GROUND WATER
REMEDIATION ALTERNATIVES

13.1 INTRODUCTION TO REMEDIATION METHODS

During the past decade, ground water scientists and engineers have devised a number of methods to contain and/or remediate soil and ground water contamination. This technology has been largely driven by ground water regulations (i.e., RCRA, CERCLA, and HSWA) relating to the transport and fate of contaminants at waste sites (see Chapter 14). Ground water remediation has gone through a revolution since 1993 due to a number of complicating issues that were discovered at numerous waste sites. Many of the original pump-and-treat systems that were installed to remove soluble contaminated plumes from the subsurface simply failed to clean up shallow ground water to acceptable water quality levels. These problems were first documented in reports by the EPA (1989; 1992), and mostly relate to difficulties in site characterization and the lack of recognition of the NAPLs problem described in detail in Chapter 11. A National Research Council publication on Alternatives to Ground Water Cleanup (NRC, 1994) indicated that the nation may be wasting large amounts

of money on ineffective remediation efforts. Other findings from the NRC are summarized below.

The remediation of a site must address two major issues: the soluble plume of contamination, which responds to site hydrogeology and may be migrating off site, and the source zone, which may contain NAPLs or residual oils where the original spill or leak occurred. It is now recognized that these source areas and soluble plumes may have to be addressed in very different ways, with greater levels of remediation or containment designed for the source area.

Examples of sources include leaking landfills, leaking pipes or tanks, spills that have sorbed to the subsurface near the water table, and either LNAPLs floating near the capillary fringe or DNAPLS residing on clay lenses below the water table or at the bottom of an aquifer (Chapter 11). The control of these complex source areas is a major challenge at every hazardous waste site and spill. Soluble plumes, on the other hand, were studied extensively over the past two decades, and traditional pump and treat systems can provide some level of control off-site or at a site boundary.

Recently ground water scientists and engineers investigated the ability of current ground water remediation technology to meet specified clean-up standards, typically the restoration of ground water to drinking water standards. An important study, completed by the EPA in 1989, evaluated the performance of 22 ground water remediation systems that had been in operation at least five years (U.S. EPA, 1989). Although contaminant removal of significant hydrocarbon mass was realized, the decrease in contaminant concentration over time was much slower than originally anticipated. Factors that were identified as major impediments to ground water restoration include:

- Contaminant factors such as nonaqueous phase liquids (NAPLs), high sorption potential, and continued leaching from source areas
- Hydrogeologic factors such as heterogeneities, low permeability units, and fractures
- Design factors such as pumping rates, recovery well locations, and screened intervals

Additional EPA research and directives have focused on the problems associated with NAPLs in the subsurface, and have concluded that "NAPLs will have significant influence on the timeframe required and/or the likelihood of achieving clean-up standards" (EPA, 1992). The NRC study (1994) concluded that it may be impractical to restore many difficult hazardous waste sites using current technology, and emerging methods may be required. For sites where conditions preclude restoration to mandated cleanup standards, the general remediation strategy described in this chapter might be applied.

The goals of a ground water remediation effort may include a range of objectives such as limiting the migration of a soluble plume off-site, isolating and containing a source area from further leaking, or treating the affected ground water aquifer down to some drinking water standard. As was discovered in the 1970s, for the control of water quality of surface

lakes and streams, it may not be technologically or economically feasible to remediate a contaminated aquifer to drinking water standards of quality. Rather, some level of protection at the fence line (or at a receptor well) to control off-site migration combined with intensive source controls may be acceptable in many cases. EPA is beginning to define a new set of goals for many hazardous waste site remediations nationwide as ground water professionals learn more about the actual performance of standard remediation methods, such as pump and treat (EPA, 1992). Figure 13.1 summarizes several remedial measures currently being practiced.

Natural attenuation methods and risk-based corrective action have received enormous attention in recent years (Chapter 12). These methods give more credit to the attenuation (dispersion, dilution, biodegradation, etc.) processes that might be operating in an aquifer between the point of disposal and any downgradient receptors. But care must be taken to assure, through well-designed monitoring programs, that concentrations are decreasing in time and that plumes are shrinking in size. Otherwise, we may end up with even more complex problems to deal with in the future.

13.2 REMEDIAL ALTERNATIVES

Once a site has been well characterized for hydrogeology and contaminant concentrations, alternatives for control and remediation can be selected and combined to provide an overall cleanup strategy. Choosing a remedial technology is a function of the type of contaminant, site hydrogeology, source characteristics, and the location of the contaminant in the subsurface. The variation of hydraulic conductivity (K) or transmissivity (T) of a formation is one of the most important parameters of interest. Thus, the ultimate success or failure of any remediation system is a direct function of the ability of the aquifer to transport fluids, both water and contaminant, nutrients, NAPLs, and vapor or air. Well mechanics dictate that pumping and injection rates of liquids and vapors are directly related to aquifer properties. Many of these issues will be addressed in detail in this chapter.

Knowledge of the reactivity or biodegradability of a contaminant in the subsurface is vital for determining whether in situ treatment processes will work. Chapters 7 and 8 indicated that levels of electron acceptors, such as dissolved oxygen, are crucial to the design of a bioremediation system. The ability of an injection system or infiltration system to deliver nutrients or additional electron acceptors to a desired location in a plume is a function of both hydraulic conditions and reactions in the subsurface. Chemical reactions and sorption of organics onto the soil matrix, which might occur during a remediation effort, must also be addressed in detail as part of the design phase of any remediation (Chapter 7).

If pure product or NAPL exists at or near the water table in the form of separate phase fluid, the problem of removal may be greatly complicated. As described in Chapter 11, float-
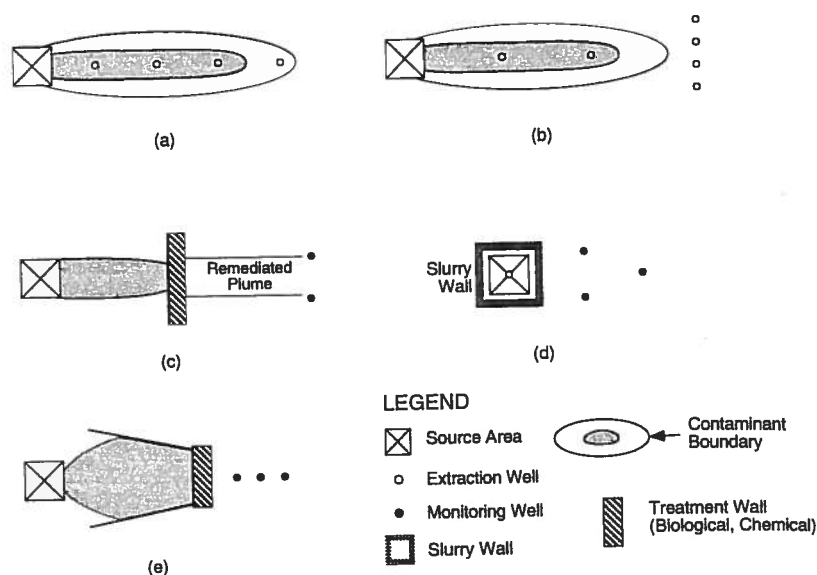
(a)

(b)

Remediated
Plume

(c)

Slurry
Wall

(d)

(e)

LEGEND

⊠ Source Area

○ Extraction Well

● Monitoring Well

☐ Slurry Wall

⬭ Contaminant Boundary

▨ Treatment Wall (Biological, Chemical)

Figure 13.1 Remedial options and source control. (a) Standard pump and treat. (b) Fence line pump and treat. (c) Treatment wall system. (d) slurry wall system. (e) Funnel and gate system.

ing product on the water table (LNAPL) is easier to deal with than denser than water contaminants (DNAPLs), which can sink to lower regions of the aquifer and cannot be easily removed. Thus, depending on the site hydrogeology, it is often necessary to combine a limited pumping system with other techniques (bioremediation, soil vapor extraction, skimming of NAPL) in order to complete remediation in the saturated and vadose zones near a hazardous waste site.

The generally accepted remediation strategies for cleanup of subsurface contamination problems include:

1. Complete source removal (i.e., excavation)
2. Source or plume containment (barriers, hydraulic control)
3. Mass reduction methods
   A. Bioremediation
   B. Soil vapor extraction
   C. Natural attenuation

The above methods, while not the only ones in use, represent the most prevalent and successful ones being applied at many hazardous waste sites today. The remainder of the chapter describes various classes and specific emerging remediation methods in detail. Section 13.3 addresses issues of source control where NAPLs may be present. Section 13.4 reviews traditional pump and treat and hydraulic containment, since so many of the older systems are still in existence. Section 13.5 explains the basics of bioremediation as it applies and has been implemented at field sites. A case study is presented at the end of the chapter. Section 13.6 describes soil vapor extraction with a detailed case study at the end of the chapter. Section 13.7 presents NAPL issues and a detailed case study. Section 13.8 discusses some of the new and emerging technologies that have been tried at a number of experimental sites such as Hill Air Force Base (AFB) in Utah and Dover AFB in Delaware. Section 13.9 presents several detailed case studies of actual field site remediation efforts.

The field of remediation technology is changing rapidly, and new methods are constantly being devised and tested by many research and development groups in the United States and abroad. Several major conferences each year provide a forum for presenting and comparing new methods of ground water cleanup. In particular, the Battelle conferences on *In Situ* and On-Site Bioremediation (1991 to 1999) and on Remediation of Chlorinated and Recalcitrant Compounds (1998) contain many excellent up-to-date methodologies and examples from field sites and laboratory settings that should be of interest. The interested reader should consult the general literature from the Association of Ground Water Scientists and Engineers, the American Society of Civil Engineers, the American Geophysical Union, and the American Chemical Society.

13.3 CONTAINMENT METHODS FOR SOURCE CONTROL

Because of the limitations of conventional pump and treat systems, interest in physical containment methods has increased, primarily for isolating source zones to limit migration of plumes. The containment option is designed to control the spread of contaminants in the subsurface by the use of physical containment methods or hydrodynamic controls. Containment is usually restricted to source areas of a spill or leak from a pond, tank, or landfill, or to contaminated ground water in the immediate vicinity of a source. Hydraulic or hydrodynamic controls usually involve some injection or pumping of ground water via a series of wells surrounding the source or in the immediate plume area (Section 13.4). Physical containment measures are designed to isolate contaminated soil and ground water from the local environment and to minimize any downgradient migration.

Isolation techniques for the surface and subsurface include excavation and removal of the contaminated soil and ground water; barriers to ground water flow such as caps, liners, and cutoff walls; and surface water controls, which are described in order. The NRC (1994; 1997) and Pankow and Cherry (1996) provide thorough reviews of remedial methods for NAPLs, contaminated ground water, and contaminated soils. The Battelle conferences de-

scribed above also present numerous examples of successful and unsuccessful remediation schemes.

13.3.1 Excavation Methods

A pit is usually dug to remove the soil, or pumping wells are installed to control the plume, and the excavated soil is transported to a secured site, such as a landfill or surface impoundment, for disposal (Ehrenfeld and Bass, 1984). This practice is generally no longer permitted in most areas. In recent years, contaminated soil is often sent to a hazardous waste incinerator for complete thermal destruction of organic contaminants. The ground water is pumped out and can be treated using a variety of techniques. The problem in excavation and removal to another location is the high cost, except for small amounts of soil as in the case of underground storage tanks. However, removal of contaminated soil and ground water to a more environmentally appropriate location may be necessary if *in situ* containment or treatment poses problems or initiates litigation. An obvious difficulty associated with excavation and removal is that total removal may be impossible when the contamination extends deep into the subsurface, the contaminants occur beneath a facility or building, or NAPLs are present.

13.3.2 Barriers to Ground Water Flow

Physical barriers used to prevent the flow of ground water include slurry walls, grout curtains, sheet piling, and compacted liners or geomembranes (NRC, 1994). Low permeability barriers for NAPL control are described in Section 13.7. Typical barriers may be used to contain contaminated ground water or leachate or prevent the flow of clean ground water into a zone of contamination. A barrier that completely encircles a contaminated region will provide better containment than a straight barrier, because ground water can flow around the ends. Some of these barriers should be used along with a pumping or collection system for improved hydraulic control across the liner or slurry wall.

Slurry wall aquifers with sandy surficial soil less than 60 ft in depth and underlain by an impermeable layer of fine grain deposits or bedrock are most amenable to slurry wall construction (Need and Costello, 1984). Construction of a slurry wall entails excavating a narrow trench (2 to 5 ft wide) surrounding the contaminated zone (Figure 13.2). The slurry acts to maintain the trench during excavation and is usually a mixture of soil or cement, bentonite, and water (Ehrenfeld and Bass, 1984). The trench is generally excavated through the aquifer and into the bedrock. Installation of a slurry wall at depths greater than 60 ft is difficult. Several books are available on detailed design issues related to slurry wall construction. (Johnson et al., 1985) provides a useful series of papers on slurry walls, based on a symposium sponsored by the ASTM.

There are two different methods for construction of slurry walls. Trenches constructed using a cement-bentonite (C-B) mixture are allowed to set whereas those constructed with a soil-bentonite (S-B) mixture are backfilled and solidified with appropriate materials. Solidification of the trench may be accomplished by backfilling with soil mixed with bentonite, soil
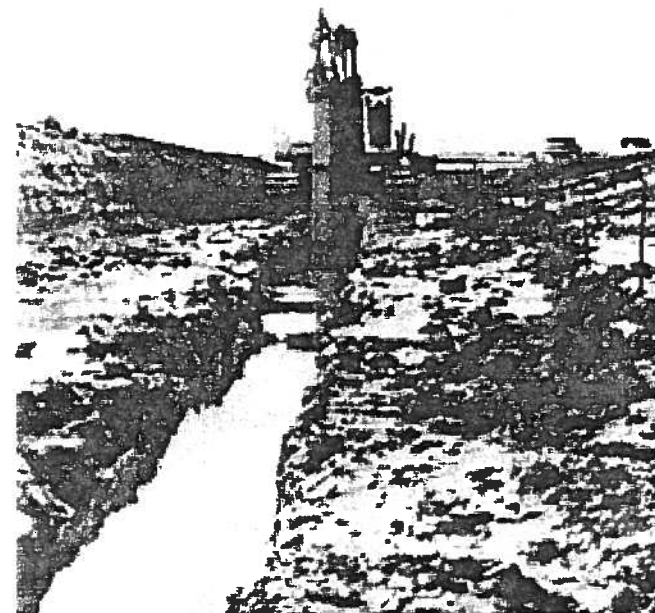
Figure 13.2 Trenching in progress. Source: Ryan, 1985 © ASTM.

mixed with cement, concrete, and asphaltic emulsion, or a combination of these with synthetic membranes (Tallard, 1985; Lynch et al., 1984). The chosen materials should be compatible with the *in situ* soil and contaminant regime. Depending on the backfill material used, the permeability of the resulting barrier may range from 10^{-6} to 10^{-8} cm/sec (Nielson, 1983). An S-B slurry cutoff wall was chosen for the first cleanup financed by the EPA's Superfund program (Ayres et al., 1983).

Grout curtains are another type of physical barrier. They are constructed by injecting grout (liquid, slurry, or emulsion) under pressure into the ground through well points (Canter and Knox, 1986). Ground water flow is impeded by the grout that solidifies in the interstitial pore space. The curtain is made contiguous by injecting the grout into staggered well points that form a two- or three-row grid pattern (Ehrenfeld and Bass, 1984). Spacing of the well points for grout injection and the rates of injection are critical. Premature solidification occurs when the injection rate is too slow, whereas the soil formation is fractured when the rate is too fast. Soil permeability is decreased and soil-bearing capacity is increased after the grout properly solidifies. Chemical or particulate grouting is most effective in soils that

are of sand-sized grains or larger. The expense of grouting and the potential for contamination-related problems in the grout limit its usefulness in the ground water area.

Sheet piling involves driving interlocking sections of steel sheet piling into the ground. The sheets are assembled before use by slotted or ball-and-socket type connections and are driven into the soil in sections. The piles are driven through the unsaturated zone and the aquifer down into the consolidated zone using a pile driver. After driving the barrier into the consolidated material, the piles remaining above ground are usually cut off. The connections between the steel sheets are not initially watertight; however, fine grained soil particles eventually fill the gaps and the barrier generally becomes more impermeable to ground water flow. The interlocks can be grouted to seal the joints between individual sheets. Sheet piling may be less effective in coarse, dense material because the interlocking web may be disrupted during construction. New developments in the technology have significantly reduced the potential for leakage through these walls (Starr and Cherry, 1994). Sheet piles have been used at a number of experimental sites to isolate contaminated zones from one another with some success (Bedient et al., 1999).

Liners represent another type of physical barrier and are often used in conjunction with surface water controls and caps (Canter and Knox, 1986). Liners are often used to protect ground water from leachate resulting from landfills containing hazardous materials. The type of liner used depends on the type of soil and contaminants that are present. Liners include polyethylene, polyvinyl chloride (PVC), many asphalt-based materials, and soil-bentonite or cement mixtures. Polyvinyl chloride liners have hydraulic conductivities of less than 3.0×10^{-11} ft/sec; however, little is known about the service life of the PVC membranes (Threlfall and Dowiak, 1980). The membrane should be installed over fine-grained soil to prevent punctures. A typical liner for a landfill is depicted in Figure 13.3.

13.3.3 Surface Water Controls

These methods alter vertical migration of contaminants by controlling infiltration of surface water through the vadose zone. Caps, dikes, terraces, vegetation, and grading are used to reduce the amount of infiltration into a site and control erosion, such as at a landfill. Channels, chutes, downpipes, seepage basins, dikes, and ditches that are used to divert uncontaminated surface water away from waste sites, collect contaminated leachate, or direct contaminated water away from clean areas (Ehrenfeld and Bass, 1984; Thomas et al., 1987). Many of these techniques may be used in combinations with each other.

