute front would migrate.

Under the assumptions listed in Eq. 11.1, \( R \) is related to the sorption distribution coefficient \( K_d \) (Eq. 10.74) as

\[
R = 1 + \frac{\rho_b K_d}{n} \quad \text{(linear equilibrium sorption)}
\]

where \( \rho_b \) is the dry bulk density of the aquifer and \( n \) is porosity. This equation is derived in Section 11.7.3.

There are many situations where the simple model of retardation embodied in Eqs. 11.11 and 11.12 is not applicable. Linear sorption that obeys Eq. 10.74 is reasonable for many hydrophobic organic solutes, but it does not generally hold for metals, which are influenced by various aspects of solution and surface chemistry.

Sorption equilibrium is often not a good assumption. In many geologic materials, molecular diffusion limits the flux of solute molecules to some sorption sites. Sorption reactions are relatively fast, but in some materials a significant fraction of the potential sorption sites are not in direct contact with mobile pore water. Some pores are dead-ended, and some pores lie entirely within the mineral matrix. The water in these pores is stagnant, and molecular diffusion is the only way to move solutes through it to potential sorption sites.

Molecular diffusion is a slow process, so the solute concentration in these tiny, stagnant pockets can differ from the solute concentration in the nearby mobile water. Likewise, the sorbed concentrations on the surfaces that line these stagnant pockets differ from the sorbed concentrations on the surfaces in contact with flowing water. If the mobile water maintains a fixed concentration long enough, the solute and sorbed concentrations will become the same in the mobile water pores and in the stagnant pores. If the mobile
water concentrations are too variable, there will be disequilibrium between the mobile and immobile waters, and some diffusive mass transfer between these regions occurs. For sands from CFB Borden, Ontario, tens to hundreds of days were required in batch sorption tests for complete sorption equilibration, as shown in Figure 10.14. Similar long times for desorption were observed by Grathwohl and Reinhard (1993) in column tests, and they attributed this to diffusion-limited sorption.

Apparent effects of diffusion-limited sorption have been observed at the laboratory scale in experiments and at the field scale in tracer tests, as discussed in Section 11.6. The characteristics of diffusion-limited sorption include breakthrough curves and plumes that are asymmetric with long trailing sections, as shown in Figure 11.23. Heterogeneity in the sorption characteristics of the medium, like lenses of variable $K_d$ materials, can cause greater dispersion and tailing similar to the effects of diffusion-limited sorption.

### 11.5.4 Colloid Transport

Colloids are defined as particles suspended in water with diameters smaller than $10 \mu m \ (10^{-6} \ m)$ in diameter (McCarthy and Zachara, 1989). At this small size, gravity forces are small compared to other forces, so particles can remain in suspension for very long times. Small as colloids are, they are still much larger than most molecules, which are on the order of $10^{-10}$ to $10^{-8} \ m$.

![Breakthrough curve: plot of concentration vs. time at a point downstream from a continuous solute source (left). Profile of concentrations along the direction of flow for a pulse of solute that is advecting and dispersing (right). When the sorption is linear and at equilibrium, the breakthrough curve and pulse are symmetrical. When the sorption is nonequilibrium (diffusion-limited), the curves become skewed with long trailing sections. Nonequilibrium sorption causes greater dispersion of solutes. The plots are generated by analytic solutions of Leij et al. (1991, 1993). The two cases compared in each plot are identical except for the mode of sorption.](image-url)
Colloids can consist of small mineral fragments, bacteria, viruses, NAPL droplets, and larger organic molecules. Some colloids are generated by chemical reactions that precipitate minerals; others are generated by surface reactions that disaggregate and loosen small particles from surfaces. Colloids can also be moved from surface water to the subsurface by natural or unnatural infiltration.

Colloids are often mobile, drifting with groundwater as it flows through pore spaces. This is yet another potential mechanism for contaminant migration. The colloid itself can be a contaminant, as in NAPL droplets or certain bacteria. Sometimes the colloid itself is not a contaminant, but contaminants hitch a ride by sorbing onto colloid surfaces. Colloids have a large ratio of surface area to mass, so they have the potential to provide a significant amount of sorption.

Immobile colloids are found at mineral surfaces, at air–water interfaces in the unsaturated zone, and probably at NAPL–water interfaces (Wan and Wilson, 1994a,b). Figure 11.24 shows colloidal latex particles sorbed onto an air–water interface. What holds colloids to these surfaces is a combination of electrostatic and chemical forces (McCarthy and Zachara, 1989). Colloids tend

Figure 11.24 Sorption of colloidal latex particles (fluorescent) onto the air–water interface of an air bubble trapped in a pore. This type of sorption can significantly retard colloid migration in unsaturated zone pore waters. From Wan, J. and J. L. Wilson, 1994a, Visualization of the role of the gas–water interface on the fate and transport of colloids in porous media. Water Resources Research, 30(1), 11–23. Copyright (1994) American Geophysical Union. Reproduced by permission of American Geophysical Union.
to attach themselves to surfaces that have an electrical charge opposite the charge of the colloid surface. For example, colloids carrying a positive charge tend to attach to negatively charged silicate and oxide minerals in the matrix.

Colloids can be filtered (trapped) in porous media when most pore openings are too small to accommodate the colloids. Such filtration is the basis for many common wastewater treatment processes. If a colloid is big enough to be excluded from small, tortuous flow paths, but small enough to migrate through larger, less tortuous pathways, the colloid can migrate at an average rate that is faster than the average linear velocity $\overline{v}$ of the water. This was demonstrated in tracer tests with bacteria in a sand and gravel aquifer (Harvey et al., 1989). In these experiments, a pulse of bacteria tracer migrated significantly faster than bromide tracer, which is nonreactive and migrates at an average rate equal to $\overline{v}$.

It is difficult to obtain groundwater samples that accurately reflect the concentrations of colloids found in situ (McCarthy and Zachara, 1989). Drilling and well installation, with the associated mechanical mixing and clay-rich drilling fluids, often introduces more colloids than are present in the ambient setting. Originally immobile colloids can be mobilized by the high hydraulic gradients that occur during drilling or groundwater sampling. It is also possible that colloid chemistry is altered during sampling, as the water adjusts to changes in parameters such as pressure, temperature, dissolved oxygen, and dissolved CO$_2$.

### 11.6 Case Studies of Solute Transport

The two case studies presented here are ones where the migration of solutes were monitored with an exceptionally large number of wells, so that a fairly clear picture of the migration patterns emerged. The first was a controlled tracer test, where known masses of tracers were intentionally injected as solutes. After injection, their migration was closely monitored by repeated sampling of thousands of small wells. The tracer solution included nonreactive solutes and several reactive solutes that sorbed and biodegraded. The other case study monitored solute transport from gasoline and diesel fuel that leaked from underground storage tanks.

#### 11.6.1 CFB Borden, Ontario, Tracer Test

The Borden tracer test is described by Mackay et al. (1986), and summarized briefly here. It took place in an unconfined sand aquifer located beneath
the Canadian Forces Base Borden (CFB Borden), Ontario, during a three-year period in the early 1980s. A tracer solution containing inorganic and organic solutes was injected and allowed to migrate under natural gradients through a dense network of monitoring wells. The sand aquifer was relatively uniform, but contained lenses that ranged from silty fine sand to clean medium sand. Its porosity and bulk density averaged \( n = 0.33 \) and \( \rho_b = 1.81 \text{ g/cm}^3 \), respectively.

The source was 12 \( \text{m}^3 \) of a premixed solution of aquifer water plus known masses of seven different tracer chemicals. Two of the tracers were inorganic and nonreactive: chloride and bromide. Five were bromated or chlorinated organic compounds that were reactive: bromoform (CHBr\(_3\)), carbon tetrachloride (CCl\(_4\)), tetrachloroethylene (PCE, C\(_2\)Cl\(_4\)), 1,2-dichlorobenzene (C\(_6\)H\(_4\)Cl\(_2\)), and hexachloroethane (C\(_2\)Cl\(_6\)). The source solution was injected just below the water table through a cluster of injection wells, as shown in Figure 11.25.

The tracers migrated downd gradient under natural hydraulic gradients (no pumping) through a dense network of multilevel samplers shown in Figure 11.25. Each multilevel sampler consisted of multiple short-screen piezometers installed in a single vertical hole. There were a total of about 5000 sampling points in the array. Samples were collected during 14 separate sampling rounds during the 1038-day tracer test.

The horizontal distribution of chloride and carbon tetrachloride solutes during the test is shown in Figure 11.26. One day after injection, the chloride was distributed in an irregular, roughly circular pattern about the injection wells. The other solutes probably had a similar distribution at this early time. As time passed, the center of mass of the solute clouds translated downgradient and the clouds dispersed and became elongated in the direction of flow. The solute clouds did disperse some transverse to flow, but very little compared to the longitudinal dispersion.

It is quite clear that the chloride tracer cloud moved more rapidly than the carbon tetrachloride tracer cloud. Later in the test, the two tracers were completely separated in space. The chloride is a nonreactive tracer that is not retarded by sorption reactions. On the other hand, carbon tetrachloride sorbed to the aquifer solids, retarding its horizontal migration. This separation of different solutes due to different sorption rates is the basis of chromatographic separation techniques used in analytical chemistry.

Figure 11.26 Contours of vertically averaged solute concentrations for chloride and carbon tetrachloride at several different times during the test. The time since injection is shown next to each solute cloud. The origin of coordinates $x = y = 0$ is at the center of the injection wells. From Mackay, D. M., D. L. Freyberg, P. V. Roberts, and J. A. Cherry, 1986, A natural gradient experiment on solute transport in a sand aquifer: I. Approach and overview of plume movement, Water Resources Research, 22(13), 2017–2029. Copyright (1986) American Geophysical Union. Reproduced by permission of American Geophysical Union.

Figure 11.27 shows the vertical distribution of the chloride tracer along the axis of the plume at day 1 and then at day 462 of the test. The chloride cloud sank vertically and spread out in the longitudinal direction. Little spreading occurred in the vertical direction.

The vertical path of the center of mass of the nonreactive tracer bromide in the vertical section is shown in Figure 3.25. Initially the tracers sank significantly and later the tracers moved mostly horizontally. The initial sinking was probably due to the fact that the tracer solution was denser than the surrounding water. As the tracer dispersed and separated due to sorption, its density approached that of the surrounding water and the rate of sinking decreased.

Figure 11.28 shows the breakthrough curves for three different tracers at a sampler located just downgradient from the injection wells. The plot clearly illustrates retardation caused by sorption. Chloride, which does not sorb significantly, breaks through first, followed by carbon tetrachloride and then PCE. The PCE sorbs more than carbon tetrachloride does, so it breaks through last. All three tracers exhibit skewed breakthrough curves, with longer tailing sections than leading sections. This skewness is more evident in the sorbing tracers, and indicates that some diffusion-limited transport is occurring (see Figure 11.23). The peak chloride concentration was nearly one (nearly equal to the injected concentration), while the peak concentrations of the sorbing solutes were far below the injected concentration. The low peak concentrations for the sorbing solutes are due to mass transferred from the aqueous phase to sorption sites.
11.6 Case Studies of Solute Transport

The migration of the tracer cloud centers of mass illustrates the sorption of the different tracers in a different way (Figure 11.29). The chloride tracer moved with nearly constant velocity, on average, as the linear trend indicates. The rate of chloride transport is consistent with the estimated average linear velocity of the groundwater. The sorbing tracers all moved slower than the chloride,
each at its own rate in inverse proportion to its own retardation factor. The sorbing solute clouds decelerated as the tracer test progressed, as evidenced by the convex shape of the curves in Figure 11.29. The deceleration may be due to diffusion-limited sorption or to heterogeneity in the aquifer's sorption characteristics.

