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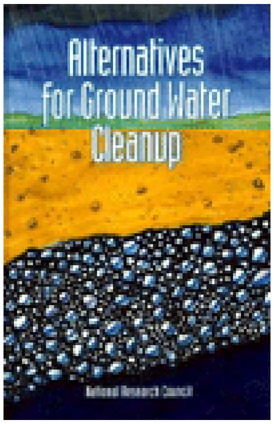

Alternatives for Ground Water Cleanup

Committee on Ground Water Cleanup Alternatives,
National Research Council

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THE NATIONAL ACADEMIES
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Alternatives for Ground Water Cleanup

Committee on Ground Water Cleanup Alternatives
Water Science and Technology Board
Board on Radioactive Waste Management
Commission on Geosciences, Environment, and Resources

NATIONAL ACADEMY PRESS
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NOTICE: The project that is the subject of this report was approved by the Governing Board of the National Research Council, whose members are drawn from the councils of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine. The members of the committee responsible for the report were chosen for their special competences and with regard for appropriate balance.

This report has been reviewed by a group other than the authors according to procedures approved by a Report Review Committee consisting of members of the National Academy of Sciences, the National Academy of Engineering, and the Institute of Medicine.

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The cover illustration shows how the elements of weather, geography, and underground strata all combine to affect our ground water.

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Preface

"A little water clears us of this deed"
Macbeth, Act II, ii

Over the past 15 years, evidence has accumulated that the nation's ground water resource, which supplies more than 50 percent of the population's drinking water, is threatened not only by excessive overdrafts but also by contamination caused by past and present industrial, agricultural, and commercial activities. In the United States, it is estimated that more than 300,000 sites may have contaminated soil or ground water requiring some form of remediation (see Table 1-2 in Chapter 1). The potential cost of these remedial activities may be as large as $750 billion in 1993 dollars to be spent over the next 20 to 30 years (see Chapter 1). The magnitude of the problem may be equally significant in other industrialized countries.

The U.S. public response to this growing perception of a threatened resource with unknown human health and ecological impacts has generally been to demand restoration of the ground water to drinking water standards (although the cleanup goal varies with the site, as discussed in Chapter 6). This goal of restoration to drinking water standards is currently the primary driver of ground water remediation activities at most sites regulated under the Comprehensive Environmental Response, Compensation, and Liability Act of 1980, also known as the Superfund act. Restoration to potable standards has also been the goal at other sites regulated under state laws and in some cases at sites regulated under the Resource Conservation and Recovery Act.

The technological response to these statutory and regulatory demands over the past decade has almost exclusively been the application of so-called "pump-and-treat" technology. Simply put, this technology involves extracting water from the ground below the water table using standard water-well technology. The extracted and contaminated water is then treated with established above-ground technologies such as air stripping or adsorption on granular activated carbon. In essence, pump-and-treat technology attempts to flush out the contaminants and to return the contaminated area to a condition in which water drawn from wells will meet drinking water standards without further treatment. However, in contrast to the suggestion from Lady Macbeth quoted above, a very large amount of water is often required to flush out even modest amounts of contaminants, and the amount of water required to rid a site of contamination is often unimaginably large. In essence, the United States has been conducting a large-scale national testing program to determine if restoration of contaminated aquifers is achievable within reasonable time frames and at an affordable cost.

The exact number of pump-and-treat systems currently in operation in the United States is unknown, but it may well exceed 3,000. A sufficient history of operation of this technology now exists to assess its efficacy. Unfortunately, and some would say not surprisingly, the effectiveness of this technology to restore contaminated aquifers seems quite limited. This has led to a widely held view that pump-and-treat is a failed technology and should be rejected as a technique for ground water remediation. Thus, the United States and other industrialized nations, as well as developing nations, are confronted with a major dilemma: how to protect human health and the environment from contaminated ground water without wasting resources pursuing technical strategies that appear unable to achieve agreed-upon societal goals. A further significant problem is how to convey these technical limitations to a public that has grown increasingly skeptical of technologists.

In response to this dilemma, the National Research Council (NRC) established a committee of experts to analyze the major technical and public policy issues arising from technical limits to aquifer remediation. The Committee on Ground Water Cleanup Alternatives was established through two boards within the NRC: the Water Science and Technology Board and the Board on Radioactive Waste Management. Financial support for this effort was provided by the Environmental Protection Agency (EPA), the Department of Energy (DOE), the Coalition on Superfund, and Chevron Corporation. The boards chose 19 experts to serve on the committee, representing a broad range of scientific and technical disciplines and stakeholders in the debate over ground water remediation.

The scope of the committee's charge included the following questions:

- What are the capabilities of pump-and-treat systems?
- What are the limits, if any, to contaminant removal from the subsurface?
- What are the capabilities of alternative or innovative technologies for subsurface remediation, and what, if any, are the barriers to the use of these technologies?
- What are the socioeconomic consequences of the possible failure of ground water remediation?
- What are the possible alternative goals for ground water remediation, and what factors should be considered in setting those goals?
- What policy alternatives should be pursued to reflect the technical limitations to aquifer remediation?

The committee undertook a thorough evaluation of existing information related to subsurface remediation. During nine meetings held over the past two years, the committee heard reports from numerous private and public groups on all aspects of ground water and soil remediation. Prominent among these were presentations by policy analysts from the EPA's Office of Solid Waste and Emergency Response (including its Technology Innovation Office), technical specialists from the EPA's Ada, Oklahoma, ground water research laboratory, researchers working on DOE efforts to deal with ground water and soil contamination at DOE facilities, and DOE employees working on technology development for environmental restoration. The committee also solicited views of industry trade groups, consultants, contractors, impacted parties, and environmental groups. Finally, the committee relied on the in-depth experience and expertise of the committee members, most of whom are recognized leaders in the technical, economic, risk, and policy debates surrounding this complex subject.

Although the committee was able to review data from only a small number of sites (approximately 80) where pump-and-treat systems have been installed, there was strong consensus that these sites represented the range of conditions encountered at the majority of sites with contaminated ground water. One dominant characteristic that surfaced in all cases was the high degree of uncertainty associated with the task of subsurface remediation. These uncertainties begin with limitations on site characterization and the ability to identify the nature and extent of the contamination in complex, multilayered, and heterogeneous geologic environments, in which key physical, chemical, or biological characteristics can vary by orders of magnitude on the scale of centimeters. They end with uncertainties about the efficacy of any subsurface remediation technology selected for the task in the face of this highly uncertain hydrogeologic and geochemical environment. In between these end points, the difficult selection of appropriate remedial actions becomes exceedingly complex due to uncertainties in analytical models used to predict the fate and transport of contaminants and uncertainties in the science of risk assessment. The problem becomes even more intractable when these uncertainties are injected into the litigious environment that exists in the United States. This unusual degree of uncertainty significantly complicates debates about the technical, institutional, and public policy strategies that should be pursued to resolve ground water contamination.

The document that follows provides in my view the most comprehensive treatment of the issues arising from technical and institutional limitations on ground water remediation yet available. Six subcommittees chaired by committee members prepared the various chapters in the report; lively debates characterized the later committee meetings as the members reviewed and discussed the subcommittees' chapters. Given the diversity of opinions and backgrounds of committee members, it was a pleasant surprise that we were able to reach a consensus on almost all issues. I wish to acknowledge the significant efforts by committee members, all of whom are heavily overcommitted but nevertheless found the time to make important contributions to the document under friendly but persistent prodding from the Water Science and Technology Board staff.

As with all such reports prepared under the auspices of the NRC, the success of the report is heavily dependent on the skills, dedication, and energy of the staff officer assigned to a committee. In this case, the Committee on Ground Water Cleanup Alternatives was extremely fortunate to have the services of Jackie MacDonald, whose contributions throughout the report are extensive. Aside from the overall management and tracking of each version of chapters or sections of chapters, Jackie demonstrated her very considerable editing skills in preparing or extensively rewriting significant sections of the report and in helping to make the report read in a consistent and comprehensible style, as opposed to sounding like a report written by 19 people. Jackie's attention to detail, persistence, enthusiasm, and commitment to hard work are inspiring, and much of the credit for the success of this document is owed to her.

Thanks are also due to several others who assisted in this project. Greg Nyce and Greicy Amjadivala efficiently managed logistical arrangements for the committee meetings. Angela Brubaker prepared the report manuscript for publication, improving the editorial details in numerous ways. Cindy Kleiman prepared technical reviews of the ecological risks of ground water contamination and analyses of alternative ground water cleanup goals. Gino Bianchi-Mosquera was responsible for much of the legwork in analyzing data from the sites listed in Appendix A and used to prepare the case studies in Chapter 3.

Finally, I wish to again acknowledge the many long hours that committee members must have spent researching, writing, and revising their contributions. I have enjoyed immensely the opportunity to work with such a talented and articulate group of professionals. I hope the reader will agree that the committee has done its task well.