Surface capping usually involves covering the contaminated area with an impermeable material, regrading to minimize infiltration of surface water, and revegetating the site (Canter and Knox, 1986). Surface caps are usually constructed using materials from one of three groups: (1) natural soils, (2) commercially designed materials, or (3) waste materials. The material used should be compatible with the soil type and contaminant regime. Examples include clay, concrete, asphalt, lime, fly ash, and mixed layers or synthetic liners. Fine-textured soils, often from on-site, are most commonly used. Several types of materials are used in combination to create a multilayer cap for a landfill (Figure 13.4).
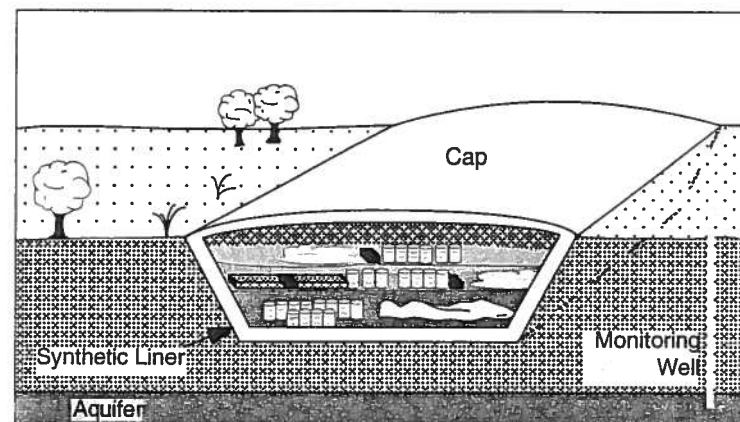
Figure 13.3 Example of synthetic liner for a hazardous-waste landfill.
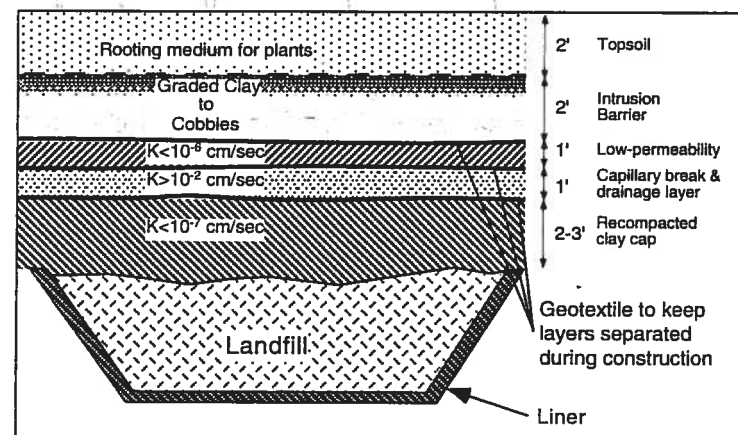

Figure 13.4 Typical multilayered cap constructed of natural soil materials.

13.4 HYDRAULIC CONTROLS AND PUMP AND TREAT SYSTEMS

Hydraulic control of ground water contamination can be designed to generally lower the water table or potentiometric surface to prevent discharge off-site, to reduce the rate of migration by removing contaminated waste, or to confine the plume to a potentiometric low created by a combination of pumping and injection wells. Maintenance on wells and pumps is particularly important for this method, and as ground water levels change, the system design may have to respond accordingly. Above ground biological or physical treatment units may be necessary to handle any contaminated water pumped by the wells.

In recent years, especially since about 1990, studies of pump and treat systems have indicated that drinking water standards may be essentially impossible to achieve in a reasonable time frame at many sites (EPA, 1989 and 1992; NRC, 1994). Between 1982 and 1992, 73% of the cleanups at Superfund sites with contaminated ground water specified the use of pump and treat technology. The effectiveness of pump and treat depends strongly on hydrogeologic and contaminant properties. For increasingly complex sites, the possibility of cleanup success decreases as discussed by the National Research Council (1994).

Several alternatives for removing contaminants via hydraulic control in the subsurface may all be part of an overall strategy for site remediation. The most popular methods have included interceptor systems, soil venting or vapor extraction (Section 13.6), and pumping or injection wells. It is not uncommon to find some or all of these methods being used at a single site, depending on the mix of chemicals and the hydrogeology of the site.

Interceptor systems use drains, a line of buried perforated pipe, and/or trenches, or an open excavation usually backfilled with gravel, to collect contaminated ground water close to the water table. These systems operate as a line of wells near the shallow water table, and are efficient at removing contamination along a linear boundary. Trenches are often used to collect nonaqueous phase liquids (LNAPLs) like crude oil or gasoline, that are light and tend to move near the capillary fringe just above the water table. Figure 13.5 shows a skimmer pump designed to selectively remove LNAPL entering the trench from a leaking UST. Trenches have also been used to collect DNAPLs from fractured limestone where a trench cuts across the fractures, is backfilled and pumped, and creates a significant zone of depression for ground water withdrawal (Figure 13.6). The trench should be designed long enough to avoid product flow around the end, and deep enough for hydraulic control to avoid the water table falling beneath the bottom of the trench during dry periods.

Pumping wells are used to extract water from the saturated zone by creating a capture zone for migrating contaminants (Figure 13.7). A major problem is the proper treatment and disposal of the contaminated water. On-site treatment facilities are usually required before water can be reinjected to the aquifer or released to the surface sanitary system. The number of wells, their locations, and the required pumping rates are the key design parameters of interest, and methods of analysis for wells are described in more detail in Chapter 3. Pumping contaminated water containing dissolved constituents can be addressed using standard well mechanics and capture zone theory which is well understood (Mercer et al., 1990). If the hy-
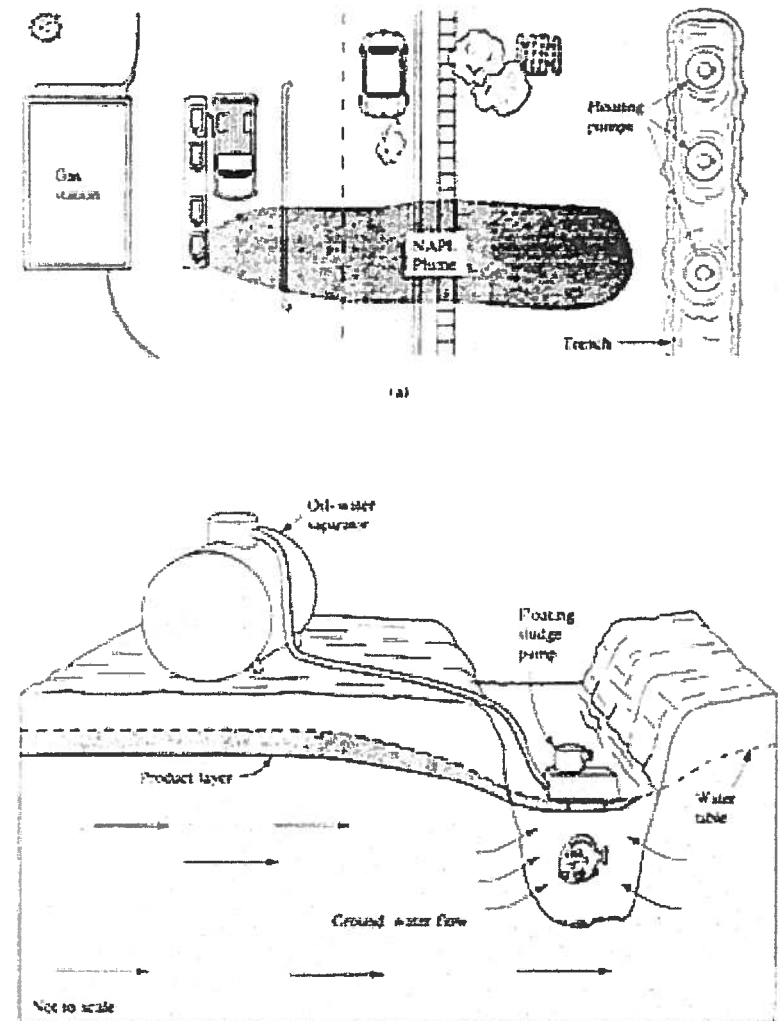
Figure 13.5 (a) Top view of LNAPL plume and interceptor trench. (b) Cross section of trench and floating pump used to capture floating product and depress the water table. Source Fetter, 1999.
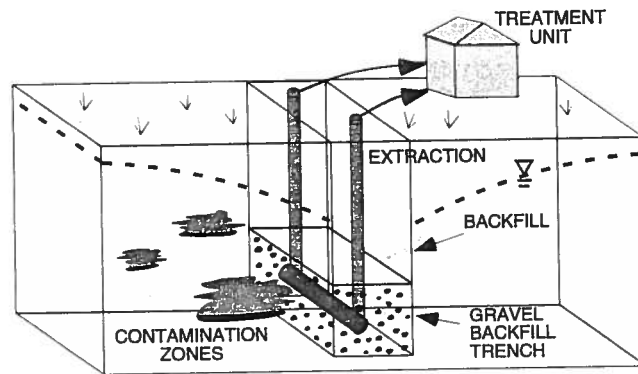
Figure 13.6 Collection Trench for DNAPL Source Zones.

drogeology is conducive to an injection or pumping system, then several design approaches can be used to develop an efficient and reliable system for contaminant removal. The most successful designs have been for relatively sandy or silty sand soils, that are very well-characterized, and ones where cleanup goals have not been too stringent.

Pilot scale pumping systems or small field demonstration projects have been used at a number of sites to evaluate the pump rates and the placement of wells in a small area of the site, before expanding to the entire site. In this way, operational policies, mechanical problems, and costs can be evaluated before attempting the larger cleanup. Careful monitoring of the system is the key to understanding how the injection/pumping pattern will respond over time. Many of the systems were originally designed without properly addressing the source area, where NAPL issues can create serious problems for standard pump and treat, vapor extraction or NAPL controls. Even with the problems associated with pump and treat designs, many sites still have these systems in place, and are providing some measure of control for off site areas.

13.4.1 Capture Zone Techniques

Pumping water containing dissolved contaminants can be addressed using standard well mechanics and capture zone theory (Chapter 3). If the hydraulic conductivity is too low or the geology is overly complex and heterogeneous, then pumping or hydraulic control may not be a feasible alternative for hazardous waste cleanup. If the hydrogeology is permeable enough for an injection pumping system, then both analytical and numerical models are available to evaluate placement and efficiency of remediation.

Javandel and Tsang (1986) developed a useful analytical method for the design of recovery well systems, based on the concept of a capture zone (Figure 13.7). More sophisti-

cated modeling approaches are described in Chapter 10 and Section 13.9 for the case of more complex sites where numerical models must be employed. The capture zone for a well depends on the pumping rate and the aquifer conditions. Ideally, the capture zone should be somewhat larger than the plume to be cleaned up, so wells can be added until sufficient pumping capacity is provided to create a useful capture zone. However, with more wells, some contaminants may pass between the wells, so well spacing becomes an important parameter as well as pumping rate. The greater the pumping rate, the larger the capture zone, so the closer the wells are placed, the better the chance of complete plume capture. Overall, the method minimizes the pumping injection rates through a proper choice of well location and distance between wells.

Javandel and Tsang (1986) use complex potential theory as the basis for a simple graphical procedure to determine the pumping rate, the number of wells, and the distance between wells. The method requires type curves for one to four wells (Figure 13.8) and values for two parameters, B the aquifer thickness (assumed to be constant) and U the specific discharge or Darcy velocity (also assumed constant) for the regional flow system. The method involves the following five steps:

1. Construct a map of the contaminant plume at the same scale as the type curves. The edge or perimeter of the plume should be clearly indicated together with the direction of regional ground water flow.

2. Superimpose the type curve for one well on the plume, keeping the x-axis parallel to the direction of regional ground water flow and along the midline of the plume so that approximately equal proportions of the plume lie on each side of the x-axis. The pumped well on the type curve will be at the
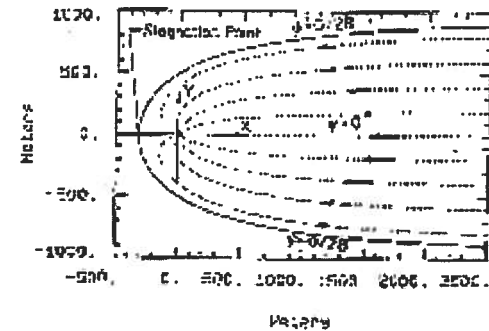

Figure 13.7 Paths of some water particles within the capture zone with Q/BU = 2000, leading to the pumping well located at the origin. Source: Javandel and Tsang, 1986.
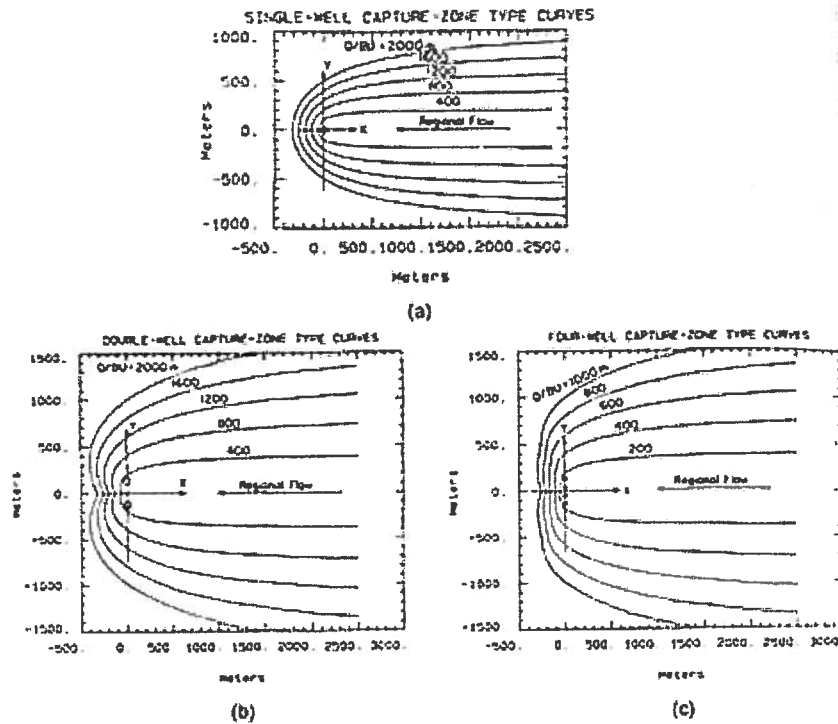
Figure 13.8 Set of type curves showing the capture zones for various values of Q/Bu. (a) Single pumping well at the origin. (b) Two pumping wells located on the Y axis. (c) Four pumping wells located on the Y axis. Source: Javandel and Tsang, 1986.

downstream end of the plume. The type curve is adjusted so that the plume is enclosed by a single Q/BU curve.

3. Calculate the single well pumping rate (Q) using the known values of aquifer thickness (B) and the Darcy velocity for regional flow (U) along with the value of Q/BU indicated on the type curve (TCV) with the equation

$$Q = B \cdot U \cdot TCV$$

4. If the pumping rate is feasible, one well with pumping rate Q is required for cleanup. If the required production is not feasible due to a lack of available drawdown, it will be necessary to continue adding wells (see step 5).

5. Repeat steps (2), (3), and (4) using the two-, three-, or four-well type curves in that order, until a single well pumping rate is calculated that the aquifer can support. The only extra difficulty comes from having to calculate the optimum spacing between wells using the following simple rules

2 wells	$Q/(BU)$
3 wells	$1.26Q/(BU)$
4 wells	$1.2Q/(BU)$

and to account for the interfacing among the pumped wells when checking on the feasibility of the pumping rates. The wells are always located symmetrically around the x-axis, as the type curves show.

Reinjecting the treated water produced by the wells will accelerate the rate of aquifer cleanup. The procedure is essentially the same as that just discussed except the type curves are reversed and the wells are injecting instead of pumping. The authors suggest that the injection wells should be moved slightly upstream of the calculated location to avoid causing parts of the plume to follow a long flow path. Their rule of thumb is to place wells half the distance between the theoretical location and the tail of the plume. The following example taken from Javandel and Tsang (1986) illustrates how the technique is used.

Example 13.1. CAPTURE ZONE

Shown on Figure 13.9 is a plume of trichloroethylene (TCE) present in a shallow confined aquifer having a thickness of 10 m, a hydraulic conductivity of 10^{-4} m/s, an effective porosity of 0.2, and a storativity of 3×10^{-5}. The hydraulic gradient for the regional flow system is 0.002 and the available drawdown for wells in the aquifer is 7 m. Given this information, design an optimum collection system.

Values of B and U are required for the calculation. B is given as 10 m, but U needs to be calculated from the Darcy equation:

$$U = K \, dh/dl \quad \text{or} \quad U = 10^{-4} \times (0.002) = 2 \times 10^{-7} \text{ m/s}$$

Now we are ready to work with the type curves following the steps just outlined.

Superposition of the type curve for one well on the plume provides a Q/BU curve of about 2500. With this number and the values of B and U, the single well pumping rate is

$$Q = B \cdot U \cdot TCV \quad \text{or} \quad 10 \cdot (2 \times 10^{-7}) \cdot 2500 = 5 \times 10^{-3} \text{ m}^3/\text{s}$$

A check is required to determine whether this pumping rate can be supported for the aquifer. The Cooper-Jacob (1946) equation provides the drawdown at the well, assuming $r = 0.2$ m and the pumping period is one year:

$$s = \log \frac{2.25Tt}{r^2 S}$$

where $Q = 5 \times 10^{-3}$ m^3/s, $T = KB = 10^{-3}$ m^2/s, $t = 1$ year or 3.15×10^7 sec, $r = 0.2$ m, and $S = 3 \times 10^{-5}$.

The pumping period represents some preselected planning horizon for cleanup. Substitution of the known values into Cooper-Jacob equation gives a drawdown of 9.85 m. Even without accounting for well loss, the calculated drawdown exceeds the 7 m available. Thus, a multiwell system is necessary.