Soon after the tracer solution was injected, the mass of sorbing solutes fell below the mass injected, due to mass transfer from the aqueous phase to sorption sites (Figure 11.30). The mass of each sorbing solute in the aqueous phase tended to decrease throughout the test. Some decreased faster than others. Hexachloroethane was essentially gone by midway through the test, and dichlorobenzene was largely gone by the end of the test. The systematic declines in the dissolved mass of hexachloroethane, dichlorobenzene, and bromoform were the result of microbial digestion of the tracer compounds. For PCE and carbon tetrachloride, the mass losses were the result of sorption, which tended to increase as the test progressed.

11.6.2 North Carolina Gasoline and Diesel Spill

At this site, leaking underground storage tanks spilled gasoline and diesel fuel into a shallow coastal plain sand aquifer that is underlain by clay. Residual LNAPL dissolved into the passing groundwater, eventually creating a long plume of solute contamination containing various hydrocarbon solutes.

In a study reported by Borden et al. (1997), the spatial and temporal trends in solute concentrations were monitored with an array of 22 multilevel well clusters, with each cluster containing two to four wells spanning different elevations. The network of monitoring wells, the plume, and the location of the leaking tanks are shown in Figure 11.31.
The distribution of MTBE and the BTEX compounds in the solute plume is illustrated in Figure 11.32. There are large differences in the extent of each solute’s plume. MTBE covers the greatest area, followed by benzene, o-xylene, m- and p-xylene, toluene, and lastly ethylbenzene. Sorption probably had little to do with the differences in solute extent; the estimated retardation factor for all solutes was close to 1.0 (Borden et al., 1997).

The significant differences in plume extent appear to be due to differing rates of biodegradation for different solutes. Borden et al. (1997) estimated the solute mass fluxes at each of the four lines of wells shown in Figure 11.31. The mass flux for each solute decreased in the downgradient direction, presumably due to microbial consumption of the solute along the flow path. Analysis of the mass flux data for lines 1 and 2 resulted in the estimated decay rates shown in Table 11.6. The decay coefficient is proportional to the rate of decay of the solute, which will be defined more precisely in the next section (Eq. 11.27). It is

Figure 11.31 Map of the gasoline plume site (a) and a vertical cross-section down the axis of the plume showing the screened intervals of clustered wells (b). The source of contamination was a group of underground storage tanks (USTs) shown at the left side of the figure. Groundwater flows from left to right. From Borden, R. C., R. A. Daniel, L. E. LeBrun, and C. W. Davis, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer, Water Resources Research, 33(5), 1105–1115. Copyright (1997) American Geophysical Union. Reproduced by permission of American Geophysical Union.
Figure 11.32  Horizontal (left) and vertical (right) distributions of MTBE and BTEX solutes in the plume. Concentration contours have units of mg/L. From Borden, R. C., R. A. Daniel, L. E. LeBrun, and C. W. Davis, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer, Water Resources Research, 33(5), 1105–1115. Copyright (1997) American Geophysical Union. Reproduced by permission of American Geophysical Union.
Table 11.6 Estimated First-Order Decay Rates Between Lines 1 and 2

<table>
<thead>
<tr>
<th>Compound</th>
<th>Decay Coefficient $\lambda$ (day$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTBE</td>
<td>0.0010 $\pm$ 0.0007</td>
</tr>
<tr>
<td>Benzene</td>
<td>0.0014 $\pm$ 0.0006</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.0063 $\pm$ 0.0010</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>0.0058 $\pm$ 0.0009</td>
</tr>
<tr>
<td>$m$-, $p$-Xylene</td>
<td>0.0035 $\pm$ 0.0009</td>
</tr>
<tr>
<td>$o$-Xylene</td>
<td>0.0017 $\pm$ 0.0006</td>
</tr>
</tbody>
</table>

Source: Borden et al. (1997).

clear that plume size is inversely related to the decay rate. The solutes with the highest decay rates (ethylbenzene and toluene) have the smallest plumes, and the solutes with the lowest decay rates (MTBE and benzene) have the largest plumes.

The distribution of several important inorganic solutes is shown in Figure 11.33. The chloride plume emanates from a salt storage facility just east of the leaking tanks, and it is not relevant to this discussion. Dissolved oxygen is low in the core of the hydrocarbon plume due to respiration reactions carried out in aerobic bacteria, consuming O$_2$ and dissolved hydrocarbons. The products of respiration are CO$_2$ and water. Elevated CO$_2$ concentrations in the core of the plume is further evidence of aerobic biodegradation. There is no clear pattern in the distribution of nitrate concentrations. Denitrification (see Table 10.13) may be a process that oxidizes some of the dissolved hydrocarbons here, but it has not caused a noticeable depression of nitrate concentrations in the core of the plume.

11.7 Modeling Solute Transport

As you can gather from the previous sections, real solute transport is very complex. So are the questions that are asked with respect to contamination, such as “Will the benzene in a gasoline contamination plume cause a concentration greater than 2 $\mu$g/L in a well that is 800 m downgradient?” No one can answer such questions with great precision, but models of transport can give useful guidance. This section outlines the basis for some of the simpler mathematical models of solute transport.
Figure 11.33  Horizontal (left) and vertical (right) distributions of chloride, oxygen, nitrate, and carbon dioxide solutes in the plume. Concentration contours have units of mg/L. From R. C. Borden, R. A. Daniel, L. E. LeBrun, and C. W. Davis, 1997, Intrinsic biodegradation of MTBE and BTEX in a gasoline-contaminated aquifer, Water Resources Research, 33(5), 1105–1115. Copyright (1997) American Geophysical Union. Reproduced by permission of American Geophysical Union.
11.7 Modeling Solute Transport

11.7.1 Modeling Dispersion and Diffusion

As solutes migrate in groundwater they tend to mix and disperse as a result of two fundamental processes:

1. Mechanical dispersion due to velocity variations (Section 11.5.1)

2. Molecular diffusion (Section 11.5.2)

Molecular diffusion is known to be governed by Fick’s first law for porous media, Eq. 11.10. There is no such universal, proven model of mass flux for the case of mechanical dispersion. It depends on the nature of spatial and transient velocity variations, which in turn depend on the nature of the medium’s heterogeneity and on transient flow phenomena. Mechanical dispersion depends on too many complex processes to be described by a simple, fundamental law of mass flux. It does, however, often result in spreading that is at least qualitatively similar to diffusive spreading. Mechanical dispersion can be modeled as though it, too, is governed by Fick’s first law, an approach that provides a reasonable representation of the processes under many circumstances.

With this Fickian approach, the effects of mechanical dispersion plus molecular diffusion are lumped together in what is called macrodispersion. One-dimensional macrodispersive flux \( F_{mx} \) is governed by an equation that is a form of Fick’s first law:

\[
F_{mx} = -nD_{mx} \frac{\partial c}{\partial x}
\]  

(11.13)

where \( n \) is porosity, \( c \) is concentration, and \( D_{mx} \) is a model parameter called the macrodispersion coefficient in the \( x \) direction. The macrodispersion coefficient consists of two terms, the first for mechanical dispersion and the second for molecular diffusion:

\[
D_{mx} = \alpha_x |\overline{v}| + T_x^* D
\]  

(11.14)

where \( \alpha_x \) is called the dispersivity in the \( x \) direction, \( |\overline{v}| \) is the magnitude of the average linear velocity of flow, \( T_x^* \) is the tortuosity in the \( x \) direction, and \( D \) is the molecular diffusion coefficient (see Eq. 11.10). In all but the lowest \( K \) materials like massive clays, mechanical dispersion causes far more dispersion than molecular diffusion does, so the diffusive term can be eliminated from Eq. 11.14:

\[
D_{mx} = \alpha_x |\overline{v}| \quad \text{(advection-dominated dispersion)}
\]  

(11.15)
Mechanical dispersion is much greater in the direction of flow than transverse to flow, so in two- or three-dimensional transport models, macrodispersion parameters are usually defined in orthogonal directions, one parallel to flow, and the other(s) transverse to flow. For transport models, the coordinate system is often a curved one, aligned with the direction of flow. For example, $D_{mx}$ and $\alpha_x$ might apply to the direction of flow, while $D_{my}$, $\alpha_y$, $D_{mz}$, and $\alpha_z$ apply to two orthogonal directions transverse to flow. In aquifers where the flow is predominantly horizontal, the transverse directions are usually chosen in the horizontal and vertical directions normal to flow.

The Fickian macrodispersion approach to transport modeling is most reasonable when the transport has the following characteristics.

- The solute is nonreactive.
- The variation in $K$ (heterogeneity) is not extreme.
- The spatial distribution of $K$ may be reasonably approximated as a space random function with log-normal distribution (normal distribution of $Y = \ln(K)$).
- The scale of heterogeneity has a finite length scale $I$.
- The scale of the plume is far larger than $I$.

Under these circumstances, modeled dispersion and the ensemble average behavior of an actual plume (plume-wide measures of dispersion) will be consistent.

For plumes that are not far larger than $I$, the appropriate longitudinal macrodispersivity $\alpha_L$ for a model depends on the scale of the plume. The appropriate $\alpha_L$ will increase by orders of magnitude as the experiment scale moves from cm (lab experiment) to tens of meters (field experiment) to hundreds of meters (plume scale). In a survey of transport models that were used to simulate solute plumes, Gelhar et al. (1992) developed the plot shown in Figure 11.34, which relates $\alpha_L$ to the extent of the modeled transport. The larger the transport scale, the larger the velocity variations that are not explicitly modeled in the velocity field $\vec{v}$, and the larger the dispersion parameters need to be to simulate dispersion due to those variations. Plots like Figure 11.34 provide only vague guidance, since there is considerable uncertainty in determining most of these values and they are specific to particular plumes and geologic materials. Numerical experiments by Janković et al. (2003, 2006), and Fiori et al. (2006) showed that for a medium with a fixed $I$, the appropriate model longitudinal dispersivity does approach a fixed value as plume scale becomes far greater than $I$. 

Janković et al. (2006) and Fiori et al. (2006) also showed that as the degree of $K$ heterogeneity (e.g., variance of $\ln(K)$) increases, plumes tend to develop long tails, due to very slow transport through the lowest-$K$ materials. Their experiments showed that in highly heterogeneous media, the leading and central parts of a plume were reasonably consistent with macrodispersion models but the trailing parts of plumes were not. Being able to accurately model the trailing edge of solute plumes would be useful for predicting contamination cleanup times, but at present this is still an unresolved challenge.