MICHAEL C. KAVANAUGH, CHAIR
COMMITTEE ON GROUND WATER CLEANUP ALTERNATIVES

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BOXES

Alternatives for Ground Water Cleanup

Executive Summary

The United States currently faces a very large ground water contamination problem. Although the total number of contaminated sites is unknown, estimates of the total number of waste sites where ground water and soil may be contaminated range from approximately 300,000 to 400,000. Recent estimates of the total cost of cleaning up these sites over the next 30 years have ranged as high as $1 trillion.

Several recent studies have raised troubling questions about whether existing technologies are capable of solving this large and costly problem. These studies focused on "pump-and-treat" systems, which involve installing wells at strategic locations to pump contaminated ground water to the surface for treatment. Pump-and-treat systems are the most common technology for ground water cleanup in the United States. The studies indicated that pump-and-treat systems may be unable to remove enough contamination to restore the ground water to drinking water standards, or that removal may require a very long time, in some cases centuries.

As a result of these studies, there is almost universal concern among groups with diverse interests in ground water contamination—from government agencies overseeing contaminated sites to industries responsible for the cleanups, environmental groups representing affected citizens, and research scientists—that the nation might be wasting large amounts of money on ineffective remediation efforts. At the same time, many of these groups are concerned that the health of current or future generations may be at risk if contaminated ground water cannot be cleaned up to make it safe for drinking. To address these concerns, the National Research Council initiated a study of ground water cleanup systems. The goals of the study were to review the performance of existing pump-and-treat systems, to determine the performance capabilities of innovative cleanup technologies, to assess whether there are scientific and technological limits to restoring contaminated ground water, to consider the public health and economic consequences of contaminated ground water, and to provide advice on whether changes in national ground water policy are needed to reflect the limits of current technology. This report presents the findings of the National Research Council's study.

The study was carried out by the Committee on Ground Water Cleanup Alternatives, appointed by the National Research Council to work under its Water Science and Technology Board and Board on Radioactive Waste Management. The committee consisted of recognized leaders in the fields of environmental engineering, hydrogeology, chemistry, epidemiology, environmental economics, and environmental law and policy. The findings of this report are based on the committee's review of original data from case studies, reports in scientific journals, presentations by experts outside the committee, evaluation of policy documents, and the extensive experience of committee members.

COMPLEXITY OF THE CONTAMINATED SUBSURFACE

Theoretically, restoration of contaminated ground water to drinking water standards is possible. However, cleanup of contaminated ground water is inherently complex and will require large expenditures and long time periods, in some cases centuries. The key technical reasons for the difficulty of cleanup include the following:

- *Physical heterogeneity:* The subsurface environment is highly variable in its composition. Very often, a subsurface formation is composed of layers of materials with vastly different properties, such as sand and gravel over rock, and even within a layer the composition may vary over distances as small as a few centimeters. Because fluids can move only through the pore spaces between the grains of sand and gravel or through fractures in solid rock and because these openings are distributed non-uniformly, underground contaminant migration pathways are often extremely difficult to predict.
- *Presence of nonaqueous-phase liquids (NAPLs):* Many common contaminants are liquids that, like oil, do not dissolve readily in water. Such liquids are known as NAPLs, of which there are two classes: light NAPLs (LNAPLs), such as gasoline, are less dense than water; dense NAPLs

(DNAPLs), such as the common solvent trichloroethylene, are more dense than water. As a NAPL moves through the subsurface, a portion of the liquid will become trapped as small immobile globules, which cannot be removed by pumping but can dissolve in and contaminate the passing ground water. Removing DNAPLs is further complicated by their tendency, due to their high density, to migrate deep underground, where they are difficult to detect and where they may remain in pools that slowly dissolve in and contaminate the ground water.

- *Migration of contaminants to inaccessible regions:* Contaminants may migrate by molecular diffusion to regions inaccessible to the flowing ground water. Such regions may be microscopic (for example, small pores within aggregated materials) or macroscopic (for example, clay layers). Once present within these regions, the contaminants can serve as long-term sources of pollution as they slowly diffuse back into the cleaner ground water.
- *Sorption of contaminants to subsurface materials:* Many common contaminants have a tendency to adhere to solid materials in the subsurface. These contaminants can remain underground for long periods of time and then be released when the contaminant concentration in the ground water decreases.
- *Difficulties in characterizing the subsurface:* The subsurface cannot be viewed in its entirety, but is usually observed only through a finite number of drilled holes. Because of the highly heterogeneous nature of subsurface properties and the spatial variability of contaminant concentrations, observations from sampling points cannot be easily extrapolated, and thus knowledge of subsurface characteristics is inevitably incomplete.

Regardless of the remediation technology chosen, these inherent complexities pose major obstacles to ground water cleanup.

PERFORMANCE OF CONVENTIONAL PUMP-AND-TREAT SYSTEMS

The committee found that at the majority of contaminated sites, the complex properties of the subsurface environment and the complex behavior of contaminants in the subsurface interfere with the ability of conventional pump-and-treat systems to achieve drinking water standards for contaminated ground water. The committee reviewed information from 77 sites where conventional pump-and-treat systems are operating (see Appendix A). At 69 of the sites, cleanup goals have not yet been reached, although it is possible that they will be reached at some of these sites in the future. The apparent success of remediation at the remaining eight sites suggests that in special circumstances, cleanup in a relatively short time period (less than a decade) may be possible.

Capabilities of Pump-and-Treat Systems

The performance of pump-and-treat systems depends directly on site conditions and contaminant chemistry. As the complexity of the site increases, the likelihood that the pump-and-treat system will meet drinking water standards decreases. Table ES-1, developed by the committee and taken from Chapter 3 of this report, shows the relative ease of ground water cleanup as a function of contaminant chemistry and subsurface hydrogeology. The committee categorized the 77 sites listed in Appendix A according to the rating system shown in this table. The conditions categorized as 1 represent those that will be easiest to remediate, while those categorized as 4 will pose the greatest technical challenge, as shown by the committee's review of the 77 sites:

- *Cleanup of sites in category 1:* At sites with conditions categorized as 1 according to the table, well-designed pump-and-treat systems generally should be able to restore the ground water to drinking water standards. Such ideal site conditions are rare in the group shown in Appendix A. For example, of the 77 sites listed, only two are categorized as 1; the pump-and-treat system reached cleanup goals at one of these sites, a service station where gasoline leaked.
- *Cleanup of sites in category 2*: Cleanup of sites in category 2 to drinking water standards is also possible but is subject to greater uncertainties than at sites in category 1. For example, 14 of the sites in Appendix A are in category 2, but cleanup goals have yet to be achieved at 10 of these sites, although it is conceivable that goals will be reached in the future.
- *Cleanup of sites in category 3*: Cleanup of sites in category 3 to drinking water standards is possible but is subject to significant uncertainties; partial cleanup may be a more realistic scenario for many such sites. For example, of the 29 sites in Appendix A in category 3, cleanup goals have been achieved at only three. All three sites were contaminated with gasoline, which biodegrades relatively rapidly, a characteristic that may have accelerated cleanup.
- *Cleanup of sites in category 4*: Cleanup of sites in category 4 to drinking water standards is unlikely. However, containing the contamination is likely to be possible at such sites. Cleanup goals have not been achieved at any of the 42 sites categorized as 4 in Appendix A.

Table ES-1 provides a useful framework for comparing the relative effectiveness of pump-and-treat systems for cleaning up sites with differ

TABLE ES-1 Relative Ease of Cleaning Up of Contaminated Aquifers as a Function of Contaminant Chemistry and Hydrogeology

	Contaminant Chemistry					
Hydrogeology	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved	Strongly Sorbed, Dissolved (degrades/ volatilizes)	Strongly Sorbed, Dissolved	Separate Phase LNAPL	Separate Phase DNAPL
Homogeneous, single layer	1[a]	1-2	2	2-3	2-3	3
Homogeneous, multiple layers	1	1-2	2	2-3	2-3	3
Heterogeneous, single layer	2	2	3	3	3	4
Heterogeneous, multiple layers	2	2	3	3	3	4
Fractured	3	3	3	3	4	4

[a] Relative ease of cleanup, where 1 is easiest and 4 is most difficult.

ent hydrogeologic and contaminant characteristics. However, it is important to realize that the categories in the table are based on the experience of committee members and a review of preexisting data for sites shown in Appendix A, not on new quantitative analyses. Even more important, the feasibility of cleanup may vary across the site. A single site may contain some regions where difficult-to-extract contaminants remain and continue to dissolve into the ground water and other regions where chemicals are primarily dissolved and no significant long-term contaminant sources are present. The part of the site containing primarily dissolved contaminants might fit category 1 or 2 according to Table ES-1, while the part of the site containing entrapped sources of contamination might fit category 3 or 4. Finally, when using a framework such as Table ES-1, it is important to realize that to some extent the feasibility of ground water cleanup depends on the cleanup goals. Returning the ground water to drinking water standards may not be possible at many sites. However, reaching less stringent goals—such as cleaning up areas containing dissolved contaminants and installing containment systems around areas with undissolved contaminants that cannot be removed—may be possible at most sites.