Superimposing the plume on the two-well type curve provides a Q/BU value of 1200, which in turn gives a Q for each of the two wells of $10 \cdot (2 \times 10^{-7}) \cdot 1200$ or 2.4×10^{-3} m^3/s. The optimum distance wells is $Q/(BU)$ or $2.4 \times 10^{-3}/[10 (2 \times 10^{-7})] = 382$ m. Again we check the predicted drawdown at each well after one year against the available 7 m. Because of symmetry, the drawdown in each well is the same. The total drawdown at one of the wells includes the contribution of that well pumping plus the second one 382 m away, based on the principal of superposition.

The calculated drawdown is 6.57 m, which is less than the available drawdown. However, well loss should be considered, which makes the two-well scheme unacceptable. Moving to a three-well scheme, Q/BU is 800 (Figure 13.9), which translates to a pumping rate of 1.6×10^{-3} m^3/s for each well. Carrying out the drawdown calculation for three wells located $1.26Q/(BU)$ or 320 meters apart provides an estimate of 5.7 m for the center well, which is comfortably less than the available drawdown. Thus, we have been able to ascertain the need for three wells, located 320 m apart, and each pumped at 1.6×10^{-3} m^3/s.

There are assumptions built into the formulation, such as constant aquifer transmissivity, fully penetrating wells, no recharge, and isotropic hydraulic conductivity, which must be satisfied by the field problem or the method will not necessarily yield a correct result. Actual field sites where boundary conditions and site heterogeneity are important issues may require analysis using numerical models as described in the next section.
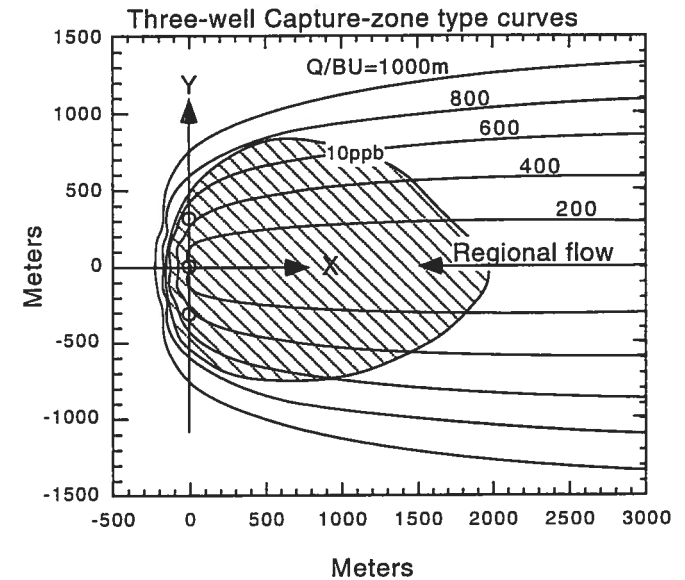
Figure 13.9 The 10-ppb contour line of TCE at the matching position with the capture zone type curve of Q/BU = 800. Source: Javandel and Tsang, 1986.

13.4.2 Analysis of Pumped Systems with Numerical Models

Ground water flow and transport modeling performed during the remedial investigation can be a powerful tool to estimate plume movement and response to various remedial schemes (see Chapter 10). Flow and contaminant transport models should be calibrated to a measured plume of contamination to the extent possible. However, caution should be used when applying models at hazardous waste sites because there can be great uncertainty whenever subsurface transport is modeled, particularly when the results of the model are based on estimated parameters. The purposes of modeling ground water flow for remediation include the following:

1. Predict concentrations of contaminants at receptor points

2. Estimate the effect of source-control actions on remediation

3. Guide the placement of monitoring wells and hydrogeologic characterization when the remedial study is conducted in phases

4. Evaluate expected remedial performance under a variety of alternative designs so that the efficiency and time of cleanup to some specified level can be predicted

The determination of whether or not to use modeling and the level of effort that should be expended is made on the basis of the objectives of the modeling, the ease with which the subsurface can be conceptualized mathematically, and the availability of data. Field data are collected to characterize the variables that govern the hydrologic and contaminant response of the site in question. Estimates based on literature values or professional judgment are frequently used as well.

Models such as the 3-D and RT3D (Clement et al., 1998) can be used to simulate flow patterns and concentration changes resulting from the operation of a pump-and-treat system. Other models are available to analyze contaminant transport such as the 2-D MOC model from Konikow and Bredehoeft (1978) and BIOPLUME III from Rifai et al. (1998). A detailed modeling example for a large pump and treat system in a complex aquifer is described in Section 13.9.

13.4.3 Optimizing Pumping-Injection Systems

Many investigators have used numerical ground water models as a tool in the design of aquifer restoration strategies because they provide a rapid means of predicting or assessing the effects of different remedial alternatives. Andersen et al. (1984) used a finite-difference ground water model as an aid in selecting an appropriate remedial action at the Lipari Landfill in New Jersey. Freeberg et al. (1987) delineated a trichloroethylene plume and used the USGS MOC Model to evaluate different withdrawal schemes at an industrial waste site. Gorelick et al. (1993) developed an entire set of optimization and simulation tools to design efficient and cost-effective capture and containment systems for ground water. However, optimization techniques have suffered because of the ill-posed ground water transport problems, and the inability to handle complex source problems involving NAPL issues.

Satkin and Bedient (1988) used the USGS MOC model to investigate various pumping and injection patterns to remediate a contaminant plume. Seven different well patterns were studied for various combinations of hydraulic gradient, maximum drawdown and aquifer dispersivity. Various cleanup levels were evaluated along with the volume of water circulated and the volume of water requiring treatment. Eight hydrogeologic conditions were modeled for the various remediation schemes. The location of a single well or multiple pumping wells requires that the capture zone encompass the entire plume. Generally, the closer a single well can be to the center of mass of contamination, the faster the cleanup time. Additional wells aligned with the axis of the plume will increase the rate of cleanup over a single well by pumping a greater volume of water.

The key hydrogeologic variables that control the rate of cleanup are well locations, pumping rates, transmissivity, dispersivity and hydraulic gradient. The three-spot, doublet, and double-cell (four wells) well patterns were effective under low hydraulic gradient condi-
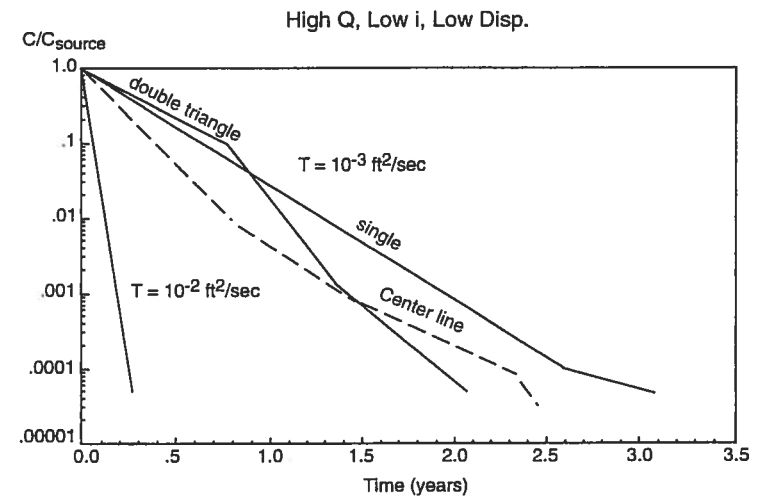
High Q, Low i, Low Disp.

Figure 13.10 Comparison of relative concentrations versus cleanup time for various well patterns for condition A. Source: Satkin and Bedient, 1988.

tions. These well patterns require on-site treatment and reinjection. The three-spot pattern performed best under a high hydraulic gradient. Finally, for a given set of well locations, and maintaining drawdown, dispersivity and hydraulic gradient constant, the cleanup time was found to be inversely related to the pumping rate for selected transmissivities. Figure 13.10 shows typical results for a selected hydrogeologic condition of low gradient and low dispersivity.

13.5 BIOREMEDIATION

The practical application of biodegradation discussed in Chapters 7 and 8 for the remediation of hazardous waste sites is termed **bioremediation**. The process, when carried out *in situ*, or in place, usually involves stimulating the indigenous subsurface microorganisms by the addition of nutrients, such as nitrogen and phosphorus, and an electron acceptor, such as oxygen, to biodegrade the contaminants of concern. The process is not new, in that some of the first systems were installed in the 1970s. Under the proper subsurface conditions, and for petroleum hydrocarbons, microorganisms can biodegrade contaminants to mineral end products such as carbon dioxide and water. Several excellent reviews have been presented in the general literature (NRC, 1993; Norris et al., 1994).
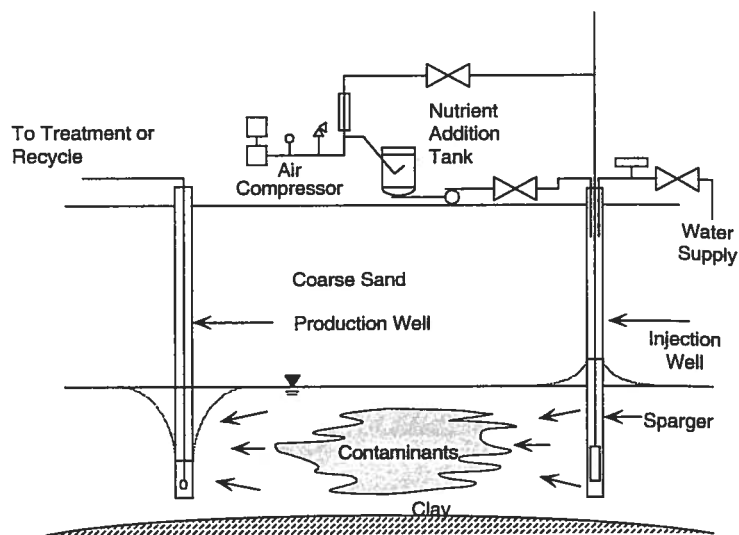
Figure 13.11 Injection system for oxygen.

In contrast with other remedial techniques that transfer the contaminants from one phase in the environment to another, *in situ* bioremediation offers partial or complete destruction of the contaminants (Chapter 7). In some cases, the natural conditions at a site provide all of the necessary materials so that the process can occur without human intervention, which is called **intrinsic bioremediation**. Engineered bioremediation systems usually require some construction of monitoring and delivery systems for the addition of nutrients or electron acceptor (Figure 13.11).

In situ bioremediation process might offer attractive economics for remediation because it precludes the need for excavation and disposal costs associated with other remediation alternatives. The method also offers an advantage where physical limitations due to the presence of structures might inhibit removal of the contaminants, and can be used to treat contaminants, which are both sorbed to the aquifer matrix and dissolved in the ground water simultaneously.

Two essential criteria must be satisfied before bioremediation can be considered a viable remediation alternative for a field site. First, the subsurface geology must have a relatively high hydraulic conductivity ($>10^{-4}$ cm/sec) to allow the transport of the electron acceptor and nutrients through the aquifer. Second, microorganisms must be present in sufficient numbers and types to degrade the contaminants of interest. It is important to keep in mind that any bioremediation project at a field site needs to be preceded by laboratory experiments

of microbial stimulation and modeling studies of nutrient delivery and transport to ensure efficient performance of the system. Enhanced aerobic bioremediation for a petroleum spill, for example, is essentially an engineered delivery of nutrients and oxygen to the contaminated zone in an aquifer.

Oxygen sources include air, pure oxygen (gaseous and liquid forms), and hydrogen peroxide. Sparging the ground water with air and pure oxygen can supply only 8 to 40 mg/L of oxygen depending on the temperature of the injection fluid (Lee et al., 1988). Hydrogen peroxide, which dissociates to form water and 1/2 molecule of oxygen, is infinitely soluble in water (Thomas and Ward 1989); however, hydrogen peroxide can be toxic to microorganisms at concentrations as low as 100 ppm. Other limitations have to do with the expense and the stability of hydrogen peroxide.

13.5.1 Engineering Design Issues

The basic steps involved in an in situ biorestoration program (Lee et al., 1988) are:

1. site investigation
2. free product investigation and recovery
3. microbial degradation enhancement study
4. system design and construction
5. operation
6. maintenance

After defining the hydrogeology, recovery of free product, if any, at the site should be completed. LNAPL can be removed using physical recovery techniques such as a dual pump system that produces water and hydrocarbon or a two-pump, two-well system that steepens the hydraulic gradient and recovers the accumulating hydrocarbon. Section 13.7 describes skimmer wells in more detail.

Prior to the initiation of a bioremediation activity, it is important to conduct a feasibility study for the biodegradation of the contaminants present at the site. First, contaminant-degrading microorganisms must be present, and second, the response of these native microorganisms to the proposed treatment method must be evaluated. In addition, the feasibility study is conducted to determine the nutrient requirements of the microorganisms. These laboratory studies provide a reliable basis for performance at the field level only if they are performed under conditions that simulate the field. A number of recent publications are available to help guide the practitioner (NRC, 1993).

The chemistry of a field site will obviously affect the types and amounts of nutrients that are required. Limestone and high mineral content soils, for example, will affect nutrient availability by reacting with phosphorous. Silts and clays at sites may induce nutrient sorption on the soil matrix, and hence decrease the amount of nutrients available for growth. In

general, a chemical analysis of the ground water provides little information about the nutrient requirements at a field site; it is mostly the soil composition that is of significance.

Feasibility studies can be completed using several different techniques. Batch culture techniques are used to measure the disappearance of the contaminant; electrolytic respirometer studies are utilized to measure the uptake of oxygen. Studies that measure disappearance of the contaminant or mineralization studies that confirm the breakdown of the contaminant to carbon dioxide and water need to be conducted. Controls to detect abiotic transformation of the pollutants and tests to detect toxic effects of the contaminants on the microflora should be included (Flathman et al. 1984; NRC, 1993; Norris et al., 1994).

For enhanced bioremediation, a system for injection of nutrients into the formation and circulation through the contaminated portion of the aquifer must be designed and constructed (Lee and Ward, 1985). The system usually includes injection and production wells and equipment for the addition and mixing of the nutrient solution (Raymond, 1978). A typical system is shown in Figure 13.11. Placement of injection and production wells may be restricted by the presence of physical structures. Wells should be screened to accommodate seasonal fluctuations in the level of the water table. Nutrients also can be circulated using an infiltration gallery; this method provides an additional advantage of treating the residual gasoline that may be trapped in the pore spaces of the unsaturated zone. Oxygen can be supplied by a number of methods including oxygen in water, pure oxygen, hydrogen peroxide, ozone, or by soil venting.

The performance of the system and proper distribution of the nutrients can be monitored by measuring the organic, inorganic, and bacterial levels in space and time. Carbon dioxide levels are also an indication of microbial activity in the formation. There are a number of field demonstrations of the bioremediation process that have been implemented over the past few years, and several examples are presented in Chapter 8 and in Dupont et al. (1998).

13.5.2 Bioremediation Demonstration Projects

Researchers from Suntech, Inc. are among the earliest pioneers who utilized bioremediation at sites contaminated with gasoline. Classic field experiments are discussed by Raymond et al. (1976) and Raymond (1978). The field study at a site in Ambler, Pennsylvania involved a leak in a gasoline pipeline that had caused the township to abandon its ground water supply wells. The free product was physically removed prior to the initiation of biodegradation studies at the site. Laboratory studies showed that the natural microbial population at the site could use the spilled high-octane gasoline as the sole carbon source if sufficient quantities of the limiting nutrients, in this case, oxygen, nitrogen and phosphate, were supplied. Pilot studies carried out in the field in several wells confirmed the laboratory findings.

Studies began in 1986 at the U.S. Coast Guard Facility in Traverse City, Michigan for fuel hydrocarbons from a large leaking fuel tank. The site was used for six years as a research field site by EPA to evaluate a number of in situ bioremediation technologies (Wilson et al., 1988). Rifai et al. (1988) and Bedient et al. (1992) applied the BIOPLUME II model to demonstrate and quantify that natural biodegradation of BTEX was occurring at the site. Several

test areas were used to test enhanced bioremediation through the subsurface injection of oxygen, hydrogen peroxide, phosphates, and nitrates. Natural biodegradation of the off-site plume was quantified based on several wells located down the plume's centerline (Bedient et al., 1992).

Researchers at Stanford University conducted an extensive field demonstration at Moffet Naval Air Station to evaluate the potential of using cometabolism in situ bioremediation of chlorinated organics. Chlorinated solvents were added to the site, along with oxygen and methane to stimulate the native microorganisms (Semprini et al., 1990; Roberts et al., 1990). There was a documented loss of contaminants: 95% of vinyl chloride, 85% of trans-DCE, 40% of cis-DCE, and 20% of TCE that had been added to the site. The researchers used a variety of methods to demonstrate biodegradation in the field including evaluation of background conditions and microbial breakdown products, conservative tracer studies, and modeling studies.

Chiang et al. (1989) evaluated the aerobic biodegradation of BTX from a natural gas plant in northern Michigan. They set up an extensive monitoring program to evaluate the effectiveness of intrinsic bioremediation in 1987, and showed that benzene concentrations dropped by 90% and the contaminant plume has shrunk considerably. Laboratory tests confirmed the potential for soil microbes to degrade the fuel contaminants at a high rate in the presence of oxygen. Finally, the BIOPLUME II was used to calibrate to the site data and to predict future conditions at the site. The model worked quite well and matched the rates measured in the field (see Chapter 8).

Since the early nineties, a larger number of successful demonstration projects on active bioremediation at field sites are now available for review. The *Handbook of Bioremediation* by Norris et al. (1994) provides detailed descriptions of the technologies available for handling both contaminated soil and ground water. A recent monograph from Dupont et al. (1998), under the innovative site remediation technology program, presents eight different case studies on bioventing, biosparging, the Raymond process, intrinsic remediation, and land farming. The reader is referred to the above references for more details than can be provided here.