The book website has a simulation of solute transport by advection through a heterogeneous region, which illustrates some of the points of the previous discussion. The simulation shows how velocity variations tend to spread solute in the direction of flow in an irregular fashion. The simulation also shows how some very low conductivity patches in the source area continue to bleed solute into the flow, creating a long tail in the plume (http://booksite.academicpress.com/9780123847058). Figure 11.35 shows a snapshot of this simulation, along with the plume-averaged one-dimensional average concentration. The one-dimensional average concentration closely resembles what a one-dimensional Fickian macrodispersion model predicts.

Another video on the book website shows a time-lapse movie of solute transport in a vertical sand tank experiment. The medium was extremely heterogeneous with clay lenses embedded in sand. The video shows a pulse of
solute migrating through the tank. After most of the pulse has passed through the tank, solute continues to bleed from the fringes of the clay lenses. In this case, a combination of slow advection and diffusive flux in the clay create the observed tailing of the plume (http://booksite.academicpress.com/9780123847058).

The most accurate estimates of macrodispersivities come from statistical analysis of tracer tests where the plume geometry was defined by a dense network of sampling wells. This was done at the Borden tracer test (Section 11.6) and at a similar test on Cape Cod in a glacial outwash sand aquifer (LeBlanc et al., 1991). The estimated macrodispersivities from these two tests are listed in Table 11.7. Compared to the Borden test, the Cape Cod test had a denser sampling network and less uncertainty in its estimates of macrodispersivity. Both sites were sandy aquifers with low to moderate levels of heterogeneity.

If solute transport is simulated with an appropriate macrodispersive model, the simulated dispersion of solute will be similar to actual dispersion on a “macro” scale. However, at a smaller scale, the actual solute plume will be more irregular or lumpy than the modeled plume. Real heterogeneous aquifers disperse contaminants into irregular, lumpy concentration

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**Table 11.7 Estimated Macrodispersivities from Tracer Tests**

<table>
<thead>
<tr>
<th>Test</th>
<th>Length of Transport (m)</th>
<th>Longitudinal $\alpha_l$ (m)</th>
<th>Transverse Horiz. $\alpha_{lh}$ (m)</th>
<th>Transverse Vert. $\alpha_{lv}$ (m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Borden</td>
<td>87</td>
<td>0.36</td>
<td>0.039</td>
<td>0.023</td>
</tr>
<tr>
<td>Cape Cod</td>
<td>216</td>
<td>0.96</td>
<td>0.018</td>
<td>0.0015</td>
</tr>
</tbody>
</table>

Sources: Freyberg (1986); Garabedian and LeBlanc (1991).
distributions that follow the pattern of heterogeneities (Fitts, 1996). On the other hand, macrodispersion models ignore the distribution of small heterogeneities, but simulate their dispersive effects as macrodispersion. As a result, macrodispersion models produce smoother concentration distributions than the real thing.

Important consequences of the smoother concentration distributions simulated by macrodispersion models can arise in reactive solute transport models. If the model is simulating more mixing that is realistic, then the simulated rates of some reactions may be higher than is realistic. In some reactions, small-scale mixing is a key factor limiting a reaction, and it is in these cases that reactive macro-scale transport models may overestimate mixing and reaction rates. Tartakovsky et al. (2009) demonstrated such effects with pore-scale reactive transport models that were compared to models that neglect pore-scale velocity variations; the largest errors occurred when advective mass transport was much larger than diffusive mass transport.

### 11.7.2 General Equations for Nonreactive Solutes

The general equations for solute transport will be derived in the simplest way possible—for one-dimensional transport of a nonsorbing, nonreactive solute. Once that equation is established, it will be extended to other, more general cases.

The general equations are derived by applying the principle of mass balance to a small rectangular element as shown in Figure 11.36. The flow and dispersive fluxes are limited to the $x$ direction only. Mass balance for the cube means that the total flux of solute mass through the boundary of the cube equals the time rate of change of solute mass stored inside the cube.

First, we will examine the mass flux through the boundaries of the cube. Two types of mass flux are considered: advective flux given by Eq. 11.9, and macrodispersive flux given by Eq. 11.13. Adding these two types of fluxes gives...
the mass flux (mass/time) in through the left side of the cube (at $x$) in the positive $x$ direction,

$$\left[ q_x c(x) - n D_{mx} \frac{\partial c}{\partial x}(x) \right] \Delta y \Delta z \quad (11.16)$$

and the mass flux out through the right side of the cube (at $x + \Delta x$) in the positive $x$ direction,

$$\left[ q_x c(x + \Delta x) - n D_{mx} \frac{\partial c}{\partial x}(x + \Delta x) \right] \Delta y \Delta z \quad (11.17)$$

The rate of change in the mass of solute stored inside the cube is

$$\frac{\partial (cn)}{\partial t} \Delta x \Delta y \Delta z \quad (11.18)$$

where $n$ is porosity. For mass balance, the flux in the left side minus the flux out the right side equals the rate of change in the mass stored within. Combining the previous three equations in this way and dividing through by $\Delta x \Delta y \Delta z$ gives

$$\left[ n D_{mx} \frac{\partial c}{\partial x}(x + \Delta x) - n D_{mx} \frac{\partial c}{\partial x}(x) - q_x c(x + \Delta x) + q_x c(x) \right] \Delta x = \frac{\partial (cn)}{\partial t} \quad (11.19)$$

In the limit as $\Delta x \to 0$, the left-hand side results in derivatives with respect to $x$ as follows:

$$\frac{\partial}{\partial x} \left( n D_{mx} \frac{\partial c}{\partial x} \right) - \frac{\partial}{\partial x} (q_x c) = \frac{\partial (cn)}{\partial t} \quad (11.20)$$

Substituting $n \bar{v}_x = q_x$ in this equation and assuming that $D_{mx}$ is independent of $x$, and that $n$ is independent of $x$ and $t$, it simplifies to

$$D_{mx} \frac{\partial^2 c}{\partial x^2} - \frac{\partial}{\partial x} (\bar{v}_x c) = \frac{\partial c}{\partial t} \quad (11.21)$$

This is the standard one-dimensional advection–dispersion equation for a nonreactive solute.

Allowing fluxes in all three dimensions would result in a similar set of terms in each direction, giving the three-dimensional advection–dispersion
11.7 Modeling Solute Transport

The equation for a nonreactive solute:

\[
D_{mx} \frac{\partial^2 c}{\partial x^2} - \frac{\partial}{\partial x} (\bar{v}_x c) + D_{my} \frac{\partial^2 c}{\partial y^2} - \frac{\partial}{\partial y} (\bar{v}_y c) + D_{mz} \frac{\partial^2 c}{\partial z^2} - \frac{\partial}{\partial z} (\bar{v}_z c) = \frac{\partial c}{\partial t} \quad (11.22)
\]

This can be written in a more compact form, making use of the gradient operator \(\nabla\), and writing the vector \((D_{mx}, D_{my}, D_{mz})\) as \(D_{mi}\) and the vector \((\bar{v}_x, \bar{v}_y, \bar{v}_z)\) as \(\bar{v}_i\):

\[
D_{mi} \nabla^2 c - \nabla (\bar{v}_i c) = \frac{\partial c}{\partial t} \quad (11.23)
\]

This is the general advection–dispersion equation for three dimensions, assuming that the porosity and macrodispersivities are constant in space and time. A few variations on this equation will now be presented.

If the flow field is steady state, \(\nabla \bar{v}_i = 0\) and \(\bar{v}_i\) can be removed from the gradient operator in Eq. 11.23 as follows:

\[
D_{mi} \nabla^2 c - \bar{v}_i \nabla c = \frac{\partial c}{\partial t} \quad \text{(steady flow)} \quad (11.24)
\]

If, in addition to steady flow, the concentration field is steady state \((\partial c/\partial t = 0)\), then Eq. 11.23 becomes

\[
D_{mi} \nabla^2 c - \bar{v}_i \nabla c = 0 \quad \text{(steady flow and concentration)} \quad (11.25)
\]

If there is no flow at all, \(\bar{v} = 0\) and Eq. 11.23 becomes the diffusion equation

\[
D_{mi} \nabla^2 c = \frac{\partial c}{\partial t} \quad \text{(no flow, diffusion only)} \quad (11.26)
\]

where in this case the coefficients \(D_{mi} = T_i^* D\) (see Eq. 11.14).

11.7.3 General Equations for Reactive Solutes

There are many variations of the advection–dispersion equation for cases where the solutes react and/or sorb to solid surfaces as they flow. A useful equation models a solute that decays at a constant rate. This would be appropriate for radioactive solutes, and sometimes for solutes that biodegrade. The
assumption is that the decay is governed by the simple first-order rate law

$$\frac{dc}{dt} = -\lambda c$$

(11.27)

where \(\lambda\) is a decay constant with dimensions of \([1/T]\). The half-life of the solute is linearly related to \(\lambda\), as shown in Eq. 10.88. When loss due to decay is added to Eq. 11.23, it becomes

$$D_{mi}\nabla^2 c - \nabla(\bar{v}_i c) - \lambda c = \frac{\partial c}{\partial t} \quad \text{(decay)}$$

(11.28)

Another facet of reaction that can be modeled is linear sorption that is always at equilibrium (Eq. 10.74 applies at all times). For this, a bit of derivation is needed to get to the final governing equation. When a solute adsorbs to the porous media, mass fluxes involving the sorbed phase must be accounted for in the solute transport equation. Assuming decay proceeds at the same rate in the aqueous and sorbed phases, Eq. 11.28 is modified as follows:

$$D_{mi}\nabla^2 c - \nabla(\bar{v}_i c) - \lambda c - \lambda c^* = \frac{\partial c}{\partial t} + \frac{\partial c^*}{\partial t}$$

(11.29)

where \(c^*\) is the sorbed mass per volume of pore water. As \(c^*\) increases, \(c\) decreases and vice versa, since the mass is being transferred from one phase to the other.

If the sorption is assumed to be linear and at equilibrium, the sorbed concentration and aqueous concentration are related by Eq. 10.74, which is repeated here in a slightly modified form:

$$cK_d = \frac{\text{sorbed mass}}{\text{mass aquifer solids}}$$

(11.30)

where \(c\) is the aqueous solute concentration, and \(K_d\) is the sorption distribution coefficient. The right side of Eq. 11.30 can be written in terms of \(c^*\), porosity \(n\), and dry bulk density \(\rho_B\) as follows:

$$cK_d = \left(\frac{\text{sorbed mass}}{\text{volume pore water}}\right) \left(\frac{\text{volume pore water}}{\text{total volume}}\right) \left(\frac{\text{total volume}}{\text{mass aquifer solids}}\right)$$

$$= (c^*)(n)\left(\frac{1}{\rho_B}\right)$$

(11.31)
Rearranging the previous equation gives $c^*$ in terms of $c$ and known constants:

$$c^* = c \left( \frac{\rho_b K_d}{n} \right) \quad (11.32)$$

Now, substituting Eq. 11.32 into 11.29 and combining the two terms with $\partial c / \partial t$, we get

$$D_{mi} \nabla^2 c - \nabla (v_i c) - \lambda c \left( 1 + \frac{\rho_b K_d}{n} \right) = \frac{\partial c}{\partial t} \left( 1 + \frac{\rho_b K_d}{n} \right) \quad (11.33)$$

The term in parentheses is the retardation factor $R$ (Eq. 11.12). Dividing both sides by $R$ shows that the effect of linear equilibrium sorption is to retard both advection and dispersion by the factor $1/R$:

$$\frac{1}{R} \left[ D_{mi} \nabla^2 c - \nabla (v_i c) \right] - \lambda c = \frac{\partial c}{\partial t} \quad \text{(sorption and decay)} \quad (11.34)$$

Comparable general equations for transport are given by van Genuchten (1981), Wexler (1992), and Charbeneau (2000).

