# C H A P T E R  1 3

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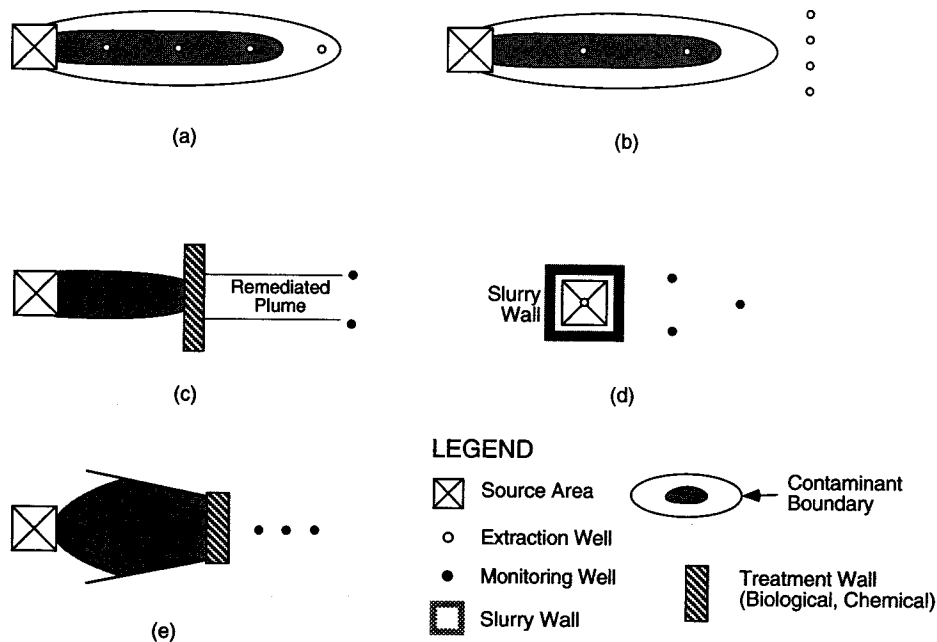
**Figure 13.1** Remedial options and source control. (a) Standard pump and treat. (b) Fence line pump and treat. (c) Treatment wall system. (d) slurry wall system. (e) Funnel and gate system.

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 $3.0 \times 10^{-11}$ 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).
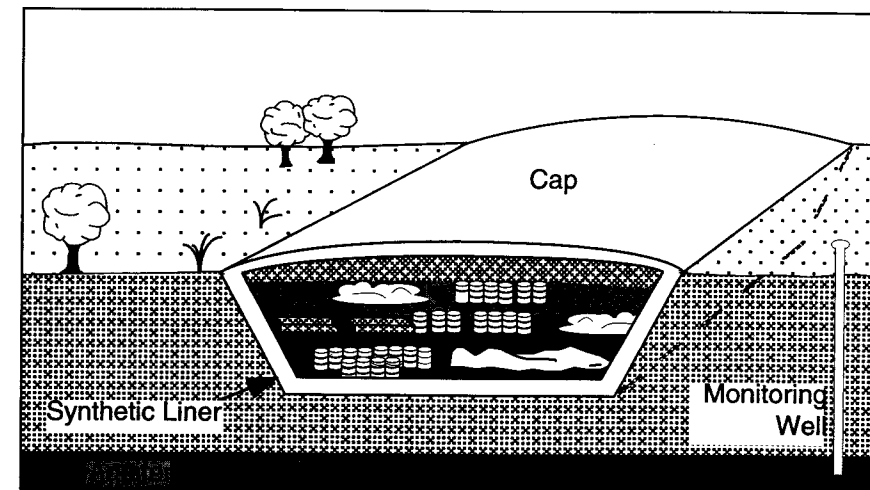