13.6 SOIL VAPOR EXTRACTION SYSTEMS

The unsaturated zone plays a key role in determining the dynamics of subsurface contaminant transport and remediation. Soil vapor extraction (SVE) is an alternative remediation strategy targeting the removal of volatile contaminants from the unsaturated zone, and results in contaminant removal from the vapor, NAPL, and aqueous phases (Rathfelder et al., 1991). Many organic substances have substantial vapor concentrations (i.e., highly volatile) compared to their solubilities. Vapor pressure and Henry's Law constant determine the degree to which the chemical will partition into the gas phase. Volatile contaminants could be more effectively recovered from the unsaturated zone by enhancing air-phase transport as opposed
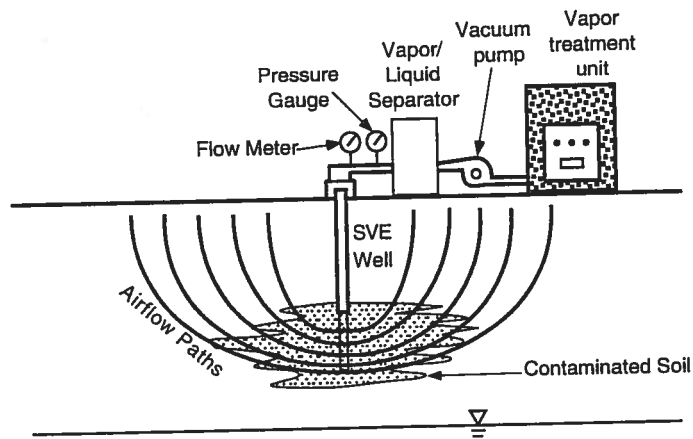
Figure 13.12 Simple vapor extraction system and the resulting pattern airflow. Source: Johnson et al., 1990.

to water-phase transport (Baehr et al., 1989). In this technique, the soil is decontaminated in place by pulling air through the soil, and the extracted gas may be discharged directly to the atmosphere or sent to an emissions control device (DePaoli et al., 1991). Advective vapor transport is induced by withdrawing air through wells that are screened in the vadose zone. As air is drawn through the pores, it will carry away the existing vapors. Thus, contaminants in the liquid and dissolved phases will volatilize and continue to be swept by the carrier air flow. As the process continues, the residual levels of soil contaminants will be effectively reduced. Figure 13.12 shows a schematic of a typical SVE system.

SVE has been successful for sites contaminated with gasoline and organic solvents that contain a large fraction of volatile components (Hutzler et al., 1989). It is extremely useful in decontaminating highly permeable soils in a relatively short time. Among the advantages of the soil vapor extraction process are that it creates a minimal disturbance of the contaminated soil, it can be constructed from standard equipment, and it is cost effective. The success of the operation depends on the rate of contaminant mass transfer from the non-aqueous and aqueous phases to the vapor phase. The feasibility of the technique is site specific. Variables to be considered include: (1) contaminant characteristics such as: contaminant volatility, boiling point, solubility, octanol/water partition coefficient; and (2) site properties such as: permeability, fraction of organic carbon, and moisture content. The decision on whether to use SVE for site remediation, or to take no action and leave the site to naturally attenuate depends on site conditions, and on the potential health risks associated with exposure.

13.6.1 System Components

A typical soil vapor extraction system such as the one shown in Figure 13.12 consists of:

1. one or more extraction wells
2. one or more air inlet or injection wells (optional)
3. piping or air headers
4. vacuum pumps or air blowers
5. flow meters and controllers
6. vacuum gauges
7. sampling ports
8. air/water separator (optional)
9. vapor treatment (optional)
10. a cap (optional)

Extraction wells are typically designed to fully penetrate the unsaturated zone to the capillary fringe. If the ground water is at a shallow depth or if the contamination is confined to near-surface soils, then the extraction wells may be placed horizontally. Extraction wells usually consist of slotted, plastic pipe placed in permeable packing. The surface of the augured column for vertical wells or the trench for horizontal wells is usually grouted to prevent the direct inflow of air from the surface along the well casing or through the trench.

It may be desirable to also install air inlet or injection wells to control airflow through zones of maximum contamination. They are constructed similarly to the extraction wells. Inlet wells or vents are passive and allow air to be drawn into the ground at specific locations. Injection wells force air into the ground and can be used in closed-loop systems (Payne et al., 1986). The function of inlet and injection wells is to enhance air movement in strategic locations and promote horizontal airflow to the extraction wells.

The pumps or blowers reduce gas pressure in the extraction wells and induce airflow to the wells. The pressure from the outlet side of the pumps or blowers can be used to push the exit gas through a treatment system and back into the ground if injection wells are used. Gas flow meters are installed to measure the volume of extracted air. Pressure losses in the overall system are measured with vacuum gauges. Sampling ports may be installed in the system at each well head, at the blower, and after vapor treatment. In addition, vapor and pressure monitoring probes may be placed to measure soil vapor concentrations and the radius of influence of the vacuum in the extraction wells.

Vapor treatment may not be required if the emission rates of chemicals are low or if they are easily degraded in the atmosphere. Typical treatment systems include liquid/vapor condensation, incineration, catalytic conversion, or granular activated carbon adsorption.

Patterns of air circulation to extraction wells have been studied in the field by direct measurements (Batchelder et al., 1986), and more recently by mathematical and experimental

modeling (Johnson et al., 1988, 1990, 1994; Krishnayya et al., 1988). Chapter 9 presented governing equations of flow and transport for the unsaturated zone. Most of the theoretical work to date has considered that any density differences in the vapor can be neglected under the forced convective conditions created by the vacuum extraction.

13.6.2 System Variables

A number of variables characterize the successful design and operation of a vapor extraction system. They may be classified as site conditions, soil properties, chemical characteristics, control variables, and response variables (Anastos et al., 1985; Envireresponse, 1987; Hutzler et al., 1989; Johnson et al., 1994).

The extent to which VOCs are dispersed in the soil, vertically and horizontally, is an important consideration in deciding if vapor extraction is preferable to other methods. The depth to ground water is also important. Where ground water is at depths of more than 40 feet and the contamination extends to the ground water, use of soil vapor extraction systems may be one of the few ways to remove VOCs from the soil (Hutzler et al., 1989; Johnson et al., 1994).

Heterogeneities influence air movement as well as the location of chemical, and the presence of heterogeneities make it more difficult to position extraction and inlet wells. There generally will be significant differences in the air conductivity of the various strata of a stratified soil. A horizontally stratified soil may be favorable for vapor extraction because the relatively impervious strata will limit the rate of vertical inflow from the ground surface and will tend to extend the influence of the applied vacuum horizontally from the point of extraction.

The soil characteristics at a particular site will have a significant effect on the applicability of vapor extraction systems. Air conductivity controls the rate at which the applied vacuum can draw air through the soil. Grain size, moisture content, soil aggregation, and stratification probably are the most important properties (Hutzler et al., 1989, Johnson et al., 1994). The soil moisture content or degree of saturation is also important in that it is easier to draw air through drier soils. The success of the soil vapor extraction in silty or clayey soils may depend on the presence of more conductive strata, as would be expected in alluvial settings, or on relatively low moisture content in the finer-grained soils.

Chemical properties will dictate whether a soil vapor extraction system is feasible. A vapor-phase vacuum extraction system is most effective at removing compounds that exhibit significant volatility at the ambient temperatures in soil. Low molecular weight, volatile compounds are favored, and vapor extraction is likely to be most effective at new sites where the more volatile compounds are still present. Compounds that have been effectively removed by vapor extraction include trichloroethene, trichloroethane, tetrachloroethene, and most gasoline constituents. Compounds that are less applicable to removal include trichlorobenzene, acetone, and heavier petroleum fuels (Payne et al., 1986; Bennedsen et al., 1985; Texas Research Institute, 1980).

Soil vapor extraction processes are flexible in that several variables can be adjusted during design or operation. These variables include the air withdrawal rate, the well spacing and

configuration, the control of water infiltration by capping, and the pumping duration. Higher air flow rates tend to increase vapor removal because the zone of influence is increased and air is forced through more of the air-filled pores. More wells will allow better control of airflow but will also increase construction and operation costs. Intermittent operation of the blowers will allow time for chemicals to diffuse from immobile water and air and permit removal at higher concentrations.

Parameters responding to soil vapor extraction system performance include air pressure gradients, VOC concentrations, moisture content, and power usage. The rate of vapor removal is expected to be primarily affected by the chemical's volatility, its sorptive capacity onto soil, the air flow rate, the distribution of air flow, the initial distribution of chemical, soil stratification or aggregation, and the soil moisture content.

13.6.3 Design Issues for Vapor Extraction Systems

Site stratigraphy, site hydrogeology, extent of spill, the chemical and physical characteristics of contaminants are key issues to be addressed prior to choosing SVE as a candidate method for site remediation. Once SVE has been selected as a possible strategy for remediation, the following procedure should be adopted for better design of SVE systems.

1. Run air permeability tests to determine site permeability.
2. Run a feasibility analysis using a screening tool to determine whether SVE is an appropriate remedial strategy for the site.
3. Run pilot tests at the site to determine the physical parameters and confirm the accuracy of the feasibility analysis.
4. Design and test the SVE system using more sophisticated modeling tools.

System design can provide data about the required number of wells, well spacing and locations, air flow rates, applied vacuum, vapor concentrations, amount of mass removed, time required for cleanup, and the residual mass remaining in soil. A detailed case study of SVE for Hill AFB is presented in Section 13.9.3.

13.6.4 Air Sparging and Hydrogen Injection

Air sparging is a relatively new technology that has been implemented at numerous sites around the country. The technique involves the forced entry of air into sparge wells or trenches under sufficient pressure to form bubbles in ground water. The bubbles sweep through the aquifer (1) to strip volatile organics from the soluble phase and from any NAPLs present along the path of bubbles, (2) to add oxygen to the water to spur the *in situ* bioremediation process, and (3) in some cases, to establish large circulation cells to move contaminated water to extraction wells. After bubbles make their way up to the unsaturated zone, an SVE system is often used to remove vapors for treatment prior to release to the atmosphere.
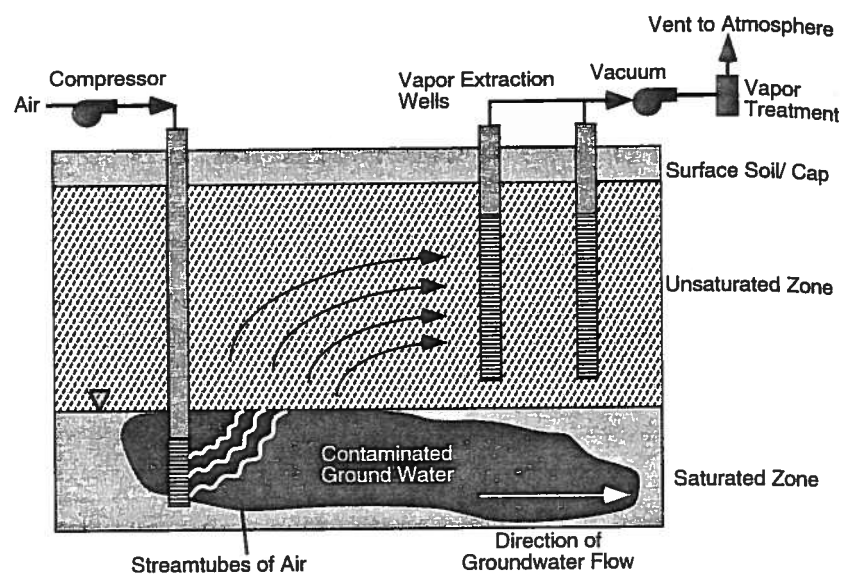
Figure 13.13 Process diagram for air sparging. Source: NRC, 1994.

It was originally assumed that sparged air would travel as bubbles dispersed throughout the contaminated zone, and would provide efficient mass transfer from the NAPL phase into the air. Recent studies indicate that air travels in air stream tubes or filaments (Ahlfield et al., 1993; Goodman et al., 1993). Current indications are that air sparging shows more promise for petroleum sites with LNAPL source zones, where the air brings oxygen that permits aerobic biodegradation to occur (Pankow and Cherry, 1996). Air sparging is more effective at treating dissolved hydrocarbon plumes than for treating source areas (Bass and Brown, 1996), and has been used as an alternative to conventional pump and treat systems (Figure 13.13).

In-situ bioremediation via direct hydrogen addition is an emerging technology designed to enhance the biodegradation of chlorinated solvents (PCE, TCE, and 1,2-DCE) in ground water and in the unsaturated zone. Based on the results of recent research, the role of hydrogen as an electron donor is now widely recognized as the key factor governing the biologically-mediated dechlorination of these common environmental contaminants (Gossett and Zinder, 1996; Carr and Hughes, 1998). Hydrogen can be delivered directly to the subsurface by a variety of means, such as dissolved in a ground water pump-and-reinjection scheme, low volume pulsed biosparging, injection of chemical reactants that produce hydrogen, electrolysis, and other methods (Fisher et al., 1998, Hughes et al., 1997).

Direct hydrogen addition is an extension of natural attenuation processes that occur at many chlorinated solvents sites, that is, hydrogen-based dechlorination where the hydrogen results from naturally-occurring fermentation substrates. The stoichiometry of the reaction (1 mg/L of hydrogen has the potential to dechlorinate 23 mg/L of PCE) and hydrogen's low cost are two strengths of this approach. This process is now being tested at several field sites around the country as part of an Air Force technology development program.

13.7 REMEDIATING NAPL SITES

13.7.1 Proven Technologies for Removing NAPLS

Chapter 11 indicated the difficulties of characterizing and remediating sites with NAPLs in the subsurface. It is now recognized that NAPLs can create a source of contamination for years or decades due to the slow dissolution process. Standard remediation methods of the eighties, such as pump and treat, only addressed the soluble part of the plume, and did little for control of NAPL source areas. A remediation technology is defined as "proven" if (1) it is commonly practiced in the field and (2) if sufficient design methodologies are available so that practitioners can apply the technology and obtain the predicted system response. An emerging technology, on the other hand, is one where some bench-scale or field-scale tests have been conducted, but detailed design procedures are not generally available. This section describes the proven approaches for removal of NAPLs from the subsurface, and Section 13.8 describes some of the more successful emerging methods for site remediation.

13.7.2 General Remediation Strategy for NAPL Sites

As restoration of ground water to drinking water standards may prove infeasible at many NAPL-affected sites, alternative approaches to managing NAPL problems should be considered. The following general management strategy divides a NAPL site into three zones:

1. dissolved phase zone
2. confirmed free-phase NAPL zone
3. potential NAPL zone (either free-phase or residual NAPL)

As shown in Figure 13.14, this classification system is based on the confirmed or suspected presence of NAPL in the aquifer. Areas where site data indicate a low probability of NAPL in the aquifer would be designated as "dissolved phase zones" where conventional remediation technologies could be applied. At many sites, the applicable cleanup standards could be at or near current drinking water standards, and pump-and-treat systems can be used to reach the required concentration levels, assuming that some controls are implemented for the source area.
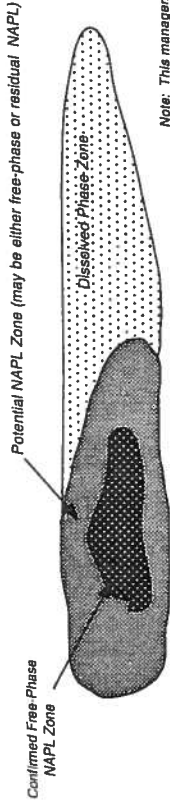
Note: This management strategy may not be applicable to all hydrogeologic settings, such as NAPL sites located over fractured metamorphic or igneous rock.

Remediation Zones at a NAPL Site

Remediation Zone	Characteristics	Remediation Goal	Remediation Technology	Potential Remediation Standard
Dissolved Phase Zone	• Low dissolved phase concentrations • No NAPL detected in monitoring wells or soil cores • Downgradient of potential NAPL Zone	Groundwater restoration of leading edge of plume.	Groundwater pump and treat.	Existing groundwater remediation standards. For example: CERCLA: Based on Risk Assessment RCRA: MCL, Background, or ACL.
Confirmed Free-Phase NAPL Zone	• NAPL observed in monitoring wells or Free-phase NAPL observed in soil cores	Prevent NAPL Migration Contain dissolved plume	Use pumping/injection wells to: • Remove free-phase NAPL • Remove potentially mobile NAPL (residual NAPL that could be mobilized under natural flow conditions at site) Operate pumping wells for long-term hydraulic containment of NAPL dissolution products	A hydraulic gradient, at least 2 - 4 times greater than highest expected natural gradient at site, must be imposed on the site until: • No further NAPL accumulation in monitoring wells is observed and • NAPL recovery rate from extraction wells reaches asymptotic response. Operate pumping wells indefinitely (until groundwater reaches current clean-up standards)
Potential NAPL Zone (may be either residual or free-phase NAPL)	• Located near potential NAPL entry points or • High dissolved phase concentrations or • NAPL observed in soil cores			

Figure 13.14 General Management Strategy for NAPL Sites

In areas where the presence of NAPL is confirmed, due to the presence of free-phase NAPL in monitoring wells, a containment strategy can be applied in place of conventional ground water remediation standards. Containment of NAPL can be achieved by imposing a relatively high hydraulic gradient across the site to remove free-phase material and to ensure that residual NAPL will remain immobilized under natural flow conditions. Some of the containment and barrier methods described in Section 13.3 could then be implemented. Operation of such a system could require a longer-term financial commitment than is currently afforded many sites.

As the presence of NAPL is difficult to confirm in the subsurface, a third zone has been defined for areas where residual and/or free-phase NAPL may be present. For example, the presence of relatively high concentrations (i.e., 1% of solubility) of dissolved organics or proximity to NAPL entry points would be sufficient to designate an area as a potential NAPL zone. The remediation approach for these areas would be identical to confirmed NAPL zones: long-term containment for NAPL and pumping to control off site migration of dissolved constituents.