### 11.7.4 Boundary Conditions

The previous sections discussed the general governing equations for solute transport. There are many different analytic and approximate solutions to these equations, each a solution for a particular set of boundary conditions. The derivation of specific solutions involves mathematics that is beyond the scope of this text, so that will not be the focus here. We will instead discuss boundary conditions in general and then examine a few useful solutions that simulate specific conditions. This brief overview will help build a general understanding of how transport parameters affect the model's output.

As was the case with flow models, a specific model is defined by its governing equation plus the specific boundary conditions that apply. For transport models, boundary conditions define aspects of mass distribution and mass flux in the modeled domain. Only one type of condition may be specified along a particular stretch of the boundary. The following is a list of the most common boundary conditions that are applied to transport models:

1. Specified mass flux at a spatial boundary
2. Specified concentration at a spatial boundary
3. Specified concentration distribution at an initial time
The first and second conditions apply to spatial boundaries through time, while the third one specifies conditions through space at an initial time.

When specifying the first, mass flux boundary condition, it is the total flux (advective plus dispersive) that is fixed. The specified flux boundary condition equation follows from the definitions of advective flux and macrodispersive flux, Eqs. 11.9 and 11.13, respectively:

\[ q_b c - n D_{mb} \frac{\partial c}{\partial b} = F_b \quad \text{(at boundary)} \quad (11.35) \]

where \( q_b \) is the specific discharge normal to the boundary, \( c \) is concentration, \( n \) is porosity, \( D_{mb} \) is the macrodispersion coefficient in the direction normal to the boundary, \( \frac{\partial c}{\partial b} \) is the concentration gradient normal to the boundary, and \( F_b \) is the specified flux across the boundary (mass/time/area). For a no-flux boundary, \( F_b = 0 \).

The second type of condition requires a fixed concentration along a boundary:

\[ c = c_b \quad \text{(at boundary)} \quad (11.36) \]

where \( c_b \) is the specified concentration. The boundary may be a point, a line, or a three-dimensional surface, and usually the concentration is maintained there over time.

The third type of condition is similar to the second, except that the concentration is specified over a region in space at an instant in time rather than on a boundary through time:

\[ c = c_i \quad \text{(at time } t_i \text{ in some region)} \quad (11.37) \]

### 11.7.5 One-Dimensional Solution for a Step Inlet Source

This is a solution of the one-dimensional (\( x \) only) transport general equation, Eq. 11.21, that allows adsorption, but not decay (\( \Lambda = 0 \)). It applies to the following boundary conditions:

\[ c = 0 \quad (t = 0, \text{ all } x) \]
\[ c = c_0 \quad (t > 0, x = 0) \]
\[ c = 0 \quad (\text{all } t, x = \infty) \]
\[ \bar{v} = \text{constant} \quad (\text{all } t, x) \quad (11.38) \]
In this step input solution, the concentration spreads in the positive x direction from a boundary at \( x = 0 \). Initially at \( t = 0 \), there is zero concentration everywhere, but with \( t > 0 \), concentrations spread from the constant concentration \( c = c_0 \) at the boundary \( x = 0 \). These would be the conditions downgradient of a large source that starts abruptly, or in a column experiment where a fixed solute concentration is introduced abruptly at the inlet end of the column.

The following solution of Wexler (1992) is based on the similar solution without adsorption \( (R = 1) \) of Ogata and Banks (1961):

\[
c = \frac{c_0}{2} \left[ \text{erfc} \left( \frac{x - \bar{v}t}{2\sqrt{D_{m_x}t/R}} \right) + \exp \left( -\frac{\bar{v}x}{D_{m_x}} \right) \text{erfc} \left( \frac{x + \bar{v}t}{2\sqrt{D_{m_x}t/R}} \right) \right] \quad (x > = 0)
\]

(11.39)

where \( \text{erfc} \) is the complementary error function, \( \exp() = e^t \) is the exponential function, and \( D_{m_x} \) is the macrodispersion coefficient as defined by Eq. 11.14.

The complementary error function goes from \( \text{erfc}(w) = 2 \ (w \ll 0) \) to \( \text{erfc}(w) = 0 \ (w \gg 0) \). The central part of this function is graphed in Figure 11.37. There is no closed form expression for \( \text{erfc}(w) \), but it can be approximated with little error using the following polynomial expression (Abramowitz and Stegun, 1972):

\[
\text{erfc}(w) \approx \left( a_1u + a_2u^2 + a_3u^3 \right) e^{-w^2} \quad (w \geq 0)
\]

(11.40)

where

\[
u = \frac{1}{1 + 0.47047w}, \quad a_1 = 0.3480242, \quad a_2 = -0.0958798, \quad a_3 = 0.7478556
\]

(11.41)

Figure 11.37 Complementary error function, \( \text{erfc}(w) \) for \(-2 < w < 2\).
When $w$ is negative, the above can still be used to determine $\text{erfc}(w)$, by using the following identity:

$$\text{erfc}(w) = 2 - \text{erfc}(-w)$$ (11.42)

The results of this solution are shown in Figure 11.38 for some specific values of the input parameters. The argument of the exponential in Eq. 11.39 is a dimensionless number known as the Peclet number $P_e = \bar{v}x/D_{mx}$, which is a measure of the relative magnitude of advective flux vs. dispersive flux. If $P_e > 100$ or so, advection dominates, and for smaller $P_e$ dispersive transport becomes significant. In advection-dominated systems, the front of the advancing solute plume migrates roughly at the average linear velocity and the concentration $c/c_0 = 0.5$ occurs at a distance of about $x = \bar{v}t$ (see Binning, 2000). The front of the advancing plume is not an abrupt step from $c/c_0 = 0$ to $c/c_0 = 1$ because of dispersion. Dispersion smears the solute front into a more gradual transition of concentrations. When $D_{mx}$ is large, the front is smeared to a greater extent, as shown in Figure 11.38.

This solution is useful for predicting the migration of a solute front near a source that has an extensive cross-section normal to flow. It is not an appropriate model when the source presents a small cross-section normal to flow. When a source is small in cross-section, lateral dispersion becomes important, and one-dimensional dispersion is not a valid assumption. The solutions described in the next two sections simulate both longitudinal and lateral dispersion, and are appropriate for smaller sources.
11.7.6 Solution for a Pulse Point Source

Charbeneau (2000) presented a solution of Eq. 11.34 that models the migration of a pulse point source with three-dimensional dispersion, adsorption, decay, and one-dimensional flow. This solution is like the one presented by Hunt (1983), but it also includes adsorption. The flow field is assumed to be uniform in the positive $x$ direction; $\bar{v}$ is constant and independent of $x$, $y$, $z$, and $t$. At time $t = 0$, an amount of solute mass $M$ is injected at a point at $x = y = z = 0$. For a finite volume $V_0$ of water at solute concentration $c_0$, the solute mass is $M = c_0 V_0$. The solution is

$$c = \frac{M}{8n\sqrt{\pi t^3} D_{mx}D_{my}D_{mz}/R} \exp\left(-\frac{R(x - \bar{v}t/R)^2}{4D_{mx}t} - \frac{Ry^2}{4D_{my}t} - \frac{Rz^2}{4D_{mz}t} - \lambda t\right)$$

(11.43)

where $n$ is porosity, $R$ is retardation factor, and $\lambda$ is the decay constant (see Eq. 11.27). This solution depicts a cloud of solute that migrates with the average linear velocity $\bar{v}/R$ and spreads out in all three directions. Generally the longitudinal dispersion is much greater than the lateral dispersion ($D_{mx} \gg D_{my}, D_{mz}$), and the solute cloud evolves into an elongate cigar-shaped ellipsoid with the long axis in the $x$ direction.

Note that incorrect versions of equations similar to Eq. 11.43 have been widely published (e.g., Bedient et al., 1999; Domenico and Schwartz, 1998; Freeze and Cherry, 1979; and the first edition of this book). The incorrect equations lack porosity $n$ in the denominator. These textbooks each cite the article of Baetsle (1969), which has the same error.

The highest concentration in the solute cloud is found at the center of mass, where $x = \bar{v}t/R$ and $y = z = 0$. At the center of mass, the term in parentheses in Eq. 11.43 becomes $-\lambda t$, so

$$c = \frac{M}{8n\sqrt{\pi t^3} D_{mx}D_{my}D_{mz}/R} e^{-\lambda t} \quad \text{(at center of mass)}$$

(11.44)

Figure 11.39 shows concentration distributions resulting from Eq. 11.43, using input parameters that are representative of some sand aquifers. The model shown in the upper plot uses a value of $D_{mx}$ that is twice that used in the model of the lower plot. Otherwise the two models are identical. The larger longitudinal macrodispersion in the upper plot causes the modeled plume to spread more in the $x$ direction and have a lower peak concentration at the center of the plume.
Groundwater Contamination

Figure 11.39 Concentrations predicted by Eq. 11.43 for two models with slightly different parameters. Common to both models are a source mass of 250 g starting at \( x = y = z = 0 \), \( \bar{v} = 1 \) m/day, \( D_{my} = 0.1 \) m\(^2\)/day, \( D_{mz} = 0.01 \) m\(^2\)/day, \( \lambda = 0 \), \( R = 1 \), \( n = 0.25 \), and \( t = 100 \) days. The difference between the two models is that \( D_{mx} = 2 \) m\(^2\)/day in the upper one and \( D_{mx} = 0.5 \) m\(^2\)/day in the lower one. Both plots show the concentration (mg/L) distribution on the plane \( z = 0 \).

11.7.7 Other More Complex Solutions

Many analytic solutions to the advection–dispersion equations have been derived for more complicated boundary conditions. We won’t delve into the details of any of these; a few of the more useful ones are listed below:

1. Hunt (1978): solution for a nonreactive solute pulse source shaped like a parallelepiped (rectangular box). At the start time, the concentration is uniformly \( c_0 \) inside the box and zero outside the box. Hunt also presents solutions for a continuous point source.

2. Leij et al. (1991): solutions for a pulse source shaped like a parallelepiped or a cylinder. Allows for both first-order decay and linear equilibrium sorption. Also has solutions for a continuous source shaped like a rectangular inlet or a circular inlet normal to flow.
3. Leij et al. (1993): solutions for similar conditions as those of Leij et al. (1991), except that nonequilibrium sorption may be modeled.

The geometries of these solutions are illustrated in Figure 11.40. The curves of Figure 11.23 were generated by SOLITRANS, a computer program that implements the solutions of Leij et al. (1991) and Leij et al. (1993) for the continuous rectangular inlet source.