Cleanup Times for Pump-and-Treat Systems

Remediation by pump-and-treat systems is a slow process. Simple calculations for a variety of typical situations show that predicted cleanup times range from a few years to tens, hundreds, and even thousands of years. Some have advocated that ground water cleanup should be considered technically impracticable when the cleanup time is very long. Given the complex policy implications of this issue, the committee defers to the expert agencies in deciding what, if any, limits to set on cleanup time. However, the committee believes that it is important for regulators to recognize that to some extent, cleanup time can be influenced by system design. A system pumping at very low rates may have a very long predicted cleanup time, while one pumping at higher rates may have a shorter predicted cleanup time. In considering the issue of cleanup time, regulators must also be aware that estimating the cleanup time is difficult and is subject to a large number of uncertainties; typical methods used to calculate cleanup time often result in underestimates because they neglect processes that can add years, decades, or even centuries to the cleanup.

CAPABILITIES OF ENHANCED PUMP-AND-TREAT AND ALTERNATIVE TECHNOLOGIES

Numerous innovative technologies exist that have the potential to improve significantly the efficiency of ground water cleanups, especially when technologies suited to specific types of contaminants or specific hydrogeologic environments are combined. While no known technology can ensure the achievement of health-based cleanup goals at complex sites, these innovations nevertheless have the potential to increase the effectiveness and reduce the costs of ground water cleanup. Some innovative technologies—including soil vapor extraction, air sparging, and in situ bioremediation of petroleum products—are already being implemented. However, the use of innovative cleanup methods has been limited by technical, institutional, and economic barriers. As a result, conventional pump-and-treat systems are used at approximately three-quarters of sites with contaminated ground water.

For this report, the committee divided innovative technologies into two categories: enhanced pump-and-treat systems, which require the pumping of fluids, and alternative technologies, which do not require pumping.

Enhanced Pump-and-Treat Systems

Conventional pump-and-treat systems pump relatively large volumes of water with relatively low contaminant concentrations. Because of the slow rates of contaminant desorption and dissolution, these systems must displace many volumes of aquifer water to flush out contaminants. Conventional pump-and-treat systems are therefore an inherently inefficient method for removing contaminants, even if they are effective in some cases. The enhanced pump-and-treat systems listed in Table ES-2 improve the efficiency of contaminant removal and lessen pumping requirements under certain conditions. These technologies can enhance contaminant removal and destruction compared to conventional systems, but each requires pumping fluids (water, air, or water solutions) through the subsurface and will therefore have some of the same limitations as conventional pump-and-treat systems.

Alternative Technologies

Conventional pump-and-treat systems and the enhancements listed in Table ES-2 require a continuous energy input for pumping water or air. The alternative approaches listed in Table ES-3 do not require a continuous energy input and therefore may be less costly. These meth

TABLE ES-2 Enhanced Pump-and-Treat Systems

Technology	Description	Application	Limitations
Demonstrated technologies[a]			
Soil vapor extraction	Flushes air through soil above the water table	Extracts volatile contaminants above the water table	Difficulty flushing zones of low permeability and removing contaminants bound to soils
In situ bioremediation—hydrocarbons	Pumps materials through the subsurface to stimulate growth of organisms that biodegrade contaminants	Removes petroleum products and derivatives above and/or below the water table	Difficulty delivering growth-stimulating materials to zones of low permeability; slowed by presence of NAPLs; difficulty delivering adequate oxygen to the organisms
Bioventing	In situ bioremediation for zones above the water table—pumps air through the soil to stimulate growth of organisms that biodegrade contaminants	Removes petroleum products and derivatives above the water table	Similar to those for soil vapor extraction; also, adding nutrients in aqueous solution may inhibit air movement and affect sows load-bearing capacity
Developing technologies[b]			
Pulsed or variable pumping	Varies the pumping rate to allow contaminants to dissolve, desorb and/or diffuse from stagnant regions	May improve removal efficiency for sites with NAPLs and other residual contaminants	Increases cleanup time because of reduced pumping rate; other limitations similar to those of conventional pump-and-treat systems
In situ bioremediation—chlorinated solvents	Pumps materials through the subsurface to stimulate growth of organisms that biodegrade contaminants	Removes chlorinated solvents above and/or below the water table	Similar to those for in situ bioremediation of petroleum hydrocarbons; also, possible accumulation of hazardous intermediate compounds

Technology	Description	Application	Limitations
In situ bioremediation—metals	Pumps materials through the subsurface to stimulate growth of organisms that change the chemical form of metals	Dissolves metals to facilitate extraction or immobilizes them to prevent spreading	Similar to those for the other forms of in situ bioremediation
Air sparging	Injects air below the water table and captures it above the water table	Extracts volatile contaminants; promotes bioremediation	Difficulty flushing low-permeability zones; difficulty operating at depths below approximately 10 meters; difficulty extracting multicomponent mixtures
Steam-enhanced extraction	Injects steam above and/or below the water table	Volatilizes contaminants	Difficulty volatilizing contaminants from low-permeability zones
In situ thermal desorption	Adds heat above the water table by Joule heating, radio frequency heating, or other means	Improves removal of contaminants with low volatility above the water table	Difficulty distributing heat evenly throughout the contaminated zone
Soil flushing	Flushes surfactants or cosolvents below the water table	Enhances recovery of contaminants with low water solubility	Similar to those of conventional pump-and-treat systems; possibility that chemical additives may adversely affect the subsurface
In situ chemical treatment	Injects chemicals to transform contaminants in place	Chemically transforms contaminants into less hazardous products	Difficulty delivering chemicals to low-permeability zones; possibility that chemical reactions may adversely affect the subsurface; slow reaction rates

[a] For demonstrated technologies, a substantial amount of performance data exists.

[b] Developing technologies require more controlled field studies and large-scale site trials to generate reliable performance data.

TABLE ES-3 Alternative Technologies

Technology	Description	Application	Limitations
Intrinsic bioremediation	Allows natural contaminant biodegradation to occur without human intervention other than careful monitoring	May remove easily degraded contaminants such as petroleum products under proper conditions	Lack of operating history for judging effectiveness
Physical containment	Contains contamination with cutoff walls, caps, or liners, or by solidifying soil	Can prevent off-site contaminant migration and improve control of pump-and-treat systems	Long-term reliability uncertain
In situ reactive barriers	Treat contaminated water as it passes through a physical barrier containing reactive chemicals, organisms, or activated carbon	Can treat a variety of contaminants by chemical, physical, or biological removal	Pilot tested but not yet tested for full-scale operation

ods show promise, but they are in the development stage, and their long-term effectiveness has not yet been demonstrated. In addition, some of these methods contain, rather than clean up, the contamination, and the methods that do result in cleanup may be much slower than the more energy-intensive approaches.

Barriers to Implementing Enhancements and Alternatives

A variety of barriers have discouraged those involved in ground water cleanup from assuming the risks associated with using innovative technologies that lack proven track records. The most significant barriers include the following:

- allocation of liability if a technology fails;
- inability to raise sufficient capital for successful commercialization;
- lack of vendors for some innovations;
- federal regulations specifying that any contractor involved in the selection or testing of a technology is ineligible for construction;
- lack of testing facilities;
- lack of cost and efficiency information;
- lack of adequate technical expertise among consultants and regulators; and
- the requirement to construct a pump-and-treat system if the innovative technology fails to achieve cleanup goals.

While the Environmental Protection Agency (EPA), the Department of Energy, the Department of Defense, and others are implementing programs to remove these barriers, the cumulative effectiveness of these efforts is unknown. Mutual risk sharing between the government and private parties would encourage greater use of innovative technologies.

CHARACTERIZING SITES FOR GROUND WATER CLEANUP

The inability of pump-and-treat systems to reach drinking water standards at many sites to date is not just a function of site complexity and technical limitations; it is also a result of insufficient or inaccurate characterization of the problem prior to cleanup. At several sites the committee reviewed, the cleanup systems failed to contain the contamination (much less clean it up) because of poor characterization of the extent of contamination and the locations of contaminant sources. The lack of adequate characterization has often occurred even after huge sums have been spent and considerable time has elapsed in characterizing the site. Thus, whether the technology is conventional or innovative, the design of a strategy for characterizing the site is as important as the design of the cleanup system itself. In brief, site characterization studies must provide the following information:

- the extent of ground water contamination, both horizontal and vertical;
- approximate locations of long-term sources of contamination, including sources near the surface where the contamination originated and sources that developed along the path of contaminant migration (such as residual NAPLs, pools of NAPLs, and metal precipitates);
- characteristics of the hydrogeologic setting important to the design of the remediation system and to the prediction of contaminant migration; and
- data to estimate the site's restoration potential using a method such as that represented in Table ES-1.