The remediation goals outlined above can be achieved with existing, proven technologies (e.g., barriers and ground water recovery wells) to provide a significant level of protection to both human and environmental receptors. Implementation of this remediation approach requires modification of current regulatory policies regarding cleanup standards and financial assurance for corrective action programs. Note that the containment period for LNAPL sites is usually shorter than for the containment of DNAPL sites. This is due to more rapid biodegradation of fuel hydrocarbons compared to chlorinated organics, and the relative ease of dealing with floating product near the water table compared to removing DNAPLs deeper in the aquifer (See Figure 13.5 versus Figure 13.6).

13.7.3 Pumping to Remove Continuous-Phase LNAPLs

LNAPLs can be removed from the subsurface by pumping recovery wells screened at the water table or by pumping an interceptor system such as a french drain or interceptor trench (Figure 13.5). The most common approach for maximizing the recovery of LNAPL is to pump the layer relatively slowly in order to keep the LNAPL mass as a continuous flowing mass (Charbeneau et al., 1989; Abdul, 1992). Water pumping is carefully controlled to avoid smearing the LNAPL layer.

Two alternative approaches can be employed: pumping the combined ground water/LNAPL mixture with a single pump, or using two separate pumps working under a control system in order to remove the aqueous phase and nonaqueous phase separately (Blake and Lewis, 1982). For systems with significant accumulations of LNAPL, a two-pump system will provide a more efficient remediation approach. A control system comprised of two water/LNAPL interface probes is used to operate dedicated LNAPL and ground water pumps. The first interface probe is set below the intake of the LNAPL pump and keeps the LNAPL pump operating as long as there is hydrocarbon near the pump intake. The lower interface probe turns the ground water pump off if hydrocarbon level approaches the intake, and on
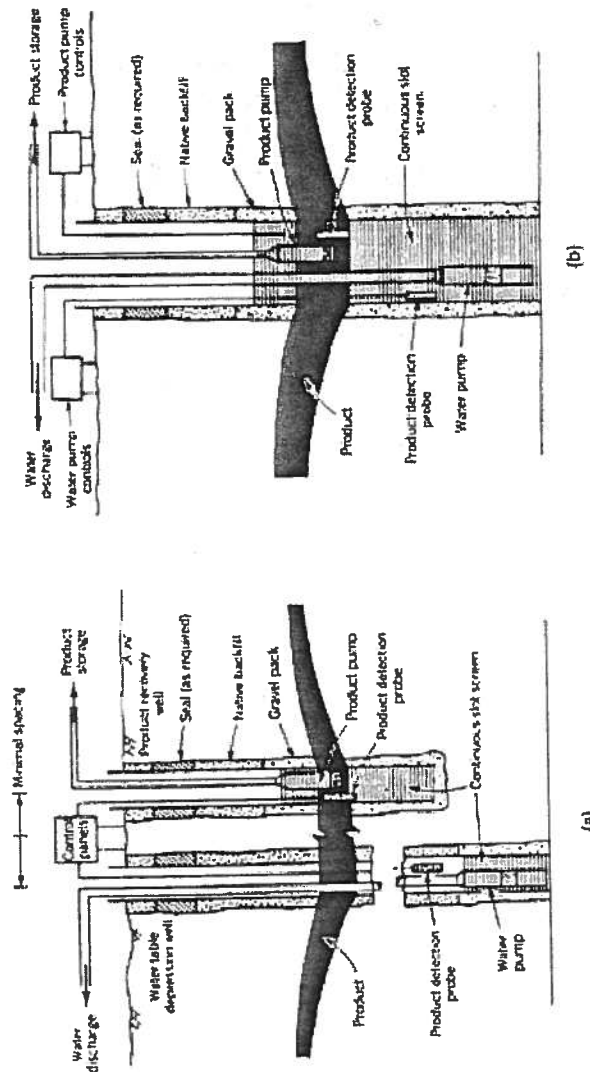
Figure 13.15 Examples of NAPL recovery systems. (a) Two-well, two-pump system. (b) One-well, two-pump system. Source: Blake and Lewis (1982).

again when there is sufficient water above the pump intake (Figure 13.15). An alternate design uses floating "skimmer" pumps and floating interface probes that move up and down on the floating hydrocarbon layer.

Once the LNAPL source area has been controlled, then natural attenuation mechanisms will usually dominate the rest of the plume and the source area, and will limit the overall extent of migration of a typical fuel hydrocarbon plume. Several recent reports from California and Texas discussed in Chapter 12, evaluated hundreds of leaking underground storage tank sites and found the average length of plume to be on the order of 200 ft in the subsurface. This limitation is largely related to the natural processes of dispersion and biodegradation acting on typical hydrocarbon plumes.

13.7.4 Pumping to Remove Continuous-Phase DNAPL

In practice, DNAPL removal is much more difficult than LNAPL removal. Source zones may have buried drums, sludge, or other pipe leaks located primarily in the shallow unsaturated zone, as well as DNAPL below the water table. The DNAPL pools and lenses are much harder to locate and the installation of recovery wells increases the risk of mobilizing DNAPL accumulations (Figure 13.6). Limited field experience indicates that some DNAPL can be mobilized by pumping, and that pumping ground water from the aquifer above the DNAPL recovery will increase yields by creating a water drive for the DNAPL pool. Trenches have been used with some success at a few sites where bedrock forms a clear vertical boundary. A detailed case study is presented in Section 13.9. Emerging and advanced remediation technologies described in Section 13.8 will be required to affect any real improvement for sites contaminated with DNAPL, since these sites are so difficult to cleanup (Pankow and Cherry, 1996).

Fractured sites containing DNAPL present an even more complex problem, since the pure phase product can penetrate deeply into fractures, creating source zones that are impossible to find or clean up in a reasonable time period. (see Figure11.11). A few fractured sites have been addressed using trench technology with some success, since a trench can potentially cut across lateral fractures and cause DNAPL to flow out and be captured by a pumping system.

13.7.5 Bioventing

While soil vapor extraction (SVE) is primarily directed at remediation of unsaturated soils, it can be adapted to the removal of volatile hydrocarbons in LNAPLs from the subsurface. In the case of bioventing just above the water table, the SVE system is operated to deliver oxygen at a slow flow rate to the indigenous microbes, thereby promoting degradation of organics in the pore space. The advantage of bioventing compared to enhanced bioremediation is that oxygen can be more easily transported in air (280mg/L O_2 in air) than in water (10 to 40 mg/L O_2 in water).

First, there will be some transport of volatile organics from contaminated ground water into an air stream being forced across the water table by a soil vapor extraction system.

However, a much more important process occurs when the water table is depressed, for example, by a ground water pumping system, thereby exposing the former saturated zone to the effects of an SVE system. In most cases, such a system will be many times more effective at removing volatile hydrocarbons when compared to conventional ground water pumping systems removing dissolved hydrocarbons. Key design parameters for these applications are presented in Section 13.6.

13.7.6 Low Permeability Enclosures

A low permeability enclosure around a DNAPL source zone will divert much of the ground water flow around the enclosure. Many types of engineered barrier technologies are available and are described elsewhere (Pankow and Cherry, 1996). Each type has its own advantages and disadvantages, depending on the underlying geology of a site, and the relative complexity of the system. Keyed and hanging enclosures are both possible, where the first has the wall set into an aquitard at the bottom of the aquifer, and the second has the wall set deeper than the DNAPL zone (Figure 13.16). Often pumping inside the enclosure is used to cause upward flow at the bottom of the enclosure and to maintain hydraulic control from outside influences.

Figure 13.17 shows a plume of dissolved contamination on the downstream side of an enclosure, for the case of no pumping. Even with pumping inside the enclosure, some contamination may diffuse through the wall and migrate downstream. Enclosures around source zones need not provide zero outward flux in order to effectively isolate the source, but rather the flux must be limited to meet regulatory standards at a specified location downstream. The enclosure also provides a separation of the source zone so that DNAPL removal or soil flushing with surfactants or co-solvents can take place inside the enclosure (see Section 13.9).

13.8 EMERGING REMEDIATION TECHNOLOGIES

13.8.1 Funnel and Gate Systems

The funnel and gate system for the *in situ* treatment of contaminant plumes consists of low permeability cutoff walls, with gaps (gate) that contain reactors that remove contaminants by abiotic or biological processes (Starr and Cherry, 1993). The reactive zone can also be designed to volatilize contaminants (Pankow et al., 1993). These systems have advanced rapidly from pilot scale trials to full-scale systems. Figure 13.18 shows a typical schematic in plan and profile for an aquifer that has a well-defined aquitard at depth. The treatment and gate designs are still the subject of research and demonstrations, and final designs are still being tested for particular geological settings and specific contaminants. Only a limited number of funnel and gate systems have actually been installed.
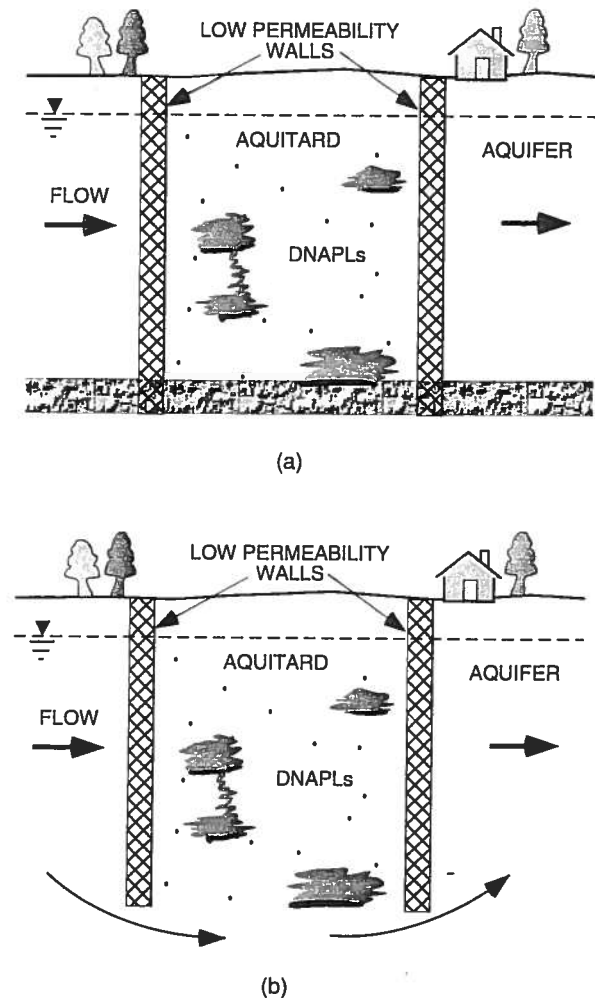
(a)

(b)

Figure 13.16 Cutoff wall enclosure: (a) keyed enclosure-groundwater is diverted laterally around the enclosure; and (b) hanging enclosure-groundwater is diverted laterally and vertically (downward) around the enclosure. Source: Pankow and Cherry, 1996.
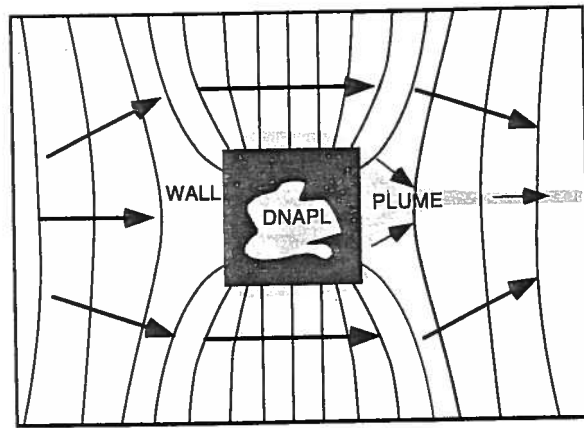
Figure 13.17 A plume of dissolved contamination downgradient of a source-zone enclosure. Dissolved contaminants diffuse through the walls to cause the plume. Source: Devlin and Parker, 1994.

A number of in situ reactive curtains are available for use in funnel and gate systems. These include in situ curtains that modify pH or Eh conditions, dissolve and cause precipitation of a mineral phase, remove materials from solution by sorption, supply nutrients that impact biodegradation, and remove materials via air sparging.

Plume management using in situ reactors has several advantages over traditional pump and treat systems. Most reactors do not require a continuous input of energy and will have fewer mechanical problems than a pumping system. Also, the reactor can be changed out as its capacity is consumed. Finally, discharge of treated water is unnecessary, which creates many regulatory problems with water disposal from pump and treat (Starr and Cherry, 1994).

A funnel and gate system includes cutoff walls and the gate. Issues such as the number of gates, the orientation with ground water flow, and the angle between the sides of the funnel are all important for design. The effect of the gate is related to the residence time and the reaction rate, which in turn depend on gate size and discharge. A number of these variables were analyzed in detail by Starr and Cherry (1994), where they simulated the steady state flow results of various geometries in a homogeneous setting typical of many unconfined sand aquifers.

Two conflicting factors are important in the design of a funnel and gate system. The discharge through a gate should be maximized so that the capture zone (Section 13.4.1) is as wide as possible, but the residence time for treatment should be as long as possible in the gate. These conflicting objectives must be balanced in the overall design in order to maintain high levels of attenuation. Effects of funnel width, gate width, gate hydraulic conductivity, funnel apex angle, orientation to regional flow direction, and retention time are all important
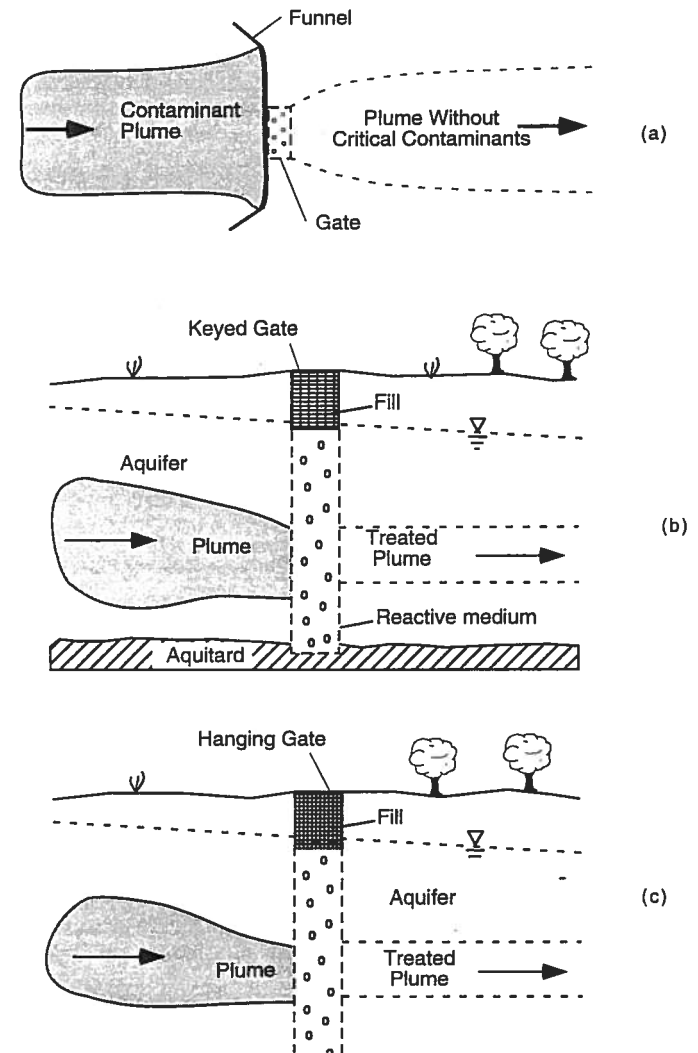
Figure 13.18 Schematic illustration of a funnel-and-gate system: (a) plan view; (b) cross-sectional view, keyed gate; and (C) cross-sectional view, hanging gate. Source: Pankow and Cherry, 1996.

aspects of the design. Starr and Cherry (1994) found that the width of the capture zone is proportional to the discharge through the gate, and the discharge can be increased by increasing the width, length, and K of the gate, or increasing the width of the funnel. Finally, residence times can be increased by making the gates longer in the direction of flow.

Treatment curtains have been recently suggested for the treatment of chlorinated solvents. Gilham and O'Hannesin (1994) describe some interesting laboratory and field studies of zero-valence iron. A substantial rate of abiotic degradation was observed for most of the chlorinated compounds tested, with iron serving as a source of electrons, although the actual degradation mechanisms are uncertain. This method may have limitations for sites with deep plumes or in fractured rock, leaving pump and treat as the only viable option for source or plume control.

13.8.2 Soil Flushing Enhancements

Enhanced pump and treat technologies include circulating steam or water containing chemical additives through a NAPL zone. Several agents can be introduced into a source zone in order to increase the mobility of NAPLs, or to increase the solubility of the NAPL or its dissolution products. The flow of water and chemicals is from injection wells or galleries to withdrawal wells where fluid is pumped into treatment units at the surface. Surfactants and cosolvents, such as ethanol or methanol, are the main types of additive chemicals used for remediation of NAPL sites (Brusseau et al., 1999). Figure 13.19 depicts a typical schematic for an enhanced soil flushing system contained in a NAPL zone at a field site.
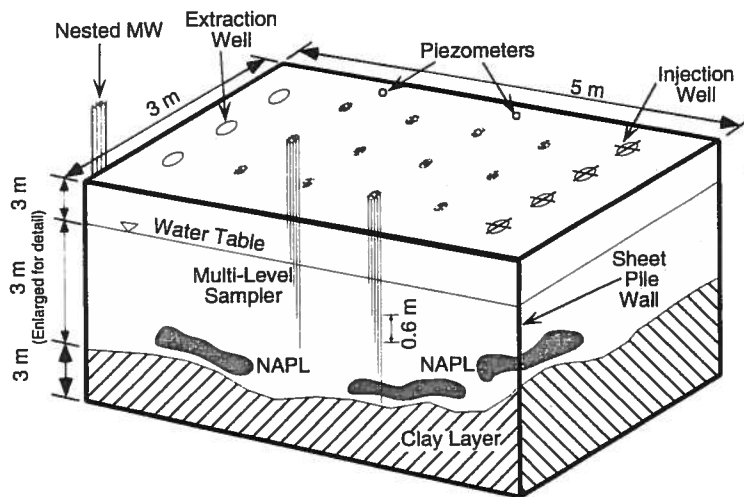

Figure 13.19 Soil Flushing, Hill AFB.