The analytic solutions listed above are quite restricted by the assumptions of a uniform flow field and a homogeneous medium. To handle heterogeneous flow fields and heterogeneous media requires more complex numerical methods, which are well beyond the scope of this book. Common numerical methods include finite differences, finite elements, and particle tracking. Some good references for detailed coverage of numerical transport modeling are Bear and Cheng (2010), Charbeneau (2000), Spitz and Moreno (1996), Rifai (1994), and Hromadka (1992).

11.8 Investigating Contamination

11.8.1 Sampling Groundwater

Groundwater sampling is a routine part of contamination studies and water supply investigations. It is usually accomplished by extracting a water sample from a well. Ideally, the sample accurately represents the chemistry of the pore water in the aquifer immediately adjacent to the screened section of the well, and the sample is analyzed quickly before reactions significantly alter the chemistry. There are many opportunities for this idealized process to fail, so care must be taken in the installation of the well, in the sampling procedure, and in preserving and analyzing the sample. This section provides a brief overview of important issues in groundwater sampling; more detailed coverage
Figure 11.41 An irregular solute plume and how it is sampled by wells. The short screens of the multilevel wells (left) are better able to define the geometry of the plume than the single long-screened well (right). As shown, the multilevel wells are installed in one borehole, with four separate screens connected to four separate solid riser pipes.

of the topic is available in books by Sanders (1998), Nielson (1991), and EPA (1993).

The construction of wells was discussed in Section 4.3. A typical well consists of a screened section of casing that allows water to move between the casing and the surrounding saturated medium, as illustrated in Figure 11.41. The screened section is isolated from other sections of the borehole by seals that prevent vertical movement of water in the borehole outside the casing.

The water that is sampled is a composite of the pore waters that surround the well screen. In some circumstances, the chemical parameter being measured will be fairly uniform over the screen length, and in others it may be quite variable. If a contaminant plume is small compared to the length of the screen, significant mixing and dilution can occur in the sample. For example, a sample with a concentration of 80 mg/L could result from a thin plume with a concentration of 500 mg/L mixing with other water outside the plume that is near zero concentration. A sample from the long-screened well illustrated in Figure 11.41 would yield a solute concentration much lower than the concentrations in the two lobes of the plume that intersect the screen. Multilevel wells, each with short screens, can better define the geometry and concentrations of a known contaminant plume (see an article by Puls and Paul (1997) for case studies demonstrating this point). Long-screened wells, on the other hand, are useful for monitoring and detecting contamination in the first place.

One potential problem is introduction of contaminants during drilling and well installation. The drilling fluid may be contaminated from its source or from the greases and oils used to lubricate the pumps that circulate the fluid. Glues used to fasten sections of plastic casing together are a source of certain
volatile organic chemicals. This problem can be avoided by using threaded casing that screws together without glue. Cement grout, sometimes used to create borehole seals, is chemically basic and tends to elevate the pH of water it contacts.

The borehole, before the well and seals are installed, is a potential conduit for contaminated water to move vertically from contaminated layers to previously clean layers. This can be prevented by maintaining a high hydraulic head in the borehole at all times during drilling, high enough so that water always flows from the borehole into the contaminated zone and not the other way around. If this is not possible, it is possible to seal the contaminated section of the borehole with casing and proper seals, and then drill deeper with a smaller diameter drill bit.

There are a variety of sampling methods that lift the water from the well to the surface. A bailer is a simple device consisting of a hollow tube with a check valve at the bottom that allows water to flow up into the tube, but prevents water from flowing down out of the tube. The bailer is lowered into the well empty and retrieved full of water.

For wells where the distance from the ground down to the water is short enough, a vacuum pump can be placed at the ground surface with its inlet tubing extending down below the water level in the well. This only works if the pump can pull a vacuum that is large enough to lift the water from the well. For most vacuum pumps, the largest lift possible is in the range 6–10 m (20–33 ft). Peristaltic pumps, which operate by squeezing a flexible plastic tubing with rollers, are able to lift water to heights near the high end of this range.

If the lift is too large for a vacuum pump, some sort of submersible pump may be used. These are installed below the water level in the well and have impellers, jets, or bladders that propel water up the outlet tubing to the surface. Some are powered by electricity and others are powered by compressed air.

Whether sampling is done with bailers or pumps, there is the possibility of contamination from the sampling devices. If a series of wells is to be sampled, care must be taken to decontaminate the sampling equipment after each well is sampled. Decontamination can be time-consuming and costly. To avoid these costs, dedicated sampling equipment is often left in each well.

Most monitoring wells are not pumped except during sampling events, so between events the water in the well may become stagnant. This stagnant water is in contact with the well casing and with the atmosphere, but no longer in contact with the aquifer matrix. Chemical reactions occur and the chemistry of this stagnant water changes from that of the in situ pore water. A good,
A representative water sample consists of water that has been pulled fresh from the pore spaces in the aquifer, not water that has been sitting for a long time in the well casing. To achieve this end, water is purged from the well for some time before collecting the sample. Parameters that are easily measured in the field like temperature, pH, Eh, and specific conductance can be monitored in the pump discharge. These change rapidly when the well is first turned on, as the well’s discharge shifts from stagnant water to fresh pore water. The parameters should stabilize once the well is steadily pumping fresh pore water.

Ideally, a groundwater sample is representative of the pore water chemistry and it stays that way until analyzed. Several undesired chemical changes can occur to samples; a few of the more common problems are listed below.

1. Volatile chemicals may be lost to evaporation when samples contact the air.

2. Dissolved oxygen levels may change when samples contact the air, and this in turn may cause various redox reactions in the sample.

3. Microbes, whether natural or not, may degrade organic constituents before analysis happens.

4. Contaminants not present in the pore water may be introduced during sampling, transport, or in the chemical testing laboratory.

Exposure to air can be minimized by avoiding methods that aerate the sample and by having the pump discharge directly into a sample container. Sample containers should be filled to the top without any head space (air above the water), and the container top should have a septum that can be pierced by a syringe to extract some of the sample in the lab without air contact. To minimize biodegradation, samples are refrigerated and analyzed within specified holding times. To check for contamination of samples in the lab and elsewhere in the process, blank samples accompany the actual samples through sampling, transport, and analysis. The blanks start off as distilled, deionized water. Solutes that show up in the analysis of blanks indicate contamination with that solute.

### 11.8.2 Sampling Pore Gases

Where there are volatile contaminants in the soil moisture of the unsaturated zone, the pore gases will also contain the contaminants, and soil gas sampling can be a useful tool. Pore gases are usually extracted using a thin hollow probe with a porous tip. The probe is driven into the ground to the desired depth,
and then a vacuum pump extracts pore gases from the probe. The gas sample is analyzed, yielding a gas concentration or partial pressure. Assuming equilibrium partitioning between the pore gas and the pore water, Henry’s law may be used to estimate the pore water concentration from the gas concentration (see Eq. 10.31).

This approach is useful only for contaminants that are volatile enough to be detected in pore gases. This method works well for most common VOC contaminants. Where a groundwater contamination plume is at the top of the saturated zone, soil gas sampling can be used to delineate the extent of the plume. A volatile compound will partition from the groundwater into pore gases just above the saturated zone. To detect such a shallow groundwater plume, pore gas samples should be collected from the base of the unsaturated zone. Where the VOC groundwater plume is at the top of the saturated zone, the overlying pore gases will contain the VOC, and where the plume is blanketed by a layer of clean water above it, the overlying pore gases sampling will lack the VOC (Figure 11.42).

### 11.8.3 Electromagnetic Surveys

Electromagnetic geophysical investigation methods were summarized in Section 4.2.5. Because contamination sources and solute plumes commonly have anomalous electromagnetic properties, these methods are useful for mapping contamination. Application of resistivity, electromagnetic, and ground-penetrating radar (GPR) surveys to contamination problems are the subject of this section.

Landfill leachate plumes, plumes from salt-storage facilities, and many other plumes have pore waters with high ionic strength compared to non-contaminated waters. Such plumes may be mapped with resistivity surveys or terrain conductivity surveys, because the plumes have anomalously low resistivity.

![Figure 11.42](image) Vertical cross-section of a VOC plume, showing where VOC-contaminated pore gases could be sampled with a pore gas survey.
Since most organic NAPLs have high resistivity compared to groundwater, it would seem logical to expect a zone of high NAPL saturation to produce a high-resistivity anomaly. Field investigations of LNAPL contamination in a sand aquifer reveal just the opposite, however (Atekwana et al., 2000; Sauck, 2000). These studies found low-resistivity anomalies corresponding to zones of high LNAPL saturations near the unsaturated/saturated zone boundary. Apparently, biodegradation of LNAPL compounds generates organic acids and carbonic acid in the pore water, which then cause dissolution of ions from minerals and mineral coatings. Pore waters near LNAPL and its degrading hydrocarbons therefore develop high TDS and low resistivity.

Terrain conductivity and GPR surveys are often used to locate buried conductive objects like pipes, tanks, or drums, which are often the source of groundwater contamination. GPR is also well suited for mapping nonconductive anomalies like voids in limestone or tunnels. Sometimes GPR surveys will reveal a strong reflector at the boundary of a pool of high LNAPL saturation, so it can be used to map the extent of LNAPL (Benson, 1995).

11.8.4 Investigating NAPLs

If you are investigating a site with organic contamination and have hopes of remediating it, some critical questions are: Is NAPL present? About how much is there? Is it mostly in the unsaturated or saturated zone? The amount and location of NAPL is the main factor in deciding what sort of remediation might work best.

It is a tricky business trying to determine the location and amount of NAPL present in the subsurface. Conventional drilling and sampling methods often miss the thin, irregular threads of residual NAPL and the isolated pools where mobile NAPL has accumulated.

Drilling itself is a hazardous activity that can create pathways where NAPLs can migrate to deeper horizons. NAPL that pools at the top of a fine-grained layer can penetrate through the layer with the help of a poorly constructed borehole. If the borehole is left open and/or has coarse backfill, the NAPL will be able to move into the backfill and migrate down through the backfill and possibly into the well casing through the screen. If it is suspected that mobile NAPL pools may be present, drilling should be done carefully and with frequent low-permeability seals to prevent vertical migration of NAPL through the backfill. Abandoned holes should be backfilled with a low-permeability grout.
It is sometimes possible to collect samples of unconsolidated materials that contain NAPL. These can yield in-place values of NAPL and water saturations if the samples are quickly sealed to prevent significant losses of volatile NAPL constituents. Although it is not always possible to see NAPL in a soil sample, its presence can be inferred from measurements of high levels of volatile gases emanating from the sample. Sometimes distinct, immiscible NAPL bubbles can be seen in pore water extracted from a sample.

The concentrations of contaminants in groundwater samples is indirect evidence about the presence of NAPL. If the aqueous concentration of an NAPL constituent approaches a quarter or even one-tenth of the equilibrium concentration for contact with the suspected NAPL, it is likely that NAPL is nearby. For example, if BTEX concentrations near a gas station are close to the levels listed in the gasoline NAPL column of Table 11.3, it is likely that somewhere nearby and hydraulically upgradient, there is gasoline NAPL.