In characterizing a site with contaminated ground water, it is important to realize that due to the complexity of the subsurface and the difficulty of observing it, perfection in site characterization is unachievable. The performance of the remediation system itself will provide additional, extremely valuable information on site characteristics that may not be possible to obtain in any other way. Data collection should continue throughout the life of the ground water cleanup system, and these data should be analyzed regularly to determine whether they are consistent with the current understanding of the site and, if not, whether changes in the remediation plan are necessary.

SETTING GOALS FOR GROUND WATER CLEANUP

This report documents that the ability of technology to restore contaminated ground water to drinking water standards is uncertain at many sites. Nevertheless, regulations under the Comprehensive Environmental Response, Compensation, and Liability Act (the Superfund law), the Resource Conservation and Recovery Act (RCRA), and similar state laws require that the water be cleaned up, usually to drinking water standards. The use of drinking water standards as cleanup goals has been questioned by many in the regulated community and others. Critics have long contended that options such as containing the contamination can protect public health, as long as the water in the containment zone is either restricted for use or treated with appropriate technology prior to use. The criticism of using drinking water standards as cleanup goals has increased because of the technical evidence that reaching these standards may not be possible in reasonable time frames at many sites. On the other hand, some people contend that drinking water standards—or stricter requirements—should be maintained as cleanup goals regardless of the capabilities of technology for two reasons: to provide an incentive against further pollution and to encourage development of improved cleanup technologies.

In the debate over ground water cleanup goals, many alternative cleanup goals have been suggested. In broad terms, these alternatives are the following:

- *complete restoration*, or removal of all traces of contamination;
- *nondegradation*, or removal of contamination to natural background levels or to detection limits;
- *health-based standards*, such as the drinking water standards used as cleanup goals at most sites today;
- *technology-based standards*, which would require cleanup to the capabilities of the best available technology;
- *partially restricted use standards*, meaning cleanup to allow nonpotable uses such as irrigation; and
- *containment*, meaning that contamination remains in place but systems are installed to prevent contaminant migration off site and, if necessary, to treat the ground water at the point of use.

Each of these options reduces the risk of deleterious impacts due to ground water contamination. However, the magnitude of this risk reduction and the associated economic benefits are difficult—if not impossible—to quantify. The professional community does not agree on the magnitude of health impacts of ground water contamination from hazardous waste sites for many reasons, the most important of which are difficulties in determining the extent to which humans have been and will be exposed to contamination, limitations in extrapolating toxicological effects observed in animal studies to human populations, and uncertainties in the science of epidemiology. Likewise, the total economic value of restoring contaminated ground water is unknown. Thus, a high degree of uncertainty exists, making quantitative assessment of the risks and benefits of various ground water cleanup goals extremely difficult.

Like society as a whole, the committee had diverse views about which of the various alternative cleanup goals is most appropriate and whether the current approach of requiring cleanup to drinking water standards at a large number of sites should be changed. However, the committee strongly believes that because existing ground water cleanup goals cannot be attained in reasonable time frames (decades) at a large number of sites with current technologies, regulators should set short-term objec tives for these sites based on the capabilities of current technology. While the long-term goals need not necessarily change, interim objectives are needed to acknowledge current technological limitations. In the recommendations below, the committee outlines a scenario for dividing contaminated sites into three categories, some of which would require interim objectives and some of which would not.

CONCLUSIONS AND POLICY RECOMMENDATIONS

In summary, the committee found that at many sites requiring ground water cleanup, some areas will remain contaminated above drinking water standards for the foreseeable future even when the best available technologies are used. However, the committee also found that cleaning up large portions of these sites is possible, even if limited areas remain contaminated. In addition, a wide range of developing technologies has the potential to improve the effectiveness of ground water remediation. Nevertheless, there are limits to what technology can accomplish, and existing regulatory requirements for ground water cleanup do not adequately account for these limits. The following recommendations provide guidance for modifying policies to reflect the key technical conclusions of this report.

Complexity of the Subsurface

***Conclusion*. Subsurface environments and many common contaminants have properties that interfere with decontamination efforts—regardless of the technology chosen**. These properties make finding the contaminant sources difficult, increase contaminant spreading, and cause contaminants to accumulate in zones from which they are difficult to extract. The complex interactions occurring in the subsurface are not fully understood, and therefore the effect of subsurface and contaminant properties on the ability to clean up ground water is often difficult to quantify.

***Recommendation 1.* The committee recommends that the EPA systematically evaluate its experience in cleaning up sites to improve understanding of factors that prevent achievement of health-based ground water cleanup goals** . The committee suggests that the EPA undertake an annual review of selected pump-and-treat systems based on the experience of EPA project managers throughout the United States. The analysis would be similar to a study of pump-and-treat systems at 24 sites that the EPA conducted in 1992 but would incorporate some of the improve ments in analysis suggested in this report (for example, evaluating the number of pore volumes extracted per year).

Recommendation 2. **The committee recommends that the EPA establish a standardized, centralized, broadly accessible repository for site information**. Currently, accessing the large amount of existing site data from completed and ongoing ground water remediation projects is extremely difficult. To increase the accessibility of data, the EPA could develop suggested formats for collection and analysis of site-specific information. The EPA could also establish an easily used, publicly accessible data base for sites where ground water cleanup is under way.

Performance of Conventional Pump-and-Treat Systems

Conclusion. **The ability of conventional pump-and-treat systems to reach health-based cleanup goals for contaminated ground water is highly site specific**. Although cleanup is possible at some sites, properties of the subsurface and the contaminants may make restoring contaminated ground water to drinking water standards technically infeasible with current technology in reasonable time frames (decades) at a large number of sites.

Conclusion. **Although restoring the total volume of contaminated ground water to health-based standards may not be feasible at many sites, properly designed pump-and-treat systems still provide important benefits, including containment of the contamination, retraction of the plume of dissolved contaminants, and removal of some contaminant mass from the subsurface**. Most sites with contaminated ground water contain two types of problem areas: (1) source areas and (2) dissolved plume areas. Conventional pump-and-treat systems may be effective for cleaning up plumes of dissolved contamination. However, this technology alone will be ineffective for restoring source areas such as those with significant amounts of residual NAPLs, pools of NAPLs, or metals that have precipitated.

Recommendation 1. **The committee recommends that the EPA's policy for determining whether ground water cleanup is feasible provide for the categorization of contaminated sites into three groupings corresponding to the complexity of the site**. At one extreme is a group of sites generally represented by category 1 in Table ES-l; cleaning up sites in this group to meet health-based goals should be possible with current technology. At the other extreme is a group of sites generally represent ed by category 4 in Table ES-l; current technology is highly unlikely to restore sites in this group to health-based standards in reasonable time frames (decades), and therefore these sites may warrant permanent infeasibility waivers with the concomitant selection of a new protective long-term goal. In the middle is a group of sites generally represented by categories 2 and 3 in Table ES-l; for sites in this group, attaining health-based ground water cleanup goals will be difficult or unlikely with current technology but not necessarily impossible over the long term as technology improves. The long-term cleanup goals for sites in this middle group should be temporarily superseded by interim objectives reflecting the capabilities of existing technologies. (The correlation of the three groupings with the categories of Table ES-1 is only approximate.)

Recommendation 2. **The committee recommends that the EPA assess and develop guidance on institutional strategies for preventing public exposure to contamination over the long term at sites where reaching health-based cleanup goals is infeasible with the best available technologies**. An institutional structure capable of lasting for several generations will be needed to oversee the large number of sites at which complete cleanup is infeasible with current technologies.

Recommendation 3. **The committee recommends that the EPA and other agencies identify and eliminate disincentives to early implementation of ground water remedial actions**. Ground water cleanup is more likely to be effective if initiated early. Allowing responsible parties to commit to only one phase of cleanup at a time instead of requiring them to agree to the entire remedy all at once might provide an incentive for early cleanup; the EPA should pilot test this concept to determine whether it results in faster cleanups or whether it slows the process because of the additional negotiations it would require.

Capabilities of Innovative Technologies

Conclusion. **Although innovative technologies for ground water cleanup are subject to many of the same limitations as conventional pump-and-treat systems, many of these technologies can improve the efficiency of ground water cleanup efforts**. However, important technical, economic, and institutional barriers have slowed their development.