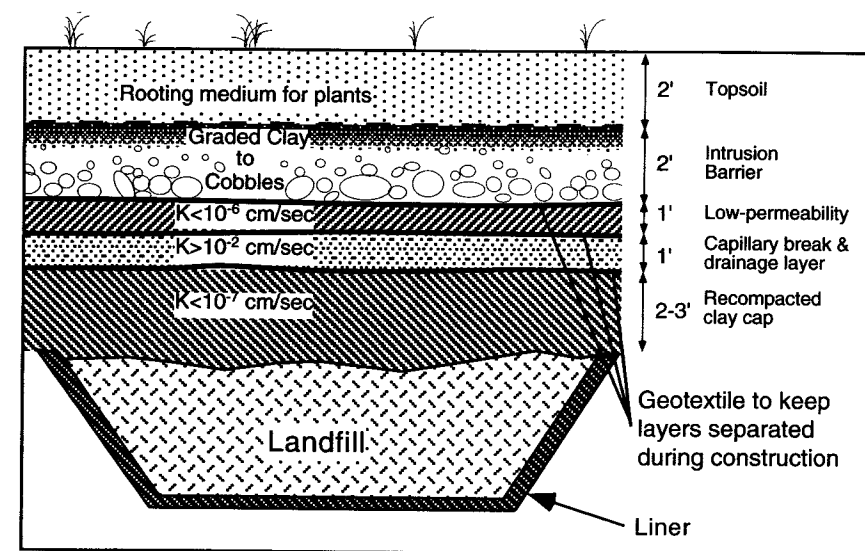**Figure 13.3** Example of synthetic liner for a hazardous-waste landfill.



**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-
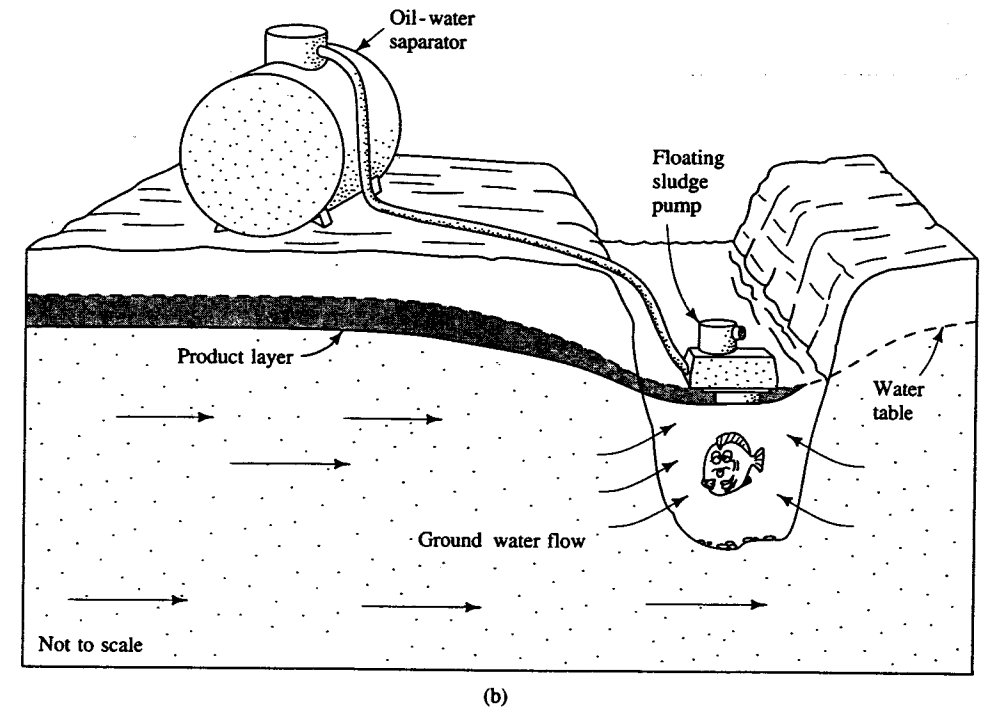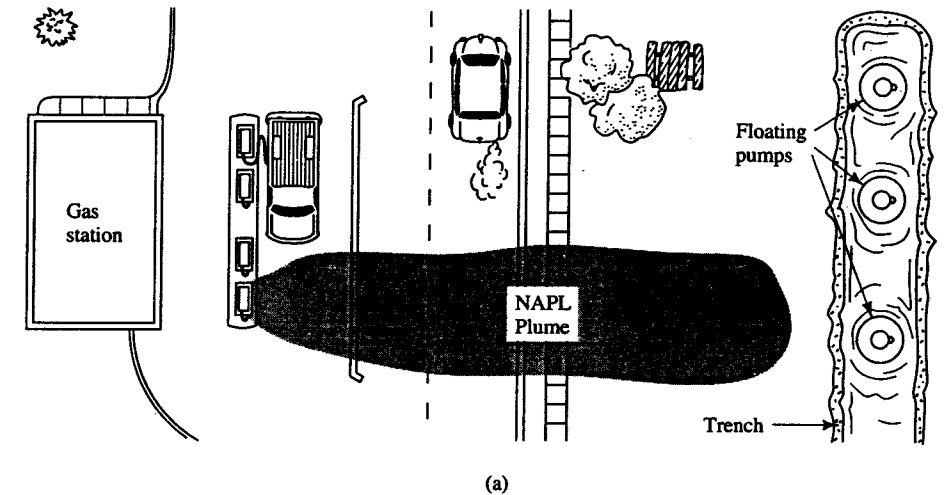
(a)