Although several researchers have reported promising results when using surfactants in laboratory trials, using surfactants to restore aquifers to drinking water conditions may be much less successful because of the presence of heterogeneities and low permeability zones in the subsurface (US EPA, 1992; Mackay and Cherry, 1989). A main impediment to the success of the process is inadequate contact of the flushing fluid with DNAPL, which might be trapped in low permeability zones. Another potential drawback to the use of these agents at DNAPL waste sites is that some of them rely on reducing the interfacial tension between the nonaqueous and aqueous phase. This can increase the potential that a residual DNAPL will mobilize downward in the saturated zone, thereby aggravating the remediation problem at a site. Finally, complete capture of the contaminated water and additives must be assured at the withdrawal wells.

Soil flushing still provides one of the only methods by which NAPLs can be solubilized or mobilized for source control. A recent text presents extensive details on the method along with results of numerous studies completed recently on the implementation and costing of surfactants and cosolvents for NAPL remediation (Lowe et al., 1999). These methods offer some promise if source zones are small and can be carefully enclosed with a barrier system to minimize any off site effects. Detailed studies of soil flushing technologies have recently been completed at Hill Air Force Base in Utah, and are described in a case study in Section 13.9.4.

Surfactant-enhanced subsurface remediation is an emerging technology for enhancing pump-and-treat remediation at complex sites. This enhancement can be due to micellar-enhanced aqueous concentrations or to reducing interfacial tensions, and ultra-high solubilization, realized along with middle phase microemulsion systems. This section briefly discusses fundamental surfactant factors critical to successful implementation of this technology (Sabatini et al., 1995; 1999).

Surfactants (surface-active-agents), otherwise known as soaps or detergents, are widely known for their cleansing characteristics, and for their foaming characteristics, which is a result of their accumulation at interfaces. Surfactants are ubiquitous, showing up in our shampoo, toothpaste, mouthwash, whipped cream, mayonnaise, and even in our cell walls. Surfactants are classified by their charge (cationic, anionic, nonionic), their origin (biosurfactants from plant or microbial production versus synthetic surfactants), and their regulatory status (direct or indirect food additive status, acceptable for discharge to wastewater treatment systems or for use in pesticide formulations). Surfactants are also characterized by their hydrophilic-lipophilic balance (HLB); surfactants with a high HLB value are water soluble while oil soluble surfactants have low HLB values.

Above a critical concentration surfactant monomers self-aggregate into micelles, and the surfactant concentration above which micelles form is known as the critical micelle concentration (CMC). The hydrophilic micelle exterior makes them highly soluble in water. Having a hydrophobic (oil like) interior, micelles are sometimes described as dispersed oil drops. When surfactant concentrations exceed the CMC, the incremental surfactant goes almost totally to formation of additional micelles. Surfactant enhanced subsurface remediation is often categorized into two systems; solubilization and mobilization.

Solubilization results from contaminant partitioning into the oil-like core of the micelle, thereby effectively increasing the aqueous solubility of the contaminant. With increasing solubility, the number of water flushes required to achieve a treatment goal decreases. At low surfactant concentrations (sub-CMC), the contaminant is present at its water solubility. Just above the CMC the solubility enhancement is minor, but increases as the surfactant concentration continues to increase above the CMC. The higher the surfactant concentration is above the CMC, the greater the number of micelles and thus the greater the solubility enhancement. Thus, to dramatically improve contaminant extraction, one should operate significantly above the CMC (an order of magnitude or more).

Mobilization refers to bulk oil displacement from the trapped residual oil (as opposed to simply enhancing the solubility). The displacement occurs due to significant reductions in interfacial tension between the NAPL and water phases. It is this interfacial tension that is largely responsible for the NAPL trapping (residual saturation) in the porous media. Significant reductions in the oil-water interfacial tension virtually eliminates the capillary forces which cause the oil to be trapped, thereby allowing the oil to readily flush out with the water. Thus, mobilization of the NAPL is maximized when ultra-low interfacial tensions are achieved.

The minimum interfacial tension occurs in middle phase microemulsion systems. By adjusting the surfactant system, it is possible to transition from normal micelles (aqueous phase), to middle phase microemulsions, to reverse micelles (oil phase inverted micelles). Careful system design will minimize the formation of mesophases in the transition region (e.g., liquid crystals), which may occur instead of the desired middle phase system. Traditionally alcohols have served this purpose while more recently hydrotropes (e.g., naphthalene sulfonates) and cosurfactants (e.g., a second surfactant) have been evaluated. Recent studies in surfactant-enhanced environmental remediation, along with prior research on surfactant enhanced oil recovery have helped advance environmental remediation technologies; (Sabatini et al., 1995; 1999).

Surfactant-enhanced subsurface remediation must be economically viable if it is to be widely implemented. In looking at two cases, Krebs-Yuill et al. (1995) determined that surfactant-enhanced remediation can be more economical than conventional pump-and-treat systems. The two most important conclusions were: (1) surfactant capital costs constitute the single largest cost in a surfactant-enhanced remediation process; and (2) decontamination of the surfactant-stream and surfactant reuse is critical. A subsequent economic study evaluated surfactant-enhanced pump-and-treat for residual zones of two acres or less (Krebbs-Yuill et al., 1996). It was shown that surfactant-enhanced remediation could be economically viable for all sites of less than one acre in size, and for 1-acre sites with residual saturation of 5% or less. For 1/4-acre sites with residual saturations of 5% or less, the cost of solubilization remediation was only 40% of the cost of pump-and-treat.

Given that surfactant reuse is crucial to the economic viability of the system, contaminant-surfactant separation and surfactant reuse needs to be a key consideration in the surfactant selection process. The ultimate goal is a surfactant system that is highly efficient in extracting the contaminant, has favorable phase behavior in the subsurface, and can efficiently be decontaminated and reused. Failure in any of these areas can render the system

uneconomical and/or infeasible, illustrating the importance of an integrated design approach. More details can be found in Lowe et al., (1999).

Cosolvents generally rely on a mixture of water and alcohols, such as ethanol and pentanol, to enhance solubilization of NAPL contaminants. In this regard, alcohols are extremely miscible, and may partition into both water and NAPL phases, and create a mixture that enhances solubility of the contaminants present at a site. Some of the most successful cosolvent flushing experiments were completed at Hill AFB in Utah, funded under SERDP/EPA, and are reported in Sillan et al. (1998) and Brusseau et al. (1999). The alcohol mixtures are used to increase the solubility of NAPL compounds so that circulation of the water/chemical mixture through the contaminated zone will remove mass more quickly than conventional pump and treat systems using water alone. Rao et al. (1997) employed a mixture of 70% ethanol, 12% n-pentanol, and 18% water to remove a multicomponent LNAPL from the Hill AFB site. Section 13.9.4 presents more details on the soil flushing experiments performed at Hill AFB in nine side-by-side comparison tests of various remediation technologies.

13.8.3 Thermally Enhanced Recovery

The use of heat to increase the mobility of NAPLs in the subsurface has been established in enhanced oil recovery (EOR) used in the petroleum industry. Specific technologies include hot water flooding or the addition of steam to reduce NAPL density and NAPL viscosity. Use of steam will also condense volatile NAPLs in front of the steam front, thereby increasing NAPL saturation and mobility (EPA, 1992). Although these technologies have removed significant amounts of NAPL in both laboratory and field pilot tests, complete removal was not achieved. Steam injection was one of the technologies tested at the Hill AFB OU1 field site, with mixed results.

13.8.4 AATDF Description

The DoD Advanced Applied Technology Demonstration Facility for Environmental Technologies (AATDF) was established by the U.S. Department of Defense (DoD) following a national competition. The program was initiated on May 1, 1993, when the DoD awarded a $19.3 million grant to a university consortium of environmental research centers led by Rice University and headed by Dr. C. Herb Ward.

The mission of the DoD/AATDF was to enhance the development of innovative technologies for the DoD by bridging the gap between academic research and proven technologies. This was accomplished by selecting the most appropriate peer-reviewed technologies for quantitative demonstrations at DoD sites.

A consortium approach was selected to implement the DoD/AATDF program. The consortium represented a unique mixture of research and engineering talent and state-of-the-science and technology in the hazardous waste remediation field. Members of the consortium included: Stanford University, University of Texas, Rice University, Lamar University, University of Waterloo and Louisiana State University. The U.S. Army Engineer Waterways

Experiment Station managed the AATDF Grant for the DoD. The DoD/AATDF was supported by five state-of-the-art consulting engineering firms: Remediation Technologies, Inc.; Battelle Memorial Institute; Geo Trans., Inc.; Arcadis Geraghty and Miller, Inc.; and Groundwater Services, Inc., along with advisory groups from the DoD, industry, and commercialization interests.

To find the best environmental remediation ideas for further demonstration, a broadly disseminated announcement was sent out to researchers in academia, government, environmental engineering and consulting companies and industry. A total of 170 preproposals were received. A peer review process narrowed the number to 40. Requests were made for full proposals. Further peer review selection resulted in 12 projects for field demonstrations. The technologies chosen targeted the DoD's main problems of soil and ground water remediation. They were aimed at providing more cost-effective solutions to difficult problems, preferably using *in situ* remediation technologies.

The results of the AATDF are being developed as a series of ten monographs (Lewis Publishers) including:

- Surfactants and cosolvents for NAPL Remediation: A Technology Practices Manual (Lowe et al., 1999)
- Sequenced Reactive Barriers for Ground water Remediation
- Modular Remediation Testing System
- Phytoremediation of Hydrocarbon-Contaminated Soil
- Steam and Electro-Heating Remediation of Tight Soils
- Soil Vapor Extraction Using Radio Frequency Heating: Resource Manual and Technology Demonstration
- Laser-Induced Fluorescence for Subsurface Contaminant Monitoring
- Reuse of Surfactants and Cosolvents for NAPL Remediation
- Remediation of Firing-Range Impact Berms
- NAPL Removal: Surfactants, Foams, and Microemulsions

13.8.5 Practicality of Containing NAPLs

Containment alternatives for NAPL sites must address several potential contaminant migration pathways. First, the migration of mobile NAPL must be stopped by (1) pumping continuous-phase NAPL until it is all trapped in the aquifer as a residual phase; (2) operation of some type of NAPL interception system, such as a NAPL interceptor trench (Figure 13.5); and (3) constructing some type of physical barrier, such as a slurry wall (Figure 13.2). Second, the vertical and lateral migration of the dissolution products in the aquifer must be curtailed using hydraulic controls or physical barriers. In some cases, natural attenuation (from dispersion, dilution, chemical degradation, and biological degradation) will stop migra-

tion of dissolved contaminants, which may be sufficient to ensure that potential receptors are protected.

At some sites facing long containment periods, the use of physical barriers such as slurry walls or treatment curtains around source areas will be cost-effective additions to the overall remediation scheme. Containment options not only minimize the migration from NAPL source areas, but they provide valuable time during which other more efficient technologies (i.e., soil flushing with surfactants) may be developed and implemented within the source area. A number of case studies showing the use of selected remediation methods are presented below. These examples represent only a limited number of possibilities, and the reader is referred to the voluminous literature that exists on the topic of ground water remediation.

13.9 CASE STUDIES OF REMEDIATION

13.9.1 Case 1: The Pump and Treat System at U.S. Air Force Plant Number 44, Tucson, Arizona — Modeling Study

Trichloroethene (TCE), 1,1-dichloroethene (DCE), and chromium have been detected in the ground water beneath the U.S Air Force Plant No. 44 site in Tucson, Arizona. Activities at this facility include development, manufacturing, testing and maintenance of missile systems from 1952 until the present. The contaminated ground water is in an extensive alluvial aquifer that Tucson uses as its principal aquifer. The Tucson area is one of the largest metropolitan areas in the country that is totally dependent on ground water for drinking water supplies, and the TCE contamination is viewed as a threat to the integrity of the water supply system. The site is listed on the National Priority List and is known as the Tucson Airport Area Superfund Site.

In 1986, prior to the pump and treat remediation system begun at the site, the area of TCE contamination was approximately 5 mi long and 1.6 mi wide. Contours of the dissolved TCE plume from measurements taken in 1986 and are shown in Figure 13.20. The maximum measured TCE concentration in 1986 was 2.7 mg/L, although concentrations as high as 15.9 ppm have been observed. The cleanup standard for TCE in this case is the drinking water standard of 5 µg/L.

TCE is a halogenated aliphatic organic compound that is typically used as an industrial cleaning solvent. In addition, reductive dehalogenation through natural biodegradation may result in production of vinyl chloride, which is a known carcinogen. TCE is denser than water, has low viscosity, is sparingly soluble in water and is fairly volatile. It has a relatively low octanol-water partition coefficient, which means that its movement in the aqueous phase is not retarded to a great degree by the organic materials in the aquifer.

Site Characterization. Results of a subsurface investigation indicate that the subsurface can be divided into four hydrogeologic units:
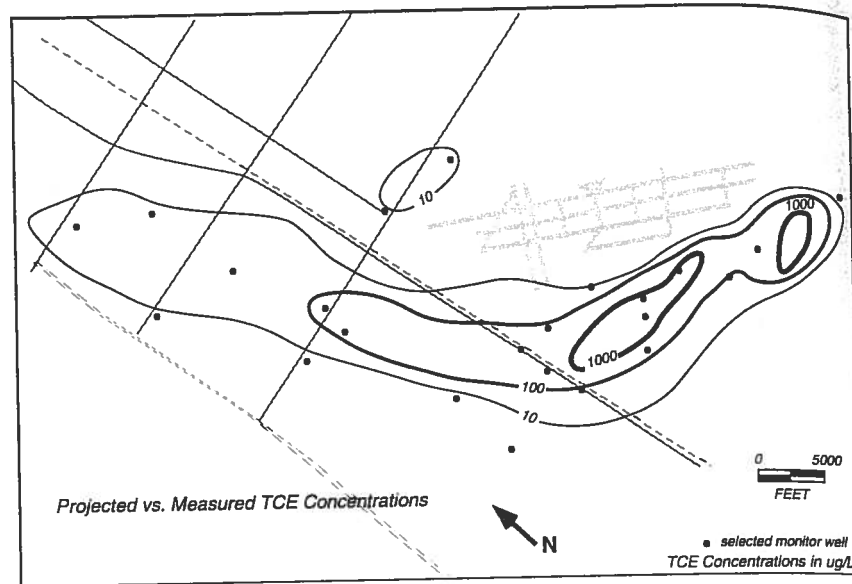
Figure 13.20 TCE Plume, Hughes Plant 44; 1986.

1. An unsaturated zone that extends from the ground surface to the water table, which is at a depth of 110 ft to 130 ft

2. An upper zone extending to a depth of 180 ft to 220 ft

3. An aquitard consisting of 100 ft to 150 ft of low permeability clay

4. A lower zone of unknown thickness

The lower portion of the unsaturated zone consists of a laterally extensive layer of relatively low permeability perching clay, which is 20 ft to 40 ft thick and which partially confines the upper aquifer. The unsaturated, upper and lower zones consist of layers of relatively low conductivity clays and sandy clays, alternating with quite permeable sand and gravel units.

Hydraulic conductivity measurements were obtained in 12 locations in the immediate vicinity of current surface impoundments from pump test data. These data indicate that hydraulic conductivity ranges from 1.5×10^{-4} ft/s to 3.1×10^{-3} ft/s for the upper zone aquifer. For clean sands and gravels, porosity measurements of 26% to 34% have been obtained for this formation. The background hydraulic gradient, calculated from water table elevation data,

is estimated to be 0.006 in the north-northwesterly direction. Ground water velocity at the site ranges from 250 to 800 ft/yr, based on an average porosity value of 25%.

Potential sources of subsurface contamination at the site include pits, ponds, trenches, and drainage ditches in which on-site disposal of solvents, wastewater, and sludge is believed to have occurred from approximately 1952 through 1977. Wastes generated during this time period include TCE, paint sludge, acids, cyanides, and alcohols. For the purpose of demonstrating pump and treat remediation in this case study, TCE is considered the contaminant of interest.

Remediation by Pump and Treat. A ground water pump and treat remediation system began operation at the site in April 1987. The pump and treat system consists of 17 extraction wells and 13 recharge wells, and the above-ground treatment plant, which utilizes ion exchange followed by air stripping, vapor phase activated carbon and pressure sand filtration. As one of the largest pump and treat systems in the United States, it was designed to treat 5000 gpm of extracted ground water. Water level elevation and contamination concentration data for the approximately 40 monitoring wells are collected monthly. The location of the extraction, recharge, and monitoring wells are shown in Figure 13.21.