Where LNAPL has accumulated at the top of the saturated zone, it may enter a well that is screened across this zone. LNAPL will enter a well when the capillary pressure in the formation is sufficient to move it into the backfill materials that surround the well screen and into the well screen itself. There is no simple relationship between the thickness of LNAPL that accumulates in a well and the distribution of LNAPL saturation in the surrounding formation.

Aral and Liao (2000) present a method for estimating the thickness of an in situ LNAPL accumulation based on bail-down tests in monitoring wells. In such a test, fluids are bailed or pumped from a well. The subsequent flow of water and LNAPL back into the well is monitored by measuring the level of the water–NAPL and NAPL–air interfaces with time. With these measurements and knowledge of the well geometry and backfill material properties, it is possible to estimate the thickness of the zone with high LNAPL saturation in the surrounding formation.

11.9 Remediating Contamination

Curing groundwater contamination problems is no small feat. The problem and its source are buried out of sight, and their spatial distribution is always uncertain. Contamination problems evolve in response to complex and intertwined physical, chemical, and biological processes, which we understand in a limited way. This discipline is young; very few remediation efforts happened before the 1970s. In the last several decades, this work has expanded
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dramatically to include thousands of different sites, some of which could be called “remediated,” while others are at least partially remediated.

The goals of remediation vary a great deal from one site to the next. Where the underlying aquifer is a valued water supply, the goal may be to rid the site of all contaminants. If the local groundwater is not used for any purpose or is already contaminated by numerous other contaminant discharges, like in so many urban areas, the aim of remediation may be much less ambitious. Lesser goals may include partial source removal, limiting further off-site migration of solutes, or perhaps just monitoring the natural bioremediation processes.

In this text, only the essentials of the current, common remediation techniques are summarized. Much more detail is available in books, conference proceedings, and journals focused on remediation. A few recent textbooks in this field are Fetter (1993), Bedient et al. (1999), Cheremisinoff (1992, 1997), Pankow and Cherry (1996), and Downey et al. (1999). This field is developing and evolving rapidly, so check recent journals and conference proceedings volumes for the latest ideas.

11.9.1 Source Removal or Isolation

Removing the source of contamination is usually at the top of the remediation priority list. Where the source is limited in extent and shallow, this is feasible and makes good sense. Most NAPL sources consist of leaking tanks or piping and the nearby soils that contain NAPL, as shown in Figures 11.3 and 11.4. The offending tanks or piping are removed, and so are NAPL–laden soils. These soils are usually treated on-site if there is space, or hauled to a spot where there is space for treatment.

There are a wide variety of treatment methods depending on the contaminants and the soils. For hydrocarbon fuels that biodegrade readily, treatment usually involves aerobic biodegradation in a pile through which air is flushed. The pile is isolated from its environs by placing an impermeable membrane under the pile and another over the top. Soils containing more hazardous and less degradable contaminants are often treated or incinerated at off-site facilities.

An alternative to source removal is source isolation: limiting the flow of water through source regions. Isolation is generally accomplished with engineered barriers that have very low hydraulic conductivity (Figure 11.43). These can be synthetic membranes, slurry walls, steel sheet pilings, injected grout, or compacted clay layers.
Synthetic membranes are generally thin, on the order of several millimeters thick. These membranes are usually made of thermoplastics or plastic geotextile fabric with embedded bentonite (a very low conductivity swelling clay). They come in large rolls, as large as can fit on a truck. When unrolled, they form long, parallel panels, overlapping at seams that are welded by heat, glue, or other means. Membranes are most often used as liners beneath excavated wastes and as covers which limit infiltration of water from above.

**Slurry walls** are used to create vertical barriers in the subsurface (Figure 11.44). One is constructed by digging a thin vertical trench, usually about 0.5–1.5 m wide. As this trench is dug, it is backfilled with a slurry of soil, bentonite, and/or cement. The trench is usually dug through more permeable soils into less permeable materials at depth, to provide an effective barrier to horizontal flow. Conventional backhoes can dig slurry walls that are up to 6 m
deep or so, and specialized trenching equipment can dig walls as deep as 50 m. Slurry wall construction works best in loose granular soils like sands and gravels, but is less effective in dense or bouldery materials like glacial till. Some references about slurry wall use in remediation include Day (1994) and Tedd et al. (1995).

Steel **sheet pilings** are sometimes used as an alternative to slurry walls to create vertical barriers. The pilings are usually corrugated to give buckling resistance, and hammered into place with a pile driver. The edges of each piling interlock, and a wall is built by driving successive interlocked panels. The standard type of sheet piling used in construction is not appropriate for barrier applications because the joints between pilings leak too much. Special pilings with better seals at the joints have been used for remediation barriers (Starr et al., 1992).

Another barrier technology is grout injection. **Grout** is a slurry of cement and/or bentonite that is injected under pressure into an open borehole, with the aim of plugging pores and reducing the hydraulic conductivity in the surrounding materials. Usually a dense network of holes is grouted in an attempt to construct a continuous barrier. Grouting is only marginally effective, because there can be no guarantee that there won’t be serious leakage through ungrouted gaps in the barrier. It is mostly used to create barriers in bedrock, where there is no practical alternative.

### 11.9.2 NAPL Recovery

In some circumstances, especially in the case of LNAPLs, NAPL can be recovered from the subsurface by means other than excavation. Because LNAPLs float on the top of the saturated zone, it is possible to concentrate and extract
11.9 Remediating Contamination

them. All that is required is a depression in the water table under the LNAPL zone. The LNAPL will slide down into the depression where it accumulates for easy extraction. The depression in the water table is created by pumping water from a well or a trench (Figure 11.45).

Usually, two pumps are employed in such a scheme: a deeper one to pump water and create the depression, and a shallower one positioned with a float to pump LNAPL. Electronic controls installed in the borehole or trench sense fluid levels and prevent overpumping on the part of either pump, so that the deep one pumps only water and the upper one pumps mostly LNAPL. If the pumped LNAPL is pure enough, it might still be recycled into some useful product. The water will most likely be contaminated with solutes from the LNAPL, and it may require treatment before being discharged back to the environment.

Sometimes only one pump is installed near the water table, and it pumps both water and LNAPL. The mixture is then routed to a tank where the NAPL and water segregate by density. The problem with this single pump technique is that the water is intimately mixed with the LNAPL, so the water becomes highly contaminated and will need expensive treatment.

Recovery of DNAPLs is much harder than recovery of LNAPLs because DNAPLs cannot easily be concentrated at shallow depth. Various techniques have been tested, but none is in widespread use or well-proven. To enhance recovery of NAPL chemicals in the vapor phase, steam and heat can be applied. To enhance recovery in the aqueous phase, surfactant molecules can be added. This increases the rate of NAPL dissolution, in much the same way that detergent increases the solubility of oil or grease on dishes.

DNAPL remediation options are discussed by Grubb and Sitar (1994) and Pankow and Cherry (1996). Most often, the only DNAPL recovered is the residual NAPL in soils excavated from the source area. DNAPL remediation typically focuses on containing plumes of aqueous-phase contamination that flow from deep, unrecovered DNAPL sources.

11.9.3 Hydraulic Control of Solute Plumes

Since it is often impossible to eliminate all sources, a key aspect of remediation is controlling solute plumes that emanate from remaining sources. The typical hydraulic control consists of well(s) located hydraulically downgradient of the source. Ideally, all of the contaminated groundwater is captured by the well(s), and no contaminated water escapes to wreak havoc further downgradient.
Example 11.5 This example illustrates how persistent NAPL sources and their resulting groundwater plumes can be. Consider a layer of unsaturated soil near the ground surface that is 1 m thick, and has PCB-1248 NAPL saturating 8% of its pore spaces. The porosity of the soil is \( n = 0.32 \). Assuming that water infiltrates down through this layer at an average rate of 0.7 m/year, calculate how long it would take for all of the PCB-1248 to dissolve away. Assume that dissolution is the only important process here.

Think of a vertical prism through this layer that is 1 m\(^2\) in cross-sectional area. First, we will calculate the mass of PCB in the prism, and then we will calculate how much dissolves from the prism each year.

The volume of contaminated soil in the prism is 1 m\(^3\), and the mass of PCB in this volume is

\[
VnS_n \rho_n = (1 \text{ m}^3)(0.32)(0.08)(1410 \text{ kg/m}^3)
= 36 \text{ kg}
\]

where \( V \) is volume of soil, \( S_n \) is NAPL saturation, and \( \rho_n \) is NAPL density (see Table 11.2).

Water flows through the 1 m\(^2\) prism at a rate of 0.7 m\(^3\)/yr. Assuming that this water contains PCB at its solubility concentration, the rate of PCB dissolution is

\[
QS = (0.7 \text{ m}^3/\text{yr})(0.054 \text{ mg/L}) \left( \frac{10^3 \text{ L}}{\text{m}^3} \right) \left( \frac{\text{kg}}{10^6 \text{ mg}} \right)
= 3.8 \times 10^{-5} \text{ kg/yr}
\]

where \( Q \) is the water flow rate and \( S \) is the solubility concentration of PCB (see Table 11.2).

Dividing the mass of PCB by the rate of dissolution gives the time required for complete dissolution:

\[
\frac{36 \text{ kg}}{3.8 \times 10^{-5} \text{ kg/yr}} = 9.5 \times 10^5 \text{ yr}
\]

The solubility of PCB is extremely low, so dissolving it away takes nearly an eternity.
Water captured by hydraulic control systems is usually treated to remove contaminants, and then discharged back to the subsurface or to surface waters. The phrase “pump and treat” is often applied to this concept. Sometimes the treatment occurs on-site, and sometimes it occurs at a local wastewater treatment plant. Discharge of treated water usually requires a permit supplied by the appropriate regulating agency (generally a state agency in the U.S.).

The geometry of the capture zone in a single well in a uniform flow field was discussed in Section 7.2.6. More sophisticated modeling is required when the area remediated has significant heterogeneity, anisotropy, or multiple wells. When designing a hydraulic control system, the objectives are to minimize the costs of pumping and treating water, while effectively containing off-site migration of dissolved contaminants. Much has been written about optimizing these systems, including books by Ahlfeld and Mulligan (2000) and Gorelick et al. (1993).

11.9.4 Soil Vapor Extraction

As shown in Figures 11.3 and 11.4, most NAPL spills leave a trail of residual NAPL in the unsaturated zone. With organic NAPLs, the nearby pore gases will contain high concentrations of the volatile compounds in the NAPL. A good way to extract contaminant mass from the subsurface is to pump these gases from the unsaturated zone, a technique known as soil vapor extraction (SVE). Because a large number of contamination problems involve spills of volatile organic compounds in NAPLs, there are many sites where SVE makes sense. Contaminants with high vapor pressures tend to partition from the NAPL phase to the vapor phase and are amenable to SVE techniques.

SVE systems commonly consist of wells that are screened in the unsaturated zone, or trenches with perforated pipe much like a horizontal well, as shown in Figure 11.46. Wells are used for deeper applications and trenches are used for shallower ones. The well or trench riser pipes are connected to a vacuum pump at the ground surface, which creates low pressure in the pipes and induces vapor flow from the surrounding unsaturated zone toward the screened section.