(b)

**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.
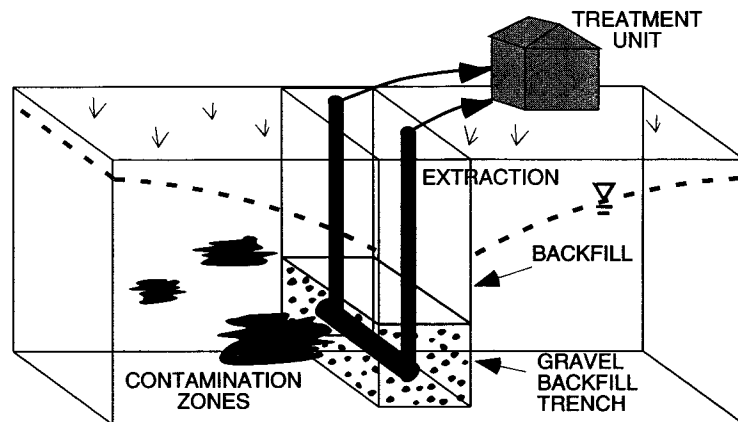
**Figure 13.6** Collection Trench for DNAPL Source Zones.

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
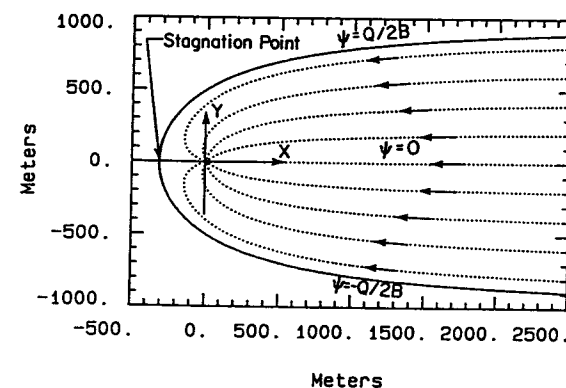


**Figure 13.7** Paths of some water particles within the capture zone with Q/BU = 2000, leading to the pumping well located at the origin. Source: Javandel and Tsang, 1986.