Recommendation. **The committee recommends that Congress investigate the possibility of charging an annual "infeasibility fee" to public and private responsible parties at sites where attaining health-based standards is not presently feasible**. Congress could investigate various options for appropriating the funds collected from this fee. The committee sees two options as having special merit. One possibility is to use some of the funds to create an applied ground water research fund to pay for a strong research program for improved ground water cleanup techniques. The other possibility is to use some of the funds to encourage use of innovative cleanup technologies by reimbursing responsible parties for testing these technologies in certain circumstances. Under this scheme, an expert panel would approve use of an innovative technology. In the event that the innovative technology fails to achieve its intended goal and the responsible party is required to construct a backup technology, the responsible party would be able to recoup some or all of its losses from the infeasibility fee fund. If the innovative technology worked, the fund would not subsidize the project. Initially the fund might apply only to Superfund sites, but if successful it might be extended to other types of sites.

Characterizing Sites

***Conclusion.* Optimization of the site characterization and management process could improve the effectiveness of ground water cleanups**. The poor performance of ground water cleanup systems is not solely a function of site complexity and technical limitations; it can also result from insufficient or inaccurate characterization of the problem prior to cleanup, leading to flawed design of the cleanup system.

***Recommendation 1.* The committee recommends establishment of expert panels to evaluate site characterization, remedy selection, and remedy performance at complex sites**. As discussed in this report, a large number of contaminated sites fit category 2 or 3 in Table ES-l, and thus design of cleanup systems for many sites will be subject to considerable uncertainties. At present, federal and state regulatory agencies have an insufficient number of technically trained staff members to address the multitude of complex sites. While not a substitute for hiring and retaining technically trained staff, expert panels could provide guidance in addressing the often difficult technical choices at these sites. The panels could also evaluate proposals for using innovative technologies that would be covered under the infeasibility fee fund discussed above. The panels could be funded by the infeasibility fee and/or by charging those responsible for cleanup at sites where the panels provide advice. The EPA should assess the feasibility of such an expert panel approach to resolving problems at complex sites.

***Recommendation 2.* The committee recommends that the EPA prepare**

new guidance documents that will lead to improved optimization of the hazardous waste site characterization process and explicitly address factors that will determine whether health-based cleanup goals are practicable. The EPA should revise existing site characterization guidance for the Superfund and RCRA programs to link the collection of specific characterization information with early action implementation steps. New guidance documents are needed to ensure that factors that may limit the ability to achieve health-based ground water cleanup goals are recognized as early as possible.

Setting Cleanup Goals

Conclusion. **Existing procedures for setting ground water cleanup goals do not adequately account for the diversity of contaminated sites and the technical complexity of ground water cleanup**. Whether goals established under existing procedures adequately protect public health and the environment, or whether they are overprotective or underprotective, is uncertain, as are the costs to society when these goals cannot be achieved.

Recommendation 1. **Although the committee recognizes that different agencies must operate under different authorities, all regulatory agencies should recognize that ground water restoration to health-based goals is impracticable with existing technologies at a large number of sites**. The complexities and limitations that this report describes are functions of the nature of the contaminants and the hydrogeology of the site, not of the identity of the agency or private party attempting to address the problem or the statutory authority or regulatory agencies involved. The EPA and other regulatory agencies should establish consistent mechanisms for deciding the restoration potential of contaminated sites, as indicated by the approach outlined in this report.

Recommendation 2. **The committee recommends that the EPA expand its efforts to inform the public about limitations of existing technologies and capabilities of innovative technologies**. From the perspective of the affected public, the Superfund program has had limited success in responding to community concerns at many sites. Although the ground water cleanup problem is technically complex, the implications of site complexities as well as the promise that innovative technologies hold to improve cleanup should be explained to the affected public. The committee recommends that the EPA include expanded efforts at community relations within the technical impracticability waiver process and revise its community relations guidance documents to include issues of technical impracticability.

1

The Ground Water Cleanup Controversy

At hazardous waste sites nationwide, industries and government agencies are spending millions of dollars trying to clean up contaminated ground water. These cleanups are required by federal and state laws passed in the last two decades—mostly in response to public concern that drinking contaminated ground water may cause cancer or other illnesses. The laws require that, in most instances, the contaminated ground water be restored to a condition that meets state and federal drinking water standards.

Recently, some have begun to question current approaches to ground water cleanup. Evidence suggests that restoring contaminated ground water to drinking water standards poses considerable technical challenges that may sometimes be insurmountable. For example, at one New Jersey site, a computer manufacturing company spent $10 million removing toxic solvents from ground water, but not long after the cleanup system was shut down the solvent concentrations in some locations returned to levels higher than before cleanup began (see Box 1-1). This company's effort and others like it have raised concern about whether the amount spent to clean up ground water is proportionate to the benefits society receives. Businesses and government agencies paying for the cleanups are calling for reconsideration of whether returning all contaminated ground water to drinking water standards is a realistic goal. At the same time, public interest groups are advocating maximum protection of the public's right to a safe water supply, both in places where the ground water is currently used for drinking and in places where it might be used in the future.

BOX 1-1 GROUND WATER CLEANUP IN SOUTH BRUNSWICK TOWNSHIP, NEW JERSEY: SYMBOL OF A BROADER PROBLEM

In 1977, toxic solvents were discovered in one of the three main wells supplying drinking water to South Brunswick Township in New Jersey. The attempt to remove this contamination has become a symbol of the broader problems with ground water cleanup nationwide.

Government investigators traced the contamination to a nearby computer manufacturing facility. The facility owner agreed to clean up the site and installed a series of pumps to extract the polluted water and eliminate the contaminants. Over the next six years, the company spent $10 million pumping out water and treating it. At the end of this period, the water in the well appeared to meet drinking water standards. However, within three years of when the company shut down the treatment system, contaminant levels in some areas near the site rose above the drinking water standards again. In one location, the contaminant concentration was twice as high as before cleanup began.

Technical experts called to the site traced the return of contamination to solvents that had migrated underground and lodged in subsurface geologic formations. These solvents were dissolving slowly into the clean ground water flowing around them. The initial pumping had removed most of the dissolved solvents but had not removed the undissolved solvents, which were recontaminating the clean ground water. As a result, the site owners had to resume pumping to prevent the contamination from spreading. In addition, they installed a million-dollar treatment system at the wellhead to provide clean drinking water.

This case is often cited as an example of the failure of conventional ground water cleanup technologies. However, as will be explained in Chapter 3, scientists have now recognized that a primary reason for the return of contamination at this site was the failure to install a containment system around the undissolved solvents. While the water within the boundaries of a containment system would not have met potable standards, the containment system would have isolated the solvents and prevented recontamination of most of the ground water. (For technical details about this site, see Box 3-3 in Chapter 3.)

REFERENCES: Stipp, 1991; EPA. 1989.

This report provides a comprehensive evaluation of the technical and policy dilemmas surrounding current ground water cleanup efforts. It assesses whether conventional and innovative cleanup technologies are capable of restoring contaminated ground water to drinking water quality. It reviews physical and chemical factors that impede cleanup regardless of the technology chosen. It discusses factors other than technical feasibility—human health, ecology, and costs—that are critical components in the ground water cleanup debate. And it provides advice on how to set policies for ground water cleanup that reflect the capabilities of technology while still protecting human health and the environment.

The report was prepared by the Committee on Ground Water Cleanup Alternatives, appointed by the National Research Council. The National Research Council appointed the committee to prepare this report because of widespread concern in the scientific community that the technical complexities of ground water cleanup, which are becoming increasingly apparent, may call for changes in ground water cleanup policies. The committee consisted of 19 experts in ground water cleanup technology, policy, and law representing a balance of viewpoints; members came from industry, government, environmental groups, academia, and con-suiting firms. The committee met nine times over a two-year period to review technical information and deliberate policy issues. The committee called upon the wider technical community to provide data related to the capabilities of ground water cleanup technologies. In addition, the committee invited people with a stake in ground water cleanup—citizens whose lives have been affected by contamination and industries that have invested large sums in cleanup—to present their viewpoints at committee meetings.

HISTORY OF GROUND WATER CLEANUP

Ground water contamination is relatively new on the nation's list of recognized environmental problems. Early environmental legislation focused on the more obvious problems: air and surface water pollution. For example, in Pittsburgh and St. Louis, air pollution was once so severe that drivers had to use headlights in the middle of the day during the winter. Along the Cuyahoga River near Cleveland, pollution was so extreme that the river caught fire—once in 1936, twice in the 1950s, and again in 1969. It was easy for the public to recognize the need to clean up surface water and air, and Congress enacted legislation to protect these resources as early as the 1940s and 1950s.[1] Ground water, however, was long believed to be naturally protected by the layers between the earth's surface and the water table, which people believed would filter out contaminants. The problem of ground water contamination did not receive widespread public recognition until the 1970s, when contamination episodes began receiving notice in the popular press. In the most publicized of these incidents—known as Love Canal—President Carter declared an emergency in Niagara Falls, New York, because of health concerns linked to ground water contamination, and many homes were evacuated.