For best efficiency, the extracted vapors have flowed through the NAPL-contaminated zone and picked up high concentrations of contaminants on their way to the extraction point. Wells or trenches have seals near the surface to prevent relatively clean air from short-circuiting the system through the backfill. Air inlet wells or trenches may be installed to allow air to enter the
subsurface at the proper depth and location so that it has to travel through the NAPL-contaminated zone before reaching an extraction well or trench.

Vapors that are extracted are usually treated to remove the contaminants, but sometimes they are released to the atmosphere. For volatile organic compounds (VOCs), treatment often consists of direct oxidation (incineration or otherwise) or filtration through granular activated carbon (GAC). GAC has a large amount of nonpolar surface area, to which VOCs sorb strongly. Used GAC with its sorbed contaminants, in turn, is usually treated off-site by processes that destroy contaminants and regenerate the carbon.

Flow of gases in the unsaturated zone is similar to the flow of water in the unsaturated zone, except that gases are more compressible than water, and gas density varies more significantly. Contaminated pore gases can be significantly denser than clean pore gases, causing contaminated vapors to sink in the unsaturated zone. When vapor flow rates are slow and the density differences are small, vapor flow can be modeled with methods that are similar to those used in groundwater flow models.

The rate of contaminant mass extraction in SVE systems is typically limited by either the rate of volatilization from the NAPL to the gas phase or the air flow rate that can be maintained. In low permeability materials like silts, clays, and tills, the air flow rates are limiting: only so much air can be drawn through the NAPL-contaminated zone.

In more permeable sands and gravels, plenty of air can be drawn through the zone, but the rate of volatilization is limiting. Under these circumstances, increasing the air flow rate will cause little change in the rate of mass removal. Optimizing SVE systems in permeable settings may involve periodic pumping, which saves operating costs and has little effect on the mass removal rate.
Attempts have been made to apply SVE concepts to the saturated zone. With a method called **air sparging**, air is pumped down a well that is screened in the saturated zone, as illustrated in Figure 11.47. As the injected air migrates back up towards the unsaturated zone, volatile contaminant molecules diffuse into it from the surrounding water and NAPL. That air, when it reaches the unsaturated zone, is extracted through typical SVE air wells. In this way, volatile contaminants are stripped from water and NAPL in the saturated zone.

In all but the coarsest gravel materials, the injected air flows through a network of fixed channels as it migrates upward, rather than bubbling randomly through the whole region around the well. It is difficult or impossible to know the distribution of these channels, but studies indicate that they are typically restricted to within a radius of a few meters of the injection well (Ahlfeld et al., 1994; Johnson et al., 1997; Lundegard and LaBrecque, 1995). The air exits the well in the uppermost part of the well screen, and often no air flows through the lower part of the screen.

The network of air channels makes the saturated zone near the well somewhat less permeable to water, but water continues to flow through this zone. The transfer of mass from the water phase to the air channels depends on the channel configurations and the rate of water flow through the zone. If there are just a few widely spaced air channels, mass transfer may be strongly limited by molecular diffusion, which is a very slow process.

SVE systems are often used to help clean up hydrocarbon fuel spills. Since hydrocarbons are mixtures of numerous compounds with varying vapor pressures, the chemistry of the extracted vapors and the remaining NAPL will
Groundwater contamination evolve with time. The high-vapor-pressure constituents are extracted most easily and constitute the bulk of the extracted contaminants at first. With time, the NAPL becomes depleted with respect to these high-vapor-pressure constituents and enriched with respect to the less volatile ones. The rate of mass extraction decreases as the remaining NAPL becomes less and less volatile, on average. As time wears on, the extracted vapors consist of larger and larger fractions of less volatile compounds.

**Example 11.6** A single vapor extraction well is installed in the middle of a source area where 250 gallons of spilled 1,1,1-TCA NAPL is trapped in the unsaturated zone. Assume that the extracted air has a 1,1,1-TCA concentration equal to 5% of its vapor pressure and that the well can pump these vapors at a rate of 100 L/minute. Estimate the total pumping time required to remove all the 1,1,1-TCA NAPL by SVE.

First, we need to calculate the mass of 1,1,1-TCA in 250 gallons, using the density reported in Table 11.2:

\[
250 \text{ gal} \left( \frac{1 \text{ L}}{0.2642 \text{ gal}} \right) \left( \frac{1.35 \text{ kg}}{\text{L}} \right) = 1277 \text{ kg}
\]

The vapor pressure of 1,1,1-TCA is 100 mm Hg and the extracted vapors are assumed to be 5% of this or 5 mm Hg. This vapor pressure must be converted into mass/volume units by first calculating the mole fraction of 1,1,1-TCA in the gas:

\[
\left( \frac{5 \text{ mm Hg}}{760 \text{ mm Hg}} \right) = 0.0066
\]

Then use the standard molar volume for gases at standard pressure and temperature (22.4 L/mol) and the formula weight for 1,1,1-TCA to calculate the mass of 1,1,1-TCA per liter of extracted vapors:

\[
0.0066 \left( \frac{\text{mol}}{22.4 \text{ L}} \right) \left( \frac{133.4 \text{ g}}{\text{mol}} \right) = \frac{0.039 \text{ g 1,1,1-TCA}}{\text{L vapor}}
\]

Next, calculate the rate of extraction of 1,1,1-TCA (mass/time):

\[
\frac{0.039 \text{ g}}{\text{L}} \left( \frac{100 \text{ L}}{\text{min}} \right) = 3.9 \text{ g/min}
\]
The time for cleanup is the total mass to be removed divided by this rate:

$$1277 \text{ kg} \left( \frac{1000 \text{ g}}{\text{kg}} \right) \left( \frac{1 \text{ min}}{3.9 \text{ g}} \right) = 3.3 \times 10^5 \text{ min} = 230 \text{ days}$$

The kind of rough estimate shown in this example can be useful when analyzing the feasibility of an SVE system. In reality, the extracted concentrations would probably decrease with time as the remaining volume of the NAPL declines. Guidelines for the design of SVE systems are given by Johnson et al. (1990).

### 11.9.5 Bioremediation

**Bioremediation** refers to the in situ destruction of contaminant molecules by reactions that occur within resident microbes. It often occurs naturally and sometimes it is aided by remediation efforts that supply needed nutrients or optimize other conditions. Most compounds in hydrocarbon fuels are fairly susceptible to biodegradation. Were it not for this fact, our hydrocarbon fuel contamination problems would be much worse than they actually are.

All near-surface groundwaters appear to support large populations of microbes. Typical microbe population densities range from $10^3$ to $10^7$ per cm$^3$ of groundwater, in both contaminated and uncontaminated waters (Ghiorse and Wilson, 1988; Suflita, 1989).

Bacteria are the most common type of microbe present, and they are the dominant agents of biodegradation. They reside on solid surfaces in the medium and make a living extracting nutrients from their environment to build cell matter and produce energy. As is generally the case in the animal world, their energy is supplied by redox reactions involving oxidation of organic matter. Six redox reactions listed in Table 10.13, starting with respiration, are some of the most common biochemical oxidation reactions in groundwater.

Respiration (aerobic biodegradation) produces more energy than the other possible biodegradation reactions, so when oxygen is present, it is usually the dominant biochemical redox process. Aerobic biodegradation is the main process by which hydrocarbon plumes are abated, but anaerobic oxidation reactions can be important when oxygen is lacking. Denitrification often occurs in the oxygen-poor core of hydrocarbon plumes.
The oxidation reactions listed in Table 10.13 are for a generic carbohydrate molecule (CH$_2$O), but similar reactions apply to other hydrocarbon molecules. For example, aerobic respiration of toluene (C$_7$H$_8$) occurs according to the following reaction:

$$C_7H_8 + 9O_2 \rightleftharpoons 7CO_2 + 4H_2O \quad (11.45)$$

Going from left to right in this reaction, carbon is oxidized and oxygen is reduced. Note that the reaction products are inorganic and harmless: carbon dioxide and water. Transformation of organic molecules to inorganic products is known as **mineralization**.

Examine the ratio of oxygen to toluene in Eq. 11.45. A mole of toluene has a mass of 92.2 g, while 9 mol of O$_2$ has a mass of 288.0 g. For each gram of toluene degraded, 3.1 g of oxygen is required. Aerobic degradation of other common hydrocarbon molecules also requires about a 3:1 ratio of oxygen mass to hydrocarbon mass.

Different hydrocarbon molecules are consumed at different rates by microbes. Some constituents of common hydrocarbon fuels are consumed rapidly while other constituents persist for a long time. The fuel spill plume illustrated in Figure 11.32 clearly shows a large variation in degradation rates, with ethylbenzene and toluene disappearing much more rapidly than MTBE and benzene. The rate of degradation of a given compound depends on many factors including the concentrations of microbes, various hydrocarbon molecules, oxygen, other nutrients, pH, and temperature. Other essential nutrients include nitrogen, phosphorus, and other elements in lesser amounts.

Often the concentration of oxygen in the water is what is most limiting. In a plume with enough dissolved hydrocarbons, oxygen is consumed by reactions like Eq. 11.45. Typical well-aerated water in the unsaturated zone has no more than about 10 mg/L of oxygen. If this water enters a hydrocarbon-contaminated zone, aerobic biodegradation can drive dissolved oxygen levels down to very low levels. Oxygen is replaced by molecular diffusion from the nearest oxygen source. In the unsaturated zone, there is plenty of air–water interface, and oxygen never has to diffuse far through the water. In the saturated zone, oxygen must diffuse long distances from the overlying unsaturated zone, a process that is extremely slow. As a result, saturated zone hydrocarbon plumes often have very low dissolved oxygen levels, like the plume shown in Figure 11.33.
When oxygen is the limiting factor, bioremediation can be enhanced by somehow supplying more oxygen. In the unsaturated zone, this can be done by injecting air into wells screened in the contaminated zone, a technique known as bioventing. This technique is similar to soil vapor extraction (Figure 11.47), except that the objective is to degrade the contaminants in situ rather than to remove them in the vapor phase. Usually, air flow rates are much smaller for bioventing than for SVE.

It is more difficult to supply oxygen to the saturated zone. Air sparging, as described in the previous section (see Figure 11.47), can be used to bring oxygen to the saturated zone. Oxygen in the air pumped down the well will diffuse into the water from bubbles as they rise to the unsaturated zone. This approach can be limited by the same factors that affect SVE applications: uncertain and limited distribution of air channels and slow molecular diffusion in the aqueous phase.

More detailed coverage of bioremediation can be found in books by Alexander (1999) and Norris et al. (1993), among others.

### 11.9.6 Engineered In Situ Reaction Zones

A recent development in remediation is the concept of an in situ reaction zone that is designed to create the proper conditions for biodegradation or some other abiotic degradation process. The zone is placed across the path of a contaminant plume. It is designed so that reactions within it reduce contaminant concentrations to acceptable levels before water exits on the downstream side.

One advantage of this concept is that it requires less equipment and maintenance than pumping water to the surface and treating it there. The system can function in a mostly passive mode, without continuous pumping. Another advantage is that since the water never leaves the subsurface, it is not subject to the strict regulations that govern discharges of treated water back into the environment.