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-
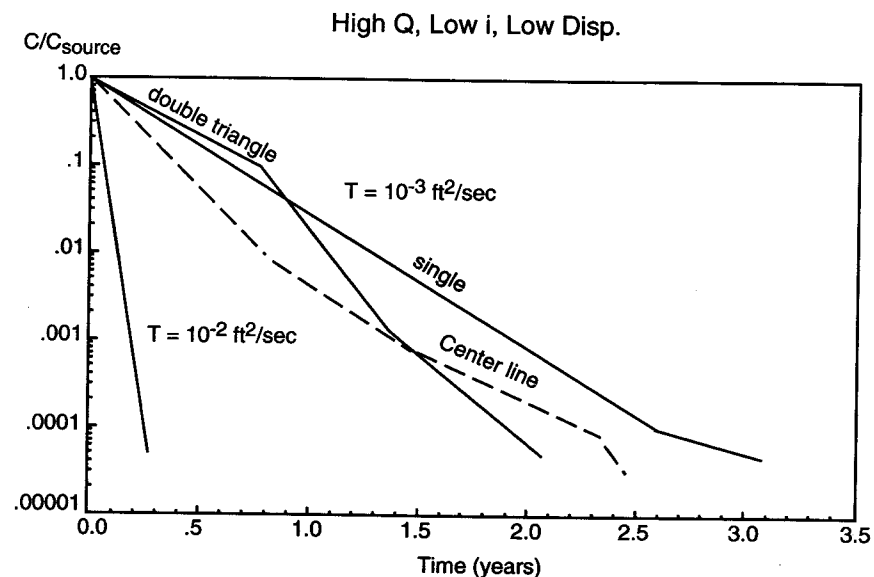


**Figure 13.10**  Comparison of relative concentrations versus cleanup time for various well patterns for condition A.  Source: Satkin and Bedient, 1988.

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).
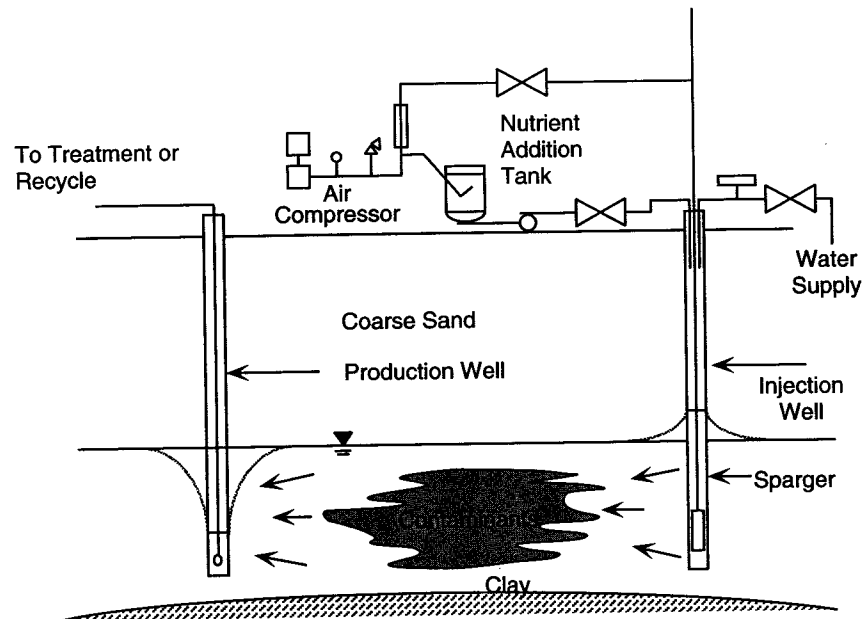
**Figure 13.11**  Injection system for oxygen.

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
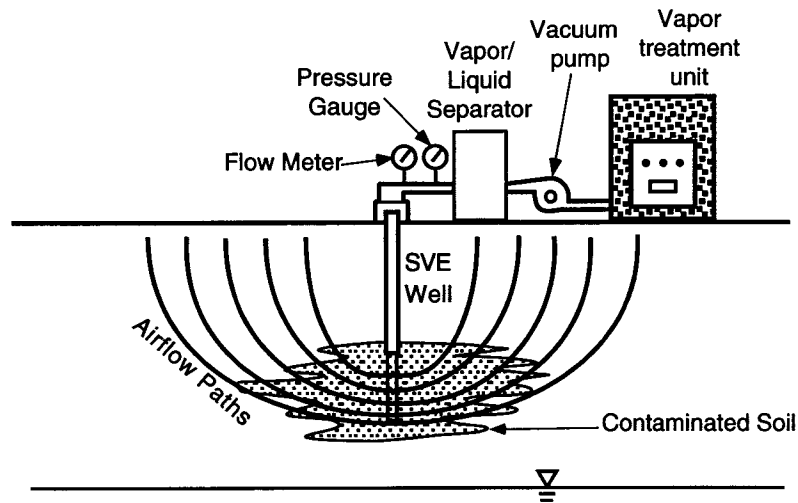
**Figure 13.12** Simple vapor extraction system and the resulting pattern airflow.
Source: Johnson et al., 1990.