Legislation

In 1980, prompted by the Love Canal incident, Congress for the first time made ground water cleanup a high national priority with the passage of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA), commonly known as the Superfund act.[2] CERCLA established a $1.6 billion federal fund (which has since grown to $15 billion), the Superfund, to pay for cleaning up abandoned hazardous waste sites (EPA, 1990; Guerrero, 1991). CERCLA also provided authority for the Environmental Protection Agency (EPA) to sue parties responsible for the contamination to recover cleanup costs; these groups have since become known as "potentially responsible parties."

In 1984, Congress broadened the nation's ground water cleanup program by amending the Resource Conservation and Recovery Act (RCRA) to require cleanup of contamination at active facilities that treat, store, or dispose of hazardous waste. To continue handling wastes, operators of active RCRA sites must agree to clean up existing pollution. RCRA also covers cleanup of contamination from leaking underground storage tanks containing petroleum products and other organic liquids.

Since the passage of CERCLA and the 1984 RCRA amendments, virtually all states have enacted laws granting them authority to require cleanup of sites with contaminated ground water (EPA, 1994). CERCLA and RCRA have strongly influenced the state laws, although some state laws are more stringent than the federal versions.

Early Research

Despite the limited public awareness of ground water contamination prior to 1980, some scientists had begun studying the problem several generations before CERCLA's passage. The earliest ground water contaminant recognized by scientists was human sewage (for a historical perspective, see Mallman and Mack, 1961). In 1854, a London doctor linked a cholera epidemic to contamination of drinking water supplies—including a neighborhood water well—with sewage. In Switzerland in 1872, a typhoid epidemic was traced to sewage contamination in a river that recharged a town's ground water supply. In 1909, two German researchers ran a series of controlled tests to investigate bacterial migration underground and established that bacteria could travel with ground water from one well to another.

As chemical use increased after World War II, isolated reports of chemical contamination of ground water appeared. In 1947, for example, hexavalent chromium from electroplating wastes was discovered in a Michigan ground water supply after homeowners complained that their water had turned yellow (Deutsch, 1961). Relatively common after the war were complaints of foaming ground water—from contamination with the surfactant alkyl benzene sulfonate that had leaked from septic systems. Recognizing the increasing potential for chemical contamination of ground water, the American Water Works Association created a task force of scientists, the Task Group on Underground Waste Disposal and Control, to study the problem in the early 1950s. The task group's first report, issued in 1952, documented that very few states were aware of the potential for ground water contamination (Middleton and Walton, 1961).

Workers sampling the contents of drums at a hazardous waste site. Courtesy of Clean Sites, Inc.

Though scientists recognized the ground water contamination problem long before the general public and government agencies, until recently only a few researchers were studying ground water cleanup technologies. At a 1961 conference on ground water contamination sponsored by the U.S. Public Health Service, one speaker remarked that because of the lack of trained ground water scientists, "there are few fields in which our ignorance is so profound" (McKee, 1961). There has been a dramatic increase in the number of ground water scientists since CERCLA's passage in 1980. Nevertheless, many of the same problems that researchers identified at the 1961 conference as key to understanding ground water contamination remain to be answered today—questions such as how geology, soil type, contaminant chemistry, and microbial activity affect the spread of contamination (McKee, 1961; McCarty, 1990).

Sources of Contamination

The primary type of ground water contamination of concern in the United States today is contamination from hazardous chemicals. The use of such chemicals is ubiquitous: substances found in contaminated ground water are used in everything from lumber treating to electronics manufacturing, fuels, food production, and agricultural chemical synthesis. When used, stored, or disposed of on land, these chemicals may eventually migrate to the ground water below.

Common causes of ground water contamination are accidental spills; intentional dumping; and leaks in storage tanks, industrial waste pits, and municipal or industrial landfills. In addition, significant quantities of contaminants may be released through routine activities such as washing of engines and rinsing of tanks. Standard application of agricultural chemicals is also a source of ground water contamination. For example, the EPA estimates that about 1 percent of all drinking water wells in the United States exceed a health-based limit for pesticides (EPA, 1992b). Although pesticide application is a potentially important source of contamination, this report focuses on the point sources of contamination found at hazardous waste sites and other sites where hazardous chemicals have leaked or spilled into the environment. Because point sources affect only a limited area, they present a more manageable problem than contamination of large areas of land with agricultural chemicals, which might far exceed the limits of cleanup technologies. Table 1-1 ranks chemicals found at hazardous waste sites in order of prevalence and gives common sources for these chemicals.

MAGNITUDE OF THE PROBLEM

Because of the widespread use and disposal of hazardous chemicals on land, the ground water contamination problem is potentially very large. However, estimates of the total number of contaminated sites have varied. In general, existing estimates have included seven categories of sites:

Excavation of a leaking underground storage tank. Courtesy of the Johns Hopkins University, Department of Geography and Environmental Engineering.

TABLE 1-1 The 25 Most Frequently Detected Ground Water Contaminants at Hazardous Waste Sites

Rank	Compound	Common Sources
1	Trichloroethylene	Dry cleaning; metal degreasing
2	Lead	Gasoline (prior to 1975); mining; construction material (pipes); manufacturing
3	Tetrachloroethylene	Dry cleaning; metal degreasing
4	Benzene	Gasoline; manufacturing
5	Toluene	Gasoline; manufacturing
6	Chromium	Metal plating
7	Methylene chloride	Degreasing; solvents; paint removal
8	Zinc	Manufacturing; mining
9	1,1,1-Trichloroethane	Metal and plastic cleaning
10	Arsenic	Mining; manufacturing
11	Chloroform	Solvents
12	1,1-Dichloroethane	Degreasing; solvents
13	1,2-Dichloroethene, trans	Transformation product of 1,1,1-trichloroethane
14	Cadmium	Mining; plating
15	Manganese	Manufacturing; mining; occurs in nature as oxide
16	Copper	Manufacturing; mining
17	1,1-Dichloroethene	Manufacturing
18	Vinyl chloride	Plastic and record manufacturing
19	Barium	Manufacturing; energy production
20	1,2-Dichloroethane	Metal degreasing; paint removal
21	Ethylbenzene	Styrene and asphalt manufacturing; gasoline
22	Nickel	Manufacturing; mining
23	Di(2-ethylhexyl)phthalate	Plastics manufacturing
24	Xylenes	Solvents; gasoline
25	Phenol	Wood treating; medicines

NOTE: This ranking was generated by the Agency for Toxic Substances and Disease Registry using ground water data from the National Priorities List of sites to be cleaned up under CERCLA. The ranking is based on the number of sites at which the substance was detected in ground water.

1. closed or abandoned hazardous waste sites requiring cleanup under CERCLA;
2. active hazardous waste treatment, storage, and disposal facilities requiring cleanup under RCRA;
3. facilities with leaking underground storage tanks (used for storing gasoline and other fuels, as well as various chemicals used in manufacturing);
4. sites managed by the Department of Energy (DOE) (contaminated with the byproducts of nuclear weapons production);

5. sites managed by the Department of Defense (DOD) (contaminated with a variety of substances, including remnants of conventional weapons manufacturing and fuels used in the nation's defense fleet);
6. federal facilities other than those managed by DOD and DOE (such as abandoned mining sites owned by the Forest Service, grain storage facilities operated by the Commodity Credit Corporation, and research laboratories managed by a variety of federal agencies); and
7. sites managed under state laws similar to CERCLA and RCRA.

Table 1-2 shows estimates of the number of sites in each of these categories as compiled from three different sources. As the table shows, the total number of sites where ground water may be contaminated is likely to be in the range of 300,000 to 400,000. However, it is extremely impor

TABLE 1-2 Number of Hazardous Waste Sites Where Ground Water May Be Contaminated

	Source of Estimate		
Site Category	EPA, 1993	Russell et al., 1991	Office of Technology Assessment, 1989
CERCLA National Priorities List	2,000	3,000	10,000
RCRA corrective action	1,500-3,500	NA	2,000-5,000
Leaking underground storage tanks	295,000	365,000	300,000-400,000
Department of Defense	7,300 (at 1,800 installations)	7,300	8,139
Department of Energy	4,000 (at 110 installations)	NA	1,700
Other federal facilities	350	NA	1,000
State sites	20,000	30,000	40,000
Total	330,150-332,150	NA	363,000-466,000

NOTE: The numbers presented in this table are estimates, not precise counts. In addition, at some of these sites, ground water may not be contaminated. For example, the EPA (1993) estimates that ground water is contaminated at 80 percent of CERCLA National Priorities List sites. There is also some overlap in site categories. For example, 7 percent of RCRA sites are federal facilities, and 23 DOE sites are on the CERCLA National Priorities List (EPA, 1993). NA indicates that an estimate comparable to the other estimates is not available from this source.

tant to recognize that the magnitude of the contamination problem varies widely at these sites. Ground water contamination from a single leaking underground storage tank at a gas station affects a relatively small area and, as discussed in Chapter 3, is relatively easy to clean up. On the other hand, contamination at CERCLA sites and at major DOE installations may be widespread and very difficult to clean up. The differences between these types of sites are illustrated by the costs of cleaning them up. According to recent EPA data, the average cost of cleaning up a leaking underground storage tank is $100,000,[3] while the average cost of cleaning up a Superfund site is $27 million (EPA, 1993). By far the bulk of the sites listed in Table 1-2 are contaminated from leaking underground storage tanks. The larger sites posing the greatest hazard to public health and the environment represent a relatively small portion of the total potential number of sites.