Monthly concentration measurements taken at the extraction and monitoring wells are used to evaluate the remediation process with respect to TCE removal. Measured TCE plumes were contoured yearly, and as can be seen from Figure 13.22, the plume area does
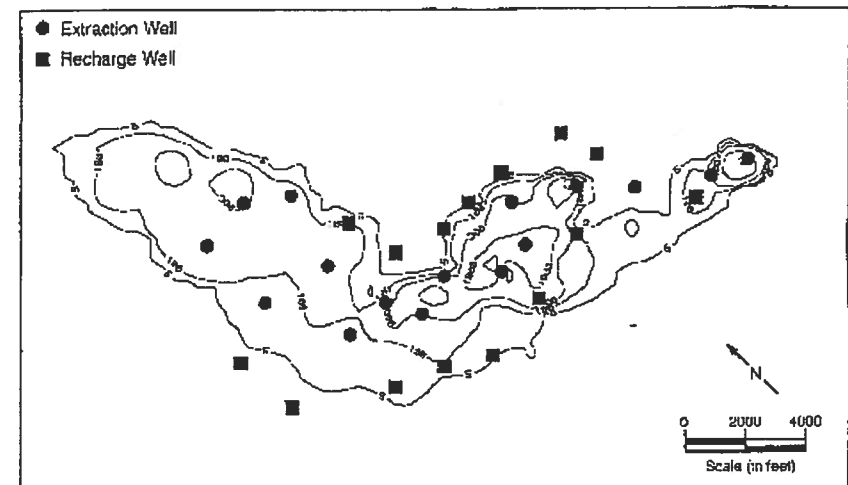

Figure 13.21 Locations of recharge and extraction wells at the Plant 44 site. Source: Burgess, 1993.

not appear to shrink a great deal through the five-year pumping period. However, concentrations do decrease through this period. Dissolved mass of the contaminated plumes may be calculated by integrating concentration contours across the area of the plume, and adjusting for porosity (Figure 13.22). The total TCE mass removed via pumping is approximately 6000 kg over 5 years. The concentration of dissolved TCE in the extracted ground water decreases during remediation, particularly in those wells with initially high TCE concentrations. In the majority of cases, the TCE concentration appears to level out between 3 and 5 years.

Modeling of the Pump and Treat System. The pump and treat system, as it applies to the Tucson site, was evaluated further through modeling with the BIOPLUME II model for transport in the aqueous phase (Burgess et al., 1993). All advection and dispersion were assumed to take place in the high permeability sand and gravel layers, which were assumed continuous in the upper zone. Based on the site characteristics and modeling results, hydraulic conductivities were found to range from 2.39×10^{-4} to 5.55×10^{-3} ft/s.

The initial distribution of potentiometric ground water elevation was determined by contouring water table elevation measurements from December 1986. The model was calibrated by varying the hydraulic conductivity as well as the model boundaries in order to obtain the water table as it existed prior to extraction. Zones of conductivity were chosen based on the shape of the water table and matched the initial field measurements well. The root mean squared (RMS) error of the modeled versus the actual potentiometric head distribution was used to determine the deviation of the simulated run from the actual data. For the flow calibration, the calculated RMS error was 4.25% (a value of less than 10-15% is desirable). The model was validated by modeling the potentiometric elevation after approximately five years of pumping and injection. The RMS error for the simulation versus actual December 1991 measurements was 7.94%, based on comparison of values at 68 locations.

The TCE plume as it appeared in December 1986 is shown as Figure 13.20. The objective of the transport calibration was to match the TCE plume as it appeared in 1986 prior to remediation startup using source locations, flowrates, and TCE concentrations. Source infiltration rates used varied from 0.001 to 0.003 cfs, and TCE concentrations of the infiltrating water varied from 400 to 10,000 ppb. The duration of source infiltration was assumed to be 20 years. Calibration is determined based on comparison of TCE concentrations at monitoring locations as well as plume area and dissolved mass. The simulated plume compares well visually with the 1986 plume. The chemical mass balance (CMB) error for the simulation, which is calculated based upon the difference between the change in dissolved mass inflow minus outflow, is 2.26% after taking into account the mass that moves beyond the model boundary during simulation. (A CMB error of < 5% is desirable).

Results of the Tucson Model. To validate the transport calibration, the December 1986 plume was modeled using the pumping and injection pattern as in the actual remediation operation. All the other aquifer parameters remained the same as in the calibration to pumped water table with the exception of the addition of the initial TCE concentration array.
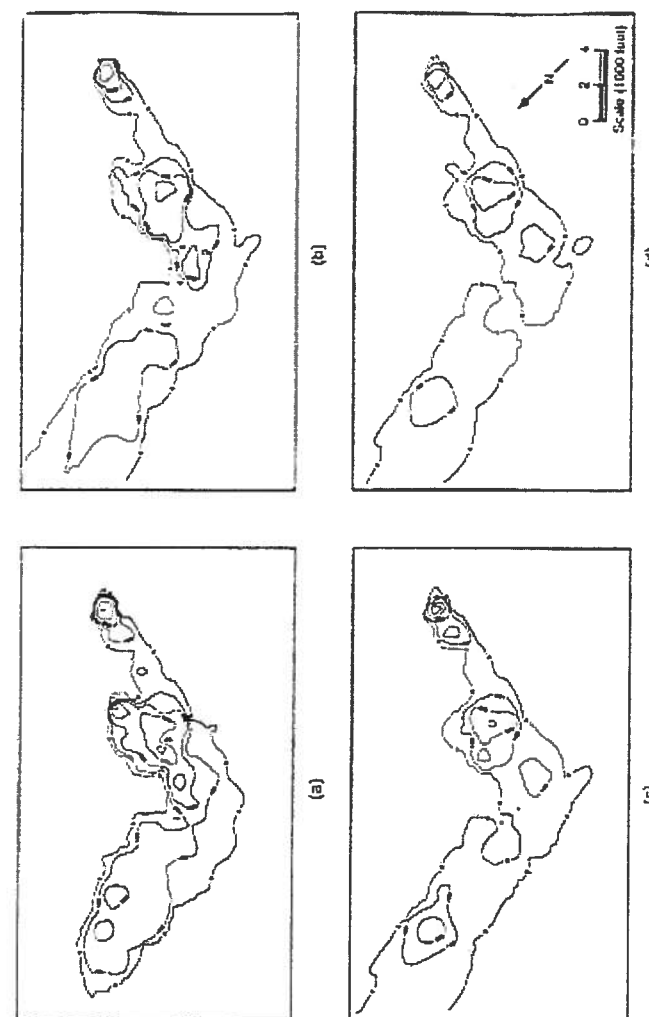
Figure 13.22   TCE plumes during remediation at the Plant 44 site, December 1986 to December 1991. Measured TCE concentrations for (a) December 1986 (ppb), (b) December 1988 (ppb), (c) December 1990 (ppb), and (d) December 1991 (ppb). Source: Burgess, 1993.

The simulation was run for five years in an attempt to predict the TCE plume in December 1991. The simulated plume compared well to the actual remediation. However, the simulated plume appeared to decrease more in area than the actual plume, a fact that may be attributed to the contouring method used. CMB errors for the remediation runs range from 0.52% to 2.36%. Overall, the model predicts that plume remediation is achieved in about 50 years, assuming that NAPLs are not a major factor at this site, which remains for further investigation (Burgess et al., 1993).

13.9.2 Case 2: Conceptual Design For a DNAPL Superfund Site

The presence of dense nonaqueous phase liquids (DNAPL) can greatly complicate ground water remediation efforts due to the downward migration of these heavy oils within an aquifer system and the difficulty of extracting DNAPL using conventional pumping methods. These problems were observed at the Motco Superfund Site near Houston, Texas, where DNAPL is present in a shallow surficial aquifer. To develop an effective scheme for DNAPL management, the aquifer remediation program for this site includes these elements (Connor et al., 1989):

- Detailed stratigraphic interpretation of the aquifer to delineate the zone of DNAPL accumulation
- A pilot recovery test to determine the effectiveness of enhanced oil recovery technologies (EOR) for mobilizing DNAPL
- A combined modeling and field study to evaluate the effect of DNAPL dissolution on future remediation activities at the site
- A conceptual remedial design for extracting mobile DNAPL and for managing residual DNAPL and DNAPL dissolution products

Given the difficulty of achieving conventional ground water clean-up standards in DNAPL-affected portions of an aquifer, an alternative approach for the management of DNAPL sites is proposed below. This approach is based on restoration of ground water quality in areas that are considered to be free of DNAPL as well as long-term containment of DNAPL and DNAPL dissolution products in zones where DNAPL presence is either confirmed or suspected based on evaluation of site data.

Delineation of DNAPL Zones. The Motco Site is a former reclamation facility that operated in the vicinity of La Marque, Texas, during the period of 1958 to 1968. Reclamation efforts involved collection and reprocessing of petrochemical residues within an 11-acre system of unlined pits. Hydrogeologic investigations have shown this area to be underlain by a surface deposit of interbedded sands, silts, and clays designated the Transmissive Zone. The Transmissive Zone, extending from the ground surface to a depth of approximately 50 ft. below grade, is in turn underlain by a stiff, high-plasticity clay layer, termed
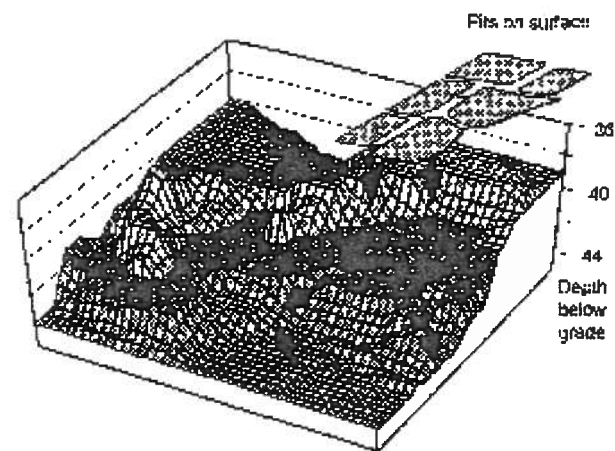
Figure 13.23 Surface map of top of clay unit, showing movement of DNAPLs down topographic valleys in TZ-3 unit.

the UC-1 Clay. DNAPL accumulations have been observed in wells screened in low spots in the shallow transmissive zone immediately atop the underlying clay stratum (see Figure 13.23).

To map the DNAPL zone, 60 boring and well logs at the site were supplemented with an additional 73 cone penetrometer logs (a geotechnical tool) to generate a continuous and laterally extensive stratigraphic record of the shallow aquifer system. The data were used to develop detailed topographic maps of the base of the transmissive zone to find DNAPL accumulation, select locations for soil borings to confirm the presence of DNAPL pools atop this clay surface, and to design a pilot test for recovery of DNAPL and affected ground water. Results of this investigation showed DNAPL to be moving through fractures and other secondary porosity features of the silt stratum, in general accordance with the base topography of the unit.

DNAPL Recovery Pilot Test. To evaluate the feasibility of pumped withdrawal of DNAPL fluids, a pilot test was conducted at the Motco Site in 1989 to compare three recovery technologies: pumping, water-flooding, and vacuum-enhanced recovery. To test the performance of pumping alone, a recovery well was installed in a zone of DNAPL accumulation and equipped with a submersible, positive displacement pump. For the vacuum-enhanced pumping scheme, the downhole pump was augmented by a wellbore vacuum, increasing the available drawdown and maximum yield of the recovery well. For the water-flooding scheme, a freshwater injection well was operated at a distance of 100 ft from a pumping well to increase the hydraulic gradient. A three-week testing program demonstrated

that some DNAPL could be removed by pumping alone, but that waterflooding and vacuum-enhanced recovery greatly increased recovery rates.

Results of the pilot test demonstrated that mobile DNAPL could be recovered from the transmissive strata by means of ground water pumping. As evidenced by DNAPL accumulation within nearby observation wells during recovery well operation, hydraulic gradients 40 to 60 times greater than normal are capable of overwhelming density forces and inducing DNAPL flow within the aquifer.

Test results indicate that any of the three pumping schemes should prove effective for ground water/DNAPL recovery from the transmissive zone. However, due to improved well yield and higher induced flow gradients, vacuum-enhanced pumping and water flooding offer significant advantages in terms of the rate and potential degree of DNAPL removal. Over a 100% increase in DNAPL production rate was observed when both enhancements were used (50 - 100 gal DNAPL/day vs. 25-50 gal/day with pumping alone).

DNAPL Dissolution Study. The pilot recovery test demonstrated that the mobile fraction of the DNAPL fluids could be removed from the water-bearing stratum using enhanced oil recovery technologies. However, a significant percentage of the DNAPL mass would remain immobilized within the aquifer matrix, possibly acting as a continued source of organic constituent release to ground water due to dissolution of soluble DNAPL components.

To quantify the effect of DNAPL dissolution on the aquifer remediation program now being planned for the Motco Site, a modeling study and in-situ field test were designed to simulate the performance of the full-scale ground water recovery system. The modeling study employed an existing dissolution relationship (Borden and Kao, 1989) which assumed equilibrium partitioning of soluble organics between water and DNAPL. On the basis of this analysis, a field test was designed to simulate the actual hydraulic conditions that might be expected during a full-scale pumping and waterflooding program for DNAPL-affected areas. One injection well and one production well, spaced 11 feet apart, were used to flush fresh water through the test area during the 30-day test period. As the test progressed, over 11,000 gallons of fresh water were drawn through the test area, resulting in significant reductions in the concentrations of key organic constituents (i.e., > 85%, see Figure 13.24).

At this site, the field dissolution test showed that approximately 50 to 100 pore volumes of fresh water may be required to achieve the current ground water recovery standards (ranging from 2 to 50 mg/L for key indicator constituents in the Class III saline aquifer) in DNAPL-affected areas. These empirical results are in good agreement with modeling predictions, which indicated that roughly a 50 pore-volume flush would be required to adequately reduce dissolution products from the residual DNAPL. As this level of flushing is probably impracticable to achieve at the site, a long-term containment system was specified to protect human health and the environment (Newell et al., 1991).

Long-Term Containment Modeling Study. To assist in the design of a long-term containment system for dissolved constituents at the Motco Site, a modeling study was conducted using the MODFLOW ground water model. To simulate the various transmissive zones and clays at the site, a 3-D model consisting of four different layers was created.
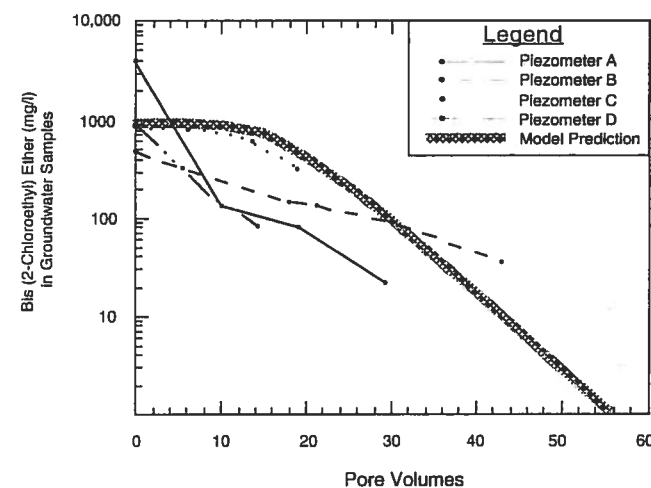
Figure 13.24 Concentration of indicator parameter versus pore volumes flushed during DNAPL dissolution pilot test.

Transmissivity and vertical conductance values were assigned to the 9200 finite difference cells using data from pump tests, slug tests, soil borings, and cone penetrometer surveys. To ensure accurate simulations, the model was calibrated using data from natural flow conditions and from the DNAPL recovery test.

Ground water pumping rates required to achieve hydraulic control of the affected areas at the site were determined for three containment system designs: (1) existing conditions, (2) partial enclosure of affected areas, (3) complete enclosure of affected areas. The existing conditions include a 900-ft long slurry wall currently in place along one side of the site. Complete enclosure of affected areas with a slurry wall reduces pumping rates required to achieve hydraulic control by approximately 10 fold, from 2.0–3.0 gpm to 0.3–0.6 gpm. Lower pumping rates will reduce the cost of treating recovered ground water, and may lead to significant cost savings during operation of the long-term containment system.

13.9.3 Case 3: Modeling a Soil Vapor Extraction Operation at Hill AFB, Utah Using VENT3D

VENT3D, a 3-D vapor flow and multicomponent transport model described in Chapter 9, was used to simulate the performance of a previously reported SVE operation at a jet (JP-4) fuel contaminated site at Hill Air Force Base, Utah, (DePaoli, 1991). Field data were used to obtain the input parameters needed to describe the subsurface air flow and contaminant re-

moval rate. The applicability of the model to this field site is demonstrated by comparing model predictions to field data. The model was then used in a predictive mode to describe the depletion of JP-4 by volatilization during the full-scale vapor extraction operation, and to predict the time frame within which cleanup goals could be achieved. This modeling effort also demonstrates the use of more sophisticated flow and transport models for describing the behavior of contaminants at field sites (El-Beshry et al., 1998; El-Beshry et al., 1999).

VENT3D (Benson, 1994), is a 3-D, finite-difference code for simulating vapor flow and transport of a multi-component mixture. The model computes the movement of compounds in the vapor phase and keeps track of the phase distribution of each compound in the other three phases, NAPL, dissolved, and sorbed using equilibrium partitioning. The model domain is divided into blocks, and each block may be given unique properties such as permeability or contaminant concentrations. Both extraction and injection wells can be simulated. Contaminant components can be present in different proportions and have different physico-chemical properties.

The site selected for this study was a fuel storage area at Hill Air Force Base (HAFB), Utah, where 102,000 L (27,000 gal = 76,500 kg) of jet fuel (JP-4) were spilled onto the ground in 1985, after an automatic filling system malfunctioned and storage tanks over-flowed. A field study of in-situ soil venting was performed at Hill AFB by Oak Ridge National Laboratory (ORNL) (DePaoli et al., 1991). A total mass of 48,000 Kg was removed from the site at the end of the 10-months SVE operation. A number of pilot tests and a full-scale SVE study were carried out at the site to demonstrate the clean-up efficiencies attainable using soil venting for remediation of fuel contaminated sites. The vent system consisted of 15 vertical vents in the main contaminated area of the site.