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; Enviresponse, 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.
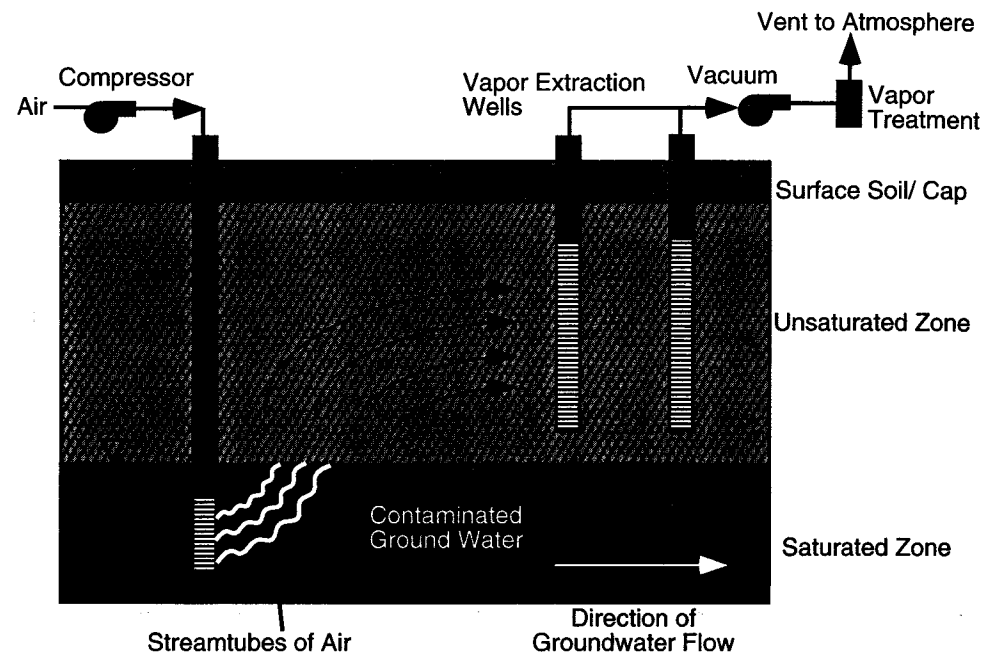
**Figure 13.13** Process diagram for air sparging. Source: NRC, 1994.

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.
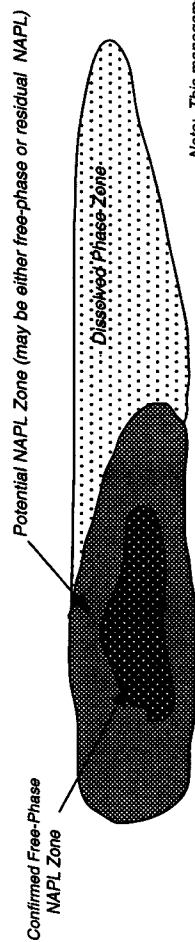
**Remediation Zones at a NAPL Site**

| 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) | 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. |
| 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 | | Operate pumping wells for long-term hydraulic containment of NAPL dissolution products | Operate pumping wells indefinitely (until groundwater reaches current clean-up standards) |

Note: This management strategy may not be applicable to all hydrogeologic settings, such as NAPL sites located over fractured metamorphic or igneous rock.

Confirmed Free-Phase NAPL Zone

Potential NAPL Zone (may be either free-phase or residual NAPL)

Dissolved Phase Zone

**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