Creosote-contaminated soil and sludges, a source of ground water contamination at a Minnesota site. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

In part because of the wide variation in contaminated sites and because the total number of sites is uncertain, estimating the total national costs of cleaning up contaminated ground water is extremely difficult. One recent, widely publicized report concluded that over the next 30 years, the nation as a whole will spend $480 billion to $1 trillion, with a "best guess" of $750 billion, cleaning up the types of sites listed in Table 1-2 (Russell et al., 1991). With 90 million households in the nation (Industrial Economics, Inc., 1991), this represents a cost of $8,000 per household. Another recent report concluded that by the year 2000, the nation will be spending nearly $24 billion per year complying with requirements for hazardous waste and underground storage tank cleanup under RCRA and site cleanups under CERCLA (Carlin et al., 1992, p. 38). Some contest the accuracy of such cost estimates because of the high level of uncer tainty associated with the magnitude of the problem and the large number of assumptions underlying the estimates. Nevertheless, the potential enormity of the costs has fueled the debate about whether the benefits the nation will receive from ground water cleanup at hazardous waste sites justify the costs.

CAPABILITIES OF CLEANUP TECHNOLOGIES

The rate at which new contaminated sites have been discovered has far exceeded the evolution of cleanup technologies (McCarty, 1990). Almost all ground water cleanup systems currently installed and planned involve variations of a technology called "pump and treat." Pump-and-treat systems operate by pumping ground water to the surface, removing the contaminants, and then either recharging the treated water into the ground or discharging it to a surface water body or municipal sewage plant (see Box 1-2).

Once ground water has been pumped to the surface, contaminants can be removed to very low levels with established technologies used to treat drinking water and wastewater. However, pumping out the water does not guarantee that all of the contaminants have been removed from beneath the site. Contaminant removal is limited by the behavior of contaminants in the subsurface a function of contaminant characteristics, site geology, and extraction system design.

When CERCLA was passed in 1980, the nation had very little experience with ground water cleanup. The details of how hydrogeology and contaminant chemistry might affect pump-and-treat systems were being investigated by a few forward-looking scientists but were not widely known in the regulatory community. As a result, the ground water cleanup efforts of the 1980s were a series of large, relatively uncontrolled experiments in whether existing technology was capable of overcoming natural physical and chemical factors that retain contaminants in the subsurface.

The first widely recognized evaluation of how the early pump-and-treat systems performed was released by the EPA in 1989 (EPA, 1989). The EPA studied 19 sites, expanding the number to 24 in an updated study published in 1992 (EPA, 1992a). Both the original 1989 report and the 1992 update found that while pump-and-treat systems may remove significant amounts of contaminant mass and prevent contaminants from spreading, most systems have so far failed to reach cleanup goals. At many of the sites studied, the contaminant concentration decreased rapidly when the pumps were first turned on, but then it leveled off and progressed toward cleanup goals much more slowly than the designers originally predicted. A 1991 study by researchers from Oak Ridge Na

BOX 1-2 THE MANY VARIETIES OF PUMP-AND-TREAT SYSTEMS

The conventional pump-and-treat system, shown in Figure 1-1, consists of a series of wells that pump contaminated water to the surface. A surface treatment unit removes the contaminants. The treated water is disposed of through wells or sprinklers that recharge the water into the ground or through pipes linking the surface treatment unit to a lake, ocean, stream, or wastewater treatment plant.

At some sites, engineers have experimented with enhancements to augment the performance of conventional pump-and-treat systems. One type of enhancement improves the efficiency of contaminant extraction by injecting surfactants, steam, or other substances underground. A second enhancement uses air to volatilize contaminants. A third enhancement involves injection of substances that help transform the contaminants in place—chemical compounds that oxidize the contaminants, for example, or oxygen that encourages microorganisms to degrade the contaminants.

In addition to their use for ground water cleanup, pump-and-treat systems may be used to clean contaminated soil between the earth's surface and the water table (a region called the vadose zone). Vadose zone pump-and-treat systems involve flushing the soil with water (to dissolve contaminants or remove them by hydraulic force) or air (to volatilize the contaminants).

This committee has included all these enhancements under the general term "pump and treat" because all involve the pumping of fluids (either water or air). More importantly, the committee wishes to emphasize that all these enhancements are subject to the same major limiting factors that affect conventional pump-and-treat systems. As discussed later in this report, no known enhancement can completely compensate for the complexities of geology and contaminant chemistry that slow cleanup efforts.

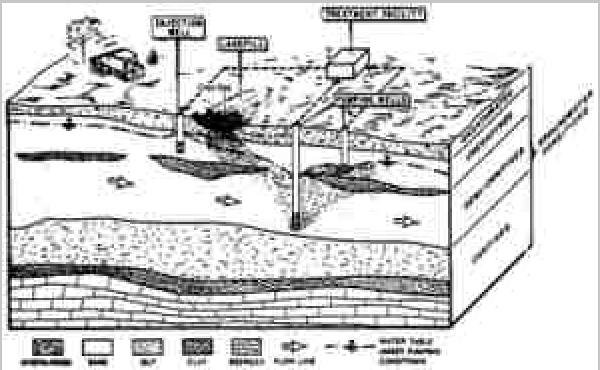
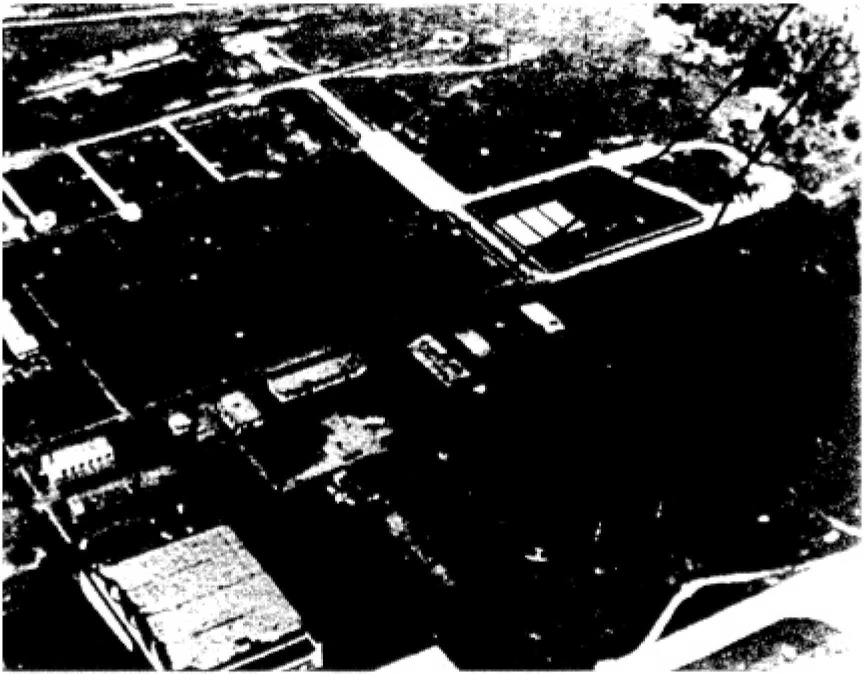


FIGURE 1-1 Example of a pump-and-treat system operating at a landfill (from Mercer et al., 1990).

tional Laboratory reached similar conclusions (Doty and Travis, 1991). Around the same time as the first EPA study, reports of the limitations of pump-and-treat systems began to receive wide notice in technical publications (see, for example, Mackay and Cherry, 1989; Travis and Doty, 1990).



Boundaries of a plume of ground water contamination originating from a spill of JP-4 jet fuel in an airline hangar (shown in the foreground). The plume is moving toward a nearby bay. Courtesy of Rice University, Department of Environmental Science and Engineering.

THE POTENTIAL CONFLICT BETWEEN TECHNOLOGY AND POLICY

The results of the studies of the late 1980s and early 1990s led many people to question whether the risk reduction that pump-and-treat systems achieve is worth their cost. Some have interpreted the studies to mean that cleaning. up ground water to health-based levels is impossible. Others are more optimistic and contend that the data are inadequate to support such an extreme conclusion, given the relatively small number of systems studied and the relatively short amount of time these systems have been operating. These people point out that the 24 systems evaluated in the 1992 EPA study had an average operating time of less than seven years.