Figure 11.48 shows some general configurations of reaction zones. The reaction zones need to be large enough to intercept the entire plume of contaminated water, and to accomplish the treatment goals. To limit the size of the reaction zone and still treat a large plume, Pankow et al. (1993) and Starr and Cherry (1994) proposed a “funnel and gate” geometry, as illustrated in the lower right of Figure 11.48. The funnel consists of engineered barriers such as slurry walls or sheet pile walls, and the gate is a more permeable zone where
treatment occurs through volatilization or some in situ reaction that destroys
the contaminant.

The reaction zone design varies depending on the chemicals that are to
be remediated. For bioremediation of hydrocarbons, the zone would probably
have a coarse backfill and distribution pipes that could be used to introduce
oxygen, nutrients, and perhaps bacteria cultures. Oxygen-releasing chemicals
like hydrogen peroxide ($H_2O_2$) or permanganate ($MnO_4^-$) could be added to
supply oxygen.

Some chlorinated hydrocarbons like TCE and PCE have been treated in
reaction zones using Fe(0) (pure iron filings, oxidation state zero) as backfill.
The redox reaction that works in this case oxidizes the iron and reduces
the chlorinated hydrocarbon, replacing chlorine atoms with hydrogen atoms
(Gillham and O’Hannesin, 1994; O’Hannesin and Gillham, 1998):

$$Fe^0 + H_2O + X – Cl \to Fe^{2+} + OH^- + X – H + Cl^- \quad (11.46)$$

where $X – Cl$ in the above represents the chlorinated hydrocarbon, and $X – H$
is this same hydrocarbon with hydrogen replacing the chlorine. Through this
type of reaction, the chlorinated ethenes PCE ($C_2Cl_4$) and TCE ($C_2HCl_3$)
are dechlorinated to become dichloroethylene (DCE, $C_2H_2Cl_2$), then vinyl
chloride ($C_2H_3Cl$), and finally ethene ($C_2H_4$).

Many other concepts for reaction zones are currently in the research phase,
which will undoubtedly lead to many new remediation technologies.
11.10 Problems

Answers are given at the back of the book for starred (*) problems.

1. If you could design the worst groundwater contaminant you could think of (it would put a lot of people at risk and be hard to remediate), what would its properties be? Think about each of the properties listed in Table 11.2. Discuss the reasons for your answers.

2. Sketch the molecular structure of the isomers 1,2-dichlorobenzene and 1,3-dichlorobenzene (like the sketches in Figure 11.6). Write the chemical formula for these isomers. Are these likely to be LNAPLs or DNAPLs? Why do you think so?

3. Sketch the molecular structure of chloroethylene (C₂H₃Cl), also known as vinyl chloride (like the sketches in Figure 11.7). Why is there only one isomer of this compound?

4. *A particular gasoline contains 2% by weight of each of these: benzene, ethylbenzene, and MTBE. Calculate the theoretical equilibrium concentrations of these three compounds for water in contact with this gasoline. Assume that the average molecular weight of all gasoline constituents is 102 g/mol.

5. For all the contaminants in Table 11.2 that have MCLs, calculate the ratios of solubility/MCL and list them in a table. Discuss the significance of this ratio. How might high solubility be a good thing?

6. *Solubility describes equilibrium between the NAPL and aqueous phases, \(K_H\) describes equilibrium between the aqueous and gas phases, and vapor pressure describes equilibrium between the NAPL and gas phases. For TCE, calculate the solubility with Eq. 11.3 and compare it to the value listed in Table 11.2 (this will require some careful unit conversions).

7. Explain why downward-migrating NAPL in the unsaturated zone initially spreads out on the top of a fine-grained layer without entering it, but may eventually be able to migrate through the layer. Use what you know about the physics of NAPL migration in your answer.

8. *Examine Figure 11.11. Consider the distribution of capillary pressure \(P_c\) in the PCE ganglia shown in the lower photo. Assume that the pressure distributions in the DNAPL and in the water are hydrostatic (there is not significant vertical flow in either phase), and that at the top of the
ganglia, the pressure in both phases is atmospheric \( (P_w = P_n = 0) \). Write an equation for capillary pressure \( P_c \) at the ganglia’s interfaces in terms of the density of the DNAPL \( \rho_n \), the density of water \( \rho_w \), and the depth below the top of the ganglia \( b_g \). Examining this equation, what is the relation between DNAPL density and its relative mobility in the saturated zone?

9. Examine Figure 11.13, and in particular the correlation of \( K \) to the position of each curve. Describe the general trend in this correlation, and explain why this makes sense.

10. *Calculate the \( x \)-direction advective flux (mass/time/area) in a plume of contamination in sand, where \( K_x = 2 \) m/day, \( \partial h / \partial x = 0.003 \), and the concentration of solute is 20 mg/L. If this plume has a cross-sectional area of 15 m\(^2\) normal to the \( x \) direction, what is the total \( x \)-direction advective mass flux in the plume (mass/time)?

11. *Using Figure 11.29 and the \( n \) and \( \rho_b \) data given in Section 11.6.1, estimate the average retardation factors \( R \) and sorption distribution coefficients \( K_d \) for carbon tetrachloride, bromoform, and PCE for the first 350 days of the test, assuming the chloride is nonreactive (its \( R = 1 \)). Do the same for the period from day 350 to 650. Discuss possible reasons for the observed differences.

12. Using the peak concentrations shown in Figure 11.28, estimate the retardation factors \( R \) for carbon tetrachloride and PCE. Compare these estimates with those you calculated in Problem 11. Explain what the reasons might be for the observed differences.

13. Would the sorption distribution coefficient \( K_d \) for benzene be higher in a peat or in a quartz sand? Explain your answer.

14. *Using Figure 11.30, estimate the ratio of sorbed mass to aqueous-phase mass for carbon tetrachloride, bromoform, and PCE at day 500 of the test. Assume that the adsorbed mass equals the injected mass minus the mass in solution (in other words, assume there is no biodegradation of the compounds). From this ratio and the \( n \) and \( \rho_b \) data given in Section 11.6.1, calculate the apparent distribution coefficients \( K_d \) at day 500. Discuss these results in comparison to the \( K_d \) values you calculated in Problem 11, giving reasons for any differences.

15. In what sort of geologic material might molecular diffusion be trivial by comparison to advection?
16. *For this problem, use the chloride plume at day 462, as shown in Figure 11.27.

(a) Estimate the molecular diffusion mass flux $F_{dx}$ of chloride in the longitudinal ($x$) direction (left to right) along the centerline of the plume from the 300 mg/L contour to the 10 mg/L contour.

(b) Estimate the advective mass flux $F_{ax}$ of chloride in the leading edge of the plume on day 462, assuming a concentration of 150 mg/L and an average linear velocity estimated from the chloride motion shown in Figure 11.29.

(c) Compare the magnitudes of the molecular diffusion flux and the advective flux you just calculated.

17. *Repeat the first part of Problem 16, but instead of calculating the molecular diffusion mass flux, calculate the macrodispersive mass flux $F_{mx}$. Use the longitudinal macrodispersivity value for the Borden tracer test listed in Table 11.7. Compare the macrodispersive flux to the molecular diffusion flux and the advective flux that you calculated in Problem 16. Explain the reasons for the different magnitudes of the fluxes.

18. Explain the reasons for the distributions of dissolved $O_2$ and $CO_2$ shown in Figure 11.33, relating them to the hydrocarbon solute distributions shown in Figure 11.32.

19. *Derive the simplest possible form of Eq. 11.39 when $\bar{v} = 0$. Explain what your resulting equation would be used to model, and what $D_{mx}$ represents in this case.

20. Using software that simulates advection and dispersion, model the migration of the chloride plume in the Borden tracer test. Use a source that is consistent with the injected mass of chloride (10.7 kg, dissolved into 12 m$^3$ of solution), use an average linear velocity based on analysis of Figure 11.29, and use the macrodispersivities listed in Table 11.7. Compare your results with those shown in Figures 11.26 and 11.27. Explain how the modeled plume changes when you double the longitudinal macrodispersivity. Explain how the modeled plume changes when you double the vertical transverse macrodispersivity.

21. Use the analytic transport solution of Eq. 11.43 to model the migration of the chloride plume in the Borden tracer test. Use a source mass of chloride equal to 10.7 kg, an average linear velocity based on analysis of Figure 11.29, and macrodispersivities listed in Table 11.7. Calculate,
using spreadsheet software, the concentration at \( t = 462 \) days along the centerline of the plume \( (20 < x < 70 \, m, \, y = z = 0) \). Make a graph of \( c \) vs. \( x \). Compare your results with those shown in Figure 11.27.

22. *Consider a cylindrical volume of soil contaminated with trichloroethylene (TCE). It is about 5 m in diameter and about 3 m deep. The porosity of the soil is about 0.30. The residual saturation of TCE NAPL averages \( S_n = 0.08 \). Assuming you could flush water through this zone at a rate of 250 L/day, estimate the minimum amount of time required to dissolve away the entire mass of TCE NAPL in the contaminated zone. Discuss how and why you think the actual volume pumped in a real cleanup situation would differ from what you just calculated.

23. At the site of a gasoline spill, there is residual saturation of gasoline within a horizontal layer that is about 2.0 m thick in the vertical direction, near the water table in a fine sand aquifer with porosity \( n = 0.33 \). In this zone the NAPL saturation is \( S_n = 0.07 \). The average infiltration and recharge rate at this location is about 50 cm/yr. The spilled gasoline contains about 1.6% benzene by weight.

(a) Calculate the mass of benzene in the 2.0 m thick residual NAPL zone, per square meter in map view.

(b) Calculate the aqueous concentration (mg/L) of benzene that you would expect in water that is in contact with and at equilibrium with this gasoline (assume the average molecular weight for molecules in the gasoline is 102 g).

(c) Calculate the advective mass flux (mg/m\(^2\)/yr) of dissolved benzene carried by the infiltration/recharge as it moves downward through the NAPL-infested zone.

(d) Estimate how long it will take the vertical infiltration of water to dissolve away all of the benzene from this NAPL zone.

(e) Assuming the gasoline contains about 8% MTBE by weight, would you expect the MTBE to persist longer or shorter than the benzene? Explain your answer.

(f) Discuss potential sources of error in your time estimate for (d).

24. *The estimated zone of contamination below the water table at a gas station cleanup site is roughly shaped like a squat cylinder with a vertical axis. The diameter of the cylinder is about 4 m, and the height of
the cylinder is about 1 m. Within this cylinder, the average total hydrocarbon concentration (dissolved + adsorbed + NAPL) is estimated to be 7000 mg/kg soil solids. The soil dry bulk density is about $\rho_b = 2.3$ kg/L.

(a) Calculate the approximate required ratio of grams of oxygen per gram of contaminant to completely oxidize the contaminant. Use the chemical formula for the oxidation of benzene ($C_6H_6$) to $CO_2$ and $H_2O$ to estimate this.

(b) Assuming that the hydraulic conductivity is $K = 1$ m/day, the natural hydraulic gradient is horizontal and equal to 0.006, and the incoming groundwater has a dissolved oxygen concentration of 5 mg/L, estimate the minimum time required for complete aerobic biodegradation of the hydrocarbons inside the cylinder.