Air permeability was appropriately estimated at 40 darcys for the horizontal permeability and 1 darcy for the vertical permeability, using a software called GASSOLVE (Falta, 1996) and data from the pilot tests conducted at the site. The initial contaminant mass was the only parameter that had to be adjusted to simulate contaminant removals during the early months of the full-scale study. The initial contaminant mass was estimated at 76,500 kg which is equal to the total spill mass. The contaminant distribution followed hydrocarbon concentrations from soil cores. The accuracy of model predictions was tested by simulating the full-scale venting operation using the estimated input parameters. VENT3D predictions were compared with observed data measured during the 10-months venting operation.

Different well configurations with different extraction rates operated during the study. The system was shutdown and restarted several times. Figures 13.25a and 13.25b show the depth averaged vacuum calculated by VENT3D and measured by ORNL from one of the flow tests. It is observed that vacuum values and contour lines are very close, except at the extraction well, where the calculated vacuum is almost half of the measured value. Overall, the model was able to adequately simulate the gas flow field based on the independently determined permeabilities.

Figure 13.26 is a plot of the observed versus calculated mass removals using 76,500 kg as the total initial contaminant mass and subdividing the fuel mixture into 10 compo-
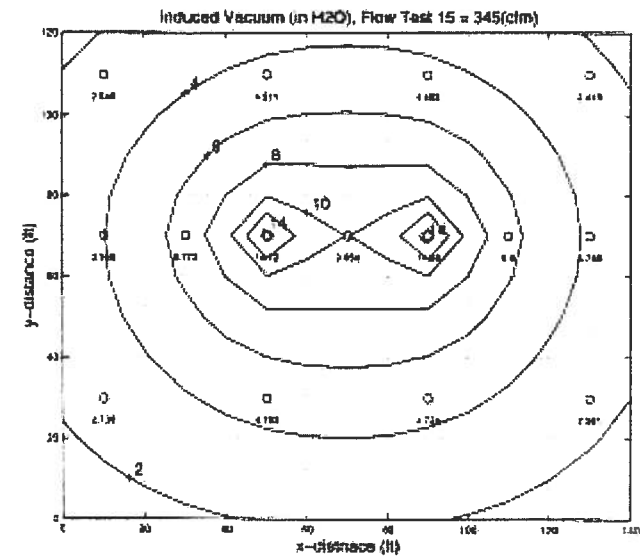
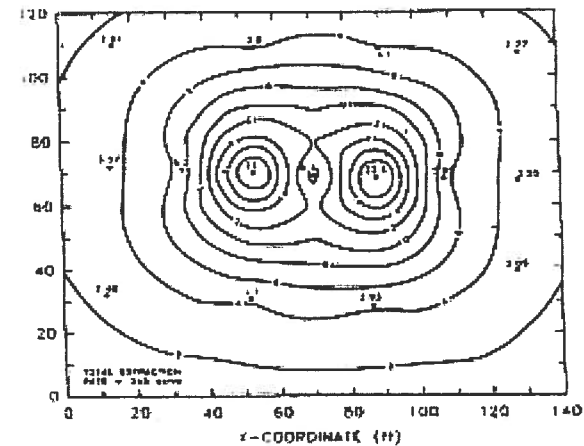Figure 13.25a VENT3D Depth Averaged Vacuum (in H_2O), Flow Test 15.

Figure 13.25b Observed Depth Averaged Vacuum (in H_2O), Flow Test 15.

nents. More details of how the field site was modeled are reported in El-Beshry et al. (1998). The initial and final (at the end of the SVE study) contaminant concentration in soil and the initial and final soil gas concentrations as predicted by VENT3D compared well.

One of the significant features of VENT3D is that it can simulate a multicomponent mixture using properties for each constituent. This causes a dilemma for fuel contamination because fuels are made up of too many compounds to account for each separately. In this study, the JP-4 was represented by 10 classes of compounds (C_5-C_{15}), categorized according to the number of carbon atoms. Each class is represented by specific physicochemical properties such as molecular weight, boiling point, vapor pressure, solubility, and octanol/water partition coefficient. Each class was represented by a single compound whose vapor pressure was the median of those in that class. The model was used to examine the effect of changes in chemical composition of jet fuel (JP-4) due to volatilization.

During vapor extraction the composition of the mixture changes, that is, the mixture loses the more volatile compounds at the beginning of the process, thus it becomes more concentrated in the less volatile components and less rich in the more volatile components. Figure 13.27 shows the changes in mass fractions of the classes in the JP-4 fuel mixture during the length of the SVE study as computed by VENT3D. The graph indicates that depletion of lighter compounds (lower carbon number) takes place while the mass fraction of the higher carbon number compounds increase because they volatilize in relatively lesser, and even insignificant, quantities.

VENT3D was successful in simulating the behavior of the SVE system during the 10-month field study. Therefore, the model was used in a predictive manner to evaluate the total time to achieve complete cleanup of the NAPL. After 10 months of operation (October 1989), actual measurements and VENT3D predictions indicated that 64% of the contamination at the site was removed, which was close to the actual removals.

13.9.4 Case 4: Surfactants and Cosolvents For Enhanced NAPL Removal at Hill AFB

Introduction. In a study funded by SERDP and USEPA, nine enhanced aquifer remediation technologies were demonstrated side-by-side at a chemical disposal pit (CDP) site at Hill Air Force Base in Utah. The demonstrations were performed inside 3 x 5 m cells, isolated from the surrounding shallow aquifer by steel sheet piling. The site was originally contaminated with an LNAPL mixture of chlorinated solvents and fuel hydrocarbons. The technologies demonstrated manipulated the solubility, mobility, and volatility of the contaminants in order to enhance the aquifer remediation over a standard "pump-and-treat" system. About 10,000 samples per cell were collected as part of tracer tests, soil flushing demonstrations, and routine characterization efforts.

The purpose of the studies was to evaluate innovative technologies for the removal of non-aqueous phase liquids (NAPL) from the saturated and, in some cases, the unsaturated
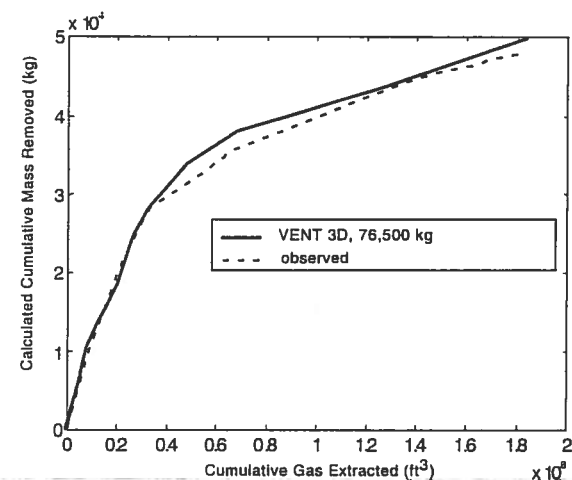
Figure 13.26 Observed and VENT3D Calculated Mass Removals during Full Scale Study at Hill AFB, Utah.
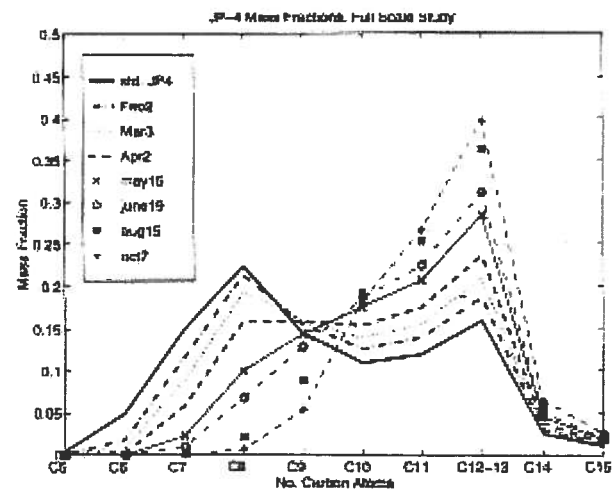

Figure 13.27 Changes in mass fractions of the different components in the JP-4 fuel mixture during the SVE study.

zone. Hill AFB's OU 1 site was chosen because all nine technologies could be demonstrated side-by-side at the location, with similar hydrogeology at a single contaminated site.

The technologies evaluated at Hill AFB included:

- air sparging/soil vapor extraction (Michigan Technological University)
- in-well aeration (University of Arizona)
- cosolvent mobilization (Clemson University)
- complexing sugar flush (University of Arizona)
- surfactant solubilization (University of Oklahoma)
- middle-phase microemulsion (University of Oklahoma)
- steam injection (Tyndall Air Force Base)
- single-phase microemulsion (University of Florida) [AATDF /EPA]
- cosolvent solubilization (University of Florida, 1995)

Site Background. The portion of the base selected for the treatability studies is known as Operable Unit 1 (OU 1), and is located near the northeastern boundary of Hill AFB. The study test cells are adjacent to chemical disposal pits 1 and 2, which had industrial liquid waste disposal sites in operation from 1952 through 1973. Wastes consisted mostly of principally petroleum hydrocarbons and spent solvents, which were periodically burned at the site.

Prior to the beginning of the enhanced remediation demonstrations at Hill AFB, Montgomery Watson, Inc. (1995, 1996) had performed site characterization and evaluation for the remedial investigation. The work included installing monitoring wells, collecting soil cores, performing slug tests, and characterizing the geology of the area. The sedimentary formation which contains the shallow aquifer on base consist of two sedimentary units, an upper sand and gravel unit and an intermediate silty clay.

The saturated portion of the upper sand and gravel phreatic aquifer has a horizontal hydraulic conductivity ranging from 10^{-1} to 10^{-2} cm/sec based on aquifer test data, and from 10^{-2} to 10^{-5} cm/sec based on slug test data. The horizontal hydraulic conductivity of the underlying clay unit ranges from 10^{-4} to 10^{-5} cm/sec based on slug test data

Chlorinated solvents, chlorinated benzenes, pesticides, PCBs, dioxins, and furans have been detected in the LNAPL associated with the chemical disposal pits. The VOC detected at the highest concentration and with the widest distribution is 1,2-DCE. The apparent free phase LNAPL thickness based on monitoring well observations ranges from 0 to 0.3 meters in the area of the proposed treatability studies. This thickness does not include residual LNAPL. High concentrations of fuel hydrocarbons and chlorinated hydrocarbons in the were also found in the subsurface soils at the CDPs.

Test Cell Operation. Each of the nine treatability study test cells has a similar layout of injection and extraction wells, multilevel ground water samplers, piezometers, and

monitoring wells. A schematic of the standard test cell is shown in Figure 13.19. During the flushing demonstrations, there was an influent tank farm (consisting of three 75,000 L tanks and three 23,000 L tanks), and an effluent tank farm (consisting of eight 75,000 L tanks and two 23,000 L tanks), along with two 23,000 L water supply tanks and related plumbing. This standard layout was used in all test cells to allow the pre- and post-treatment tracer test configurations. The multilevel samplers were used during the tracer tests and flushing studies to collect ground water and soil gas samples for analysis. The results were used to monitor flow characteristics and composition of the fluids of the tests and to adjust the treatment process, if necessary. Soil samples were collected at selected MLS locations to characterize the pretreatment soil conditions in the test cell.

Test Cell Characterization. The performance of the innovative technologies is evaluated based on the change in the amount of NAPL mass within each of the test cells, and on the amount of mass remaining in the cell after treatment. If properly designed, partitioning tracer studies can give an estimate of the distribution of NAPL within a test cell, as well as the total mass in the cell (Jin et al., 1994). Tracer studies as well as soil borings were performed to estimate the total mass of NAPL pre- and post-remediation and to evaluate the performance of each remediation technology.

Tracer Tests. Partitioning tracer tests (PTTs) were performed in all nine test cells before and after the technology demonstrations. These tests were designed to determine the spatial distribution and the total volume of NAPL within each cell. Laboratory tests were used to evaluate several tracers for use in the field tests, including: ethanol, methanol, hexanol, bromide, 2,2-dimethyl-3-pentanol, n-pentanol, and 6-methyl-2-heptanol.

During the partitioning tracer test, a small volume of solution containing low concentrations of both conservative and partitioning tracers was pumped through the cell. The conservative tracer will pass through the system unaffected by the NAPL content of the cell. The partitioning tracers will partition into the NAPL phase when they encounter it, and partition back out of the NAPL after the main mass of the tracer pulse has passed, resulting in a chromatographic separation between the partitioning and conservative tracers. This chromatographic separation is reflected in concentration breakthrough curves (BTCs) developed for the various sampling points in each cell, and allows NAPL saturations to be computed for each area of the cell (Jin et al., 1994)

Breakthrough curves for the reactive tracers were used to estimate the volume and spatial distribution of NAPL in each test cell. A minimum of three methods are used to calculate the NAPL distribution. First, the integrated mass of NAPL in the swept volume is calculated by the method of moments. Second, an inversion technique is used with a solution to the 1-D advection–dispersion equation utilizing a method of superposition to account for spatial variability along the flow path. The third method will be an inversion technique that incorporates the code developed by Gary Pope at the University of Texas. Calculations can be made for each of the MLS points and the extraction well.

Results. A surfactant solubilization and a surfactant mobilization test were conducted in two different cells at HAFB OU1 by the University of Oklahoma. In the solubilization cell, 10 pore volumes of 4.3 wt% Dowfax 8390 were flushed through the cell. Results indicated that greater than 95% recovery of the surfactant was achieved, along with removal of

roughly 50% of the contaminant (obviously additional flushing would have removed more contaminant, but this was the pre-established number of pore volumes to be conducted). The Dowfax 8390 proved to be a very robust system, although not as efficient as the middle phase system (as expected) (Sabatini et al., 1999).

In the mobilization cell a surfactant system of 2.2 wt% AOT, 2.1 wt% Tween 80, and 0.43 wt% calcium chloride was used. In this case 6.6 pore volumes of surfactant removed roughly 85% to 90% of the contaminant. The improved elution was obvious, both visually and by measured concentrations. While this system was more efficient, it required much higher operator skill to both design and implement, especially for this highly hydrophobic oil. At the same time surfactant-enhanced solubilization was much more efficient than water alone, as observed from the pre- and post-surfactant injection periods. For additional details on this field test, refer to Knox et al. (1999).

During the cosolvent flushing tests performed by the University of Florida, a mixture of water and two alcohols was used, including ethanol and n-pentanol to enhance solubilization. The 10-day cosolvent flood was followed by a 20-day period of water flushing, and one pore volume per day (3.1 L/min) was maintained throughout the tests (Rao et al., 1997; Sillan et al., 1998). Because of more than 60 sampling locations within each cell, a great deal was learned about the distribution of NAPL saturation as cosolvents were flushed through the cell. Both core analyses and pre- and post-partitioning tracer tests were used to evaluate the changes in NAPL saturations during the test. Results were encouraging after the 10-day flush, with typical removal values in the range of 75% to 85%. More details on similar tests in the general literature are summarized in Lowe et al. (1999). Overall, the soil flushing methods show promise for small NAPL source areas, but economic considerations may preclude their use for larger areas. Preliminary results from several of the test cells at

TABLE 13.1 Mass Removal Reported in Hill AFB Field demonstrations.

Project	Cell Size	Target Depth	Reported Mass Recovered*	Reported Fraction of Initial Mass Recovered*
Hill AFB, Utah- Ethanol- OU 1	3 by 5 m	4.6 to 6.1 bgs	Approx. 350 liters of NAPL	>85% Cell-Wide Basis:> 95% in the Central Flood Zone: > 75% in Bottom 0.5 m
Hill AFB, Utah OU 1- Cosolvent Mobilization - Cell No.3	3 by 5 m	5 to 9 m bgs	Not known at this time	Preliminary Estimate 80 to 90% Based on Soil Cores
Hill AFB, Utah- OU 1, Solubilization- Cell No. 5	3 by 5 m	5 to 9 m bgs	Not known at this time	45-55%
Hill AFB, Utah- OU 1, Mobilization- Cell No. 6	4 by 5 m	6 to 9 m bgs	Not known at this time	85-95%
Hill AFB, Utah - OU 1 Surfactant with Cosolvent Cell No. 8	3 by 5 m	4.9 to 7.9 m bgs	Approx. 350 liters	72% Based on Partitioning Tracer Testing, 64 to 96% Based on Soil Cores
Hill AFB, Utah - OU 2 Micellar Flood	(1 PV =15,000 gallons)	8 to 15 m bgs	511 gallons (By Partitioning Interwell Tracer Tests)	99% (By Partitioning Interwell Tracer Tests)
Hill AFB, Utah - OU 2 Foam Flood	6 to 10 m	12 to 14 m bgs	36.5 gallons of DNAPL	Approximately 90%

* Methods for mass estimates include soil cores, concentrations in produced fluids, and partitioning tracer tests.

Hill AFB are contained in the ACS publication edited by Brusseau et al. (1999). A brief summary of reported mass removals at Hill AFB is shown in Table 13.1.

SUMMARY

Chapter 13 reviews the important concepts of aquifer remediation as applied to contaminated hazardous-waste sites. Many of the flow and transport issues discussed in previous chapters are used here. Various methods of containment, hydraulic control, pump and treat, bioremediation, soil vapor extraction, and NAPL control are presented in detail, along with four complete case studies from the authors' experiences. Modern approaches to site remediation include consideration of two related but distinct problems: (1) source control near the area of greatest contamination and (2) plume control either at some downgradient boundary or for removal of soluble components. Figure 13.1 depicts several of the methods available for site cleanup; earlier pump-and-treat systems for soluble plume removal are being combined with more intensive methods near source areas. Finally, hazardous-waste site remediation is a rapidly evolving field with new technologies merging rapidly. New remediation approaches include funnel and gate systems, treatment walls, air sparging, surfactant flushing, and cosolvent flushing for NAPLs removal. Due to the performance problems of original pump-and-treat systems, new and combined remediation methods are currently being tested at a number of field sites. It is clear that no single method will emerge as superior, due to the heterogeneous nature of field sites, the complexity of the contaminants involved, the NAPL issue, and the expense involved in cleaning up a site.

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