That the ability of technology to restore contaminated ground water was in question was not known beyond a limited group of scientists when Congress enacted the major ground water cleanup laws. As a result, current ground water cleanup policies rest on the assumption that restoring contaminated ground water is technically straightforward. Regulations under CERCLA, RCRA, and their equivalents at the state level require the establishment of strict numerical concentration goals for cleanup. Under CERCLA and RCRA, cleanup goals are generally set at drinking water standards—known as "maximum contaminant levels." Under state programs, goals are sometimes stricter—such as concentrations equal to natural background levels in uncontaminated areas. In setting ground water cleanup goals, government regulators have only rarely considered whether existing technology is capable of meeting these goals.

As a result of the increasing publicity of frustrated cleanup efforts such as that described in Box 1-1, many people have criticized the existing approach to setting ground water cleanup goals. These critics contend that the setting of goals that may not be technically achievable establishes unrealistic public expectations and misuses financial resources. On the other hand, supporters of existing goals maintain that strict goals are necessary to induce the maximum level of cleanup possible and to provide the maximum level of public health protection. Supporters of existing goals also argue that these goals help encourage the development of improved technologies.

Thus, a potential for conflict has arisen between existing policies for ground water cleanup and the capabilities of existing technologies. On one hand is the desire to eliminate the health risks of ground water contamination, as mandated by law. On the other hand are reports that technology has so far been unable to reach health-based cleanup goals at many sites, despite substantial effort. Over the last few years, policy-makers in the EPA and other branches of government have recognized this potential conflict and have been reevaluating the current approach to ground water cleanup in light of new knowledge about technical limitations. This report provides information to guide these policymakers in assessing whether the nation's current ground water cleanup programs adequately reflect the capabilities of existing and emerging technologies.

NOTES

1. The first version of the Federal Water Pollution Control Act passed in 1948; the first federal air pollution legislation, providing federal grants to cities and states to study air pollution, passed in 1955.

2. Although the Resource Conservation and Recovery Act of 1976 included limited provisions for ground water cleanup at active hazardous waste sites and the Safe Drinking Water Act of 1974 called for protecting ground water from subsurface injection of waste, ground water cleanup did not receive major national emphasis until after CERCLA's passage.

3. According to the EPA (1993), the cost of cleaning up underground storage tank leaks varies widely and may be as low as $2,000 for some sites and as high as $1 million for others.

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2

Complexity of the Contaminated Subsurface

No environmental problem can be solved rationally before it has been adequately defined. This chapter presents an overview of the characteristics of contaminated ground water that must be understood in order to assess prospects for remediation. The complexities of the subsurface environment and of contaminant distribution, which are documented in this chapter, significantly complicate the cleanup task (see Box 2-1). Although this chapter focuses on factors that complicate ground water cleanup, the arguments should not be interpreted to mean that restoration of ground water is impossible on theoretical grounds. Ground water contamination by hazardous substances is by no means intractable, although at many sites it is likely to prove extraordinarily difficult, time consuming, and costly to reverse.

THE SUBSURFACE ENVIRONMENT

When contaminants enter the subsurface, they become subject to a variety of physical, chemical, and biological processes that operate beneath the ground. The design of an effective ground water cleanup system requires an understanding of these processes because they control the fate of the contaminants and the ease with which they can be extracted.

Physical Characteristics

Ground water is stored in underground formations called aquifers. There are two broad categories of aquifers: consolidated (see Figure 2-1)

BOX 2-1 COMPLEXITY OF THE CONTAMINATED SUBSURFACE: A HYPOTHETICAL EXAMPLE

Every conceivable subsurface remediation approach is subject to constraints posed by fundamental principles such as conservation of mass, conservation of energy, the theoretical limitation on energy efficiency embodied in the Second Law of Thermodynamics, and the thermodynamic relationships governing chemical and physical equilibria. Nothing in these principles precludes cleanup of contaminated sites to any desired level. However, consideration of these laws makes it evident that cleanup using presently known technology will often be extremely difficult to achieve in a reasonable period of time.

To illustrate the situation, consider a barrel of trichloroethylene (TCE) that has leaked below ground. Because the TCE disperses, it would not generally be possible to pump the chemical out in pure form; rather, the TCE must dissolve in the ground water and be removed by pumping out the water. Based on the solubility of TCE in water, more than one thousand barrels of water would have to be removed for each barrel of TCE spilled, if the water removed was saturated with TCE. In practice, however, the pumped water may contain only one-tenth or one-hundredth or one-thousandth of the amount of TCE that would be present if the water were completely saturated with TCE, because most of the water will never have been in dose enough contact to the TCE long enough to allow complete saturation. Then, for each barrel of TCE it will be necessary to pump out 10,000 or 100,000 or 1 million barrels of water. Wells placed near the TCE would speed up the process, but it is seldom possible to precisely locate the concentrated pockets of chemical contamination.

This example illustrates common elements of ground water contamination problems that greatly interfere with cleanup efforts; contaminants may be difficult to extract because they do not dissolve fully; the subsurface environment is neither simple in structure nor easy to characterize, and determining the precise location of the contamination is seldom easy.

and unconsolidated (see Figure 2-2). Unconsolidated aquifers consist of uncemented granular materials such as sand and gravel; they store water in the interstitial pore space among the grains. Consolidated aquifers consist of more or less solid rock; they store water primarily in solution channels, fractures, and joints (although in material such as sandstone, some water may also be stored in interstitial pore spaces). Layers of such formations comprise what is called the saturated ground water zone. Here, water completely fills the pore openings. Overlying the saturated zone is a zone in which the pore spaces contain both air and water and thus are not saturated with water. This zone is known as the unsaturated, or vadose, zone.

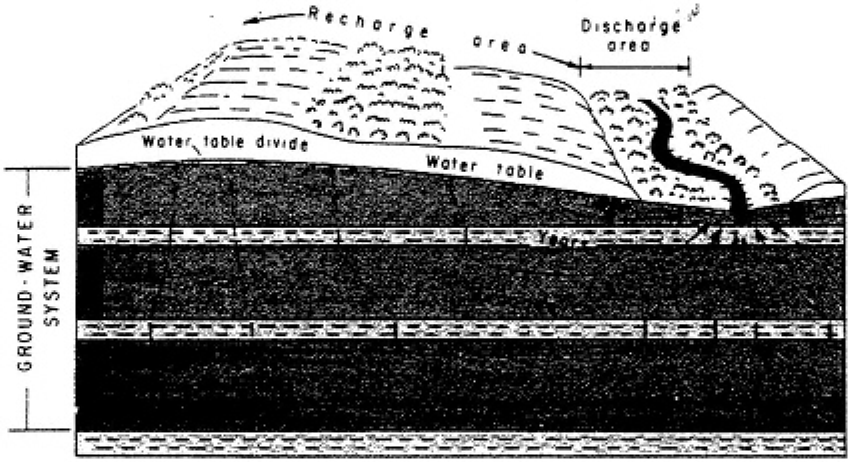


FIGURE 2-1 Simplified schematic of ground water flow in an unconsolidated aquifer. The flow lines indicate travel times to various parts of the subsurface, with longer travel times indicated by flow lines reaching deeper into the subsurface. SOURCE: Heath (1983).

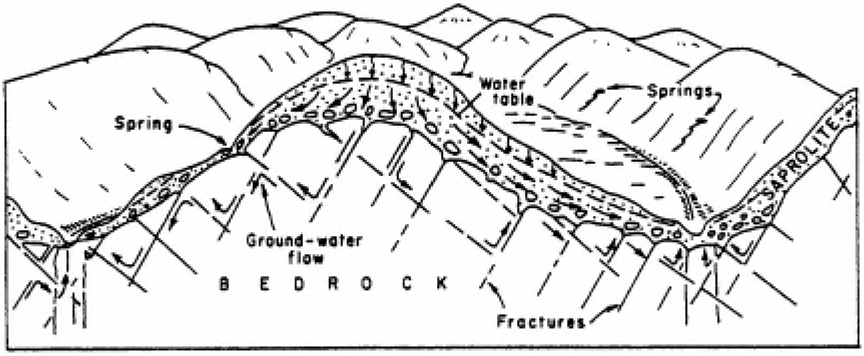


FIGURE 2-2 Simplified schematic of ground water flow in a consolidated aquifer. As the flow lines indicate, the direction of ground water flow in such aquifers depends on the locations of the fractures and thus is often tortuous and difficult to predict. SOURCE: From Heath (1980), as reprinted in LeGrand (1988).

Hydraulic Properties of Aquifers

Table 2-1 summarizes key hydraulic properties of aquifers and their importance to remediation efforts. (See the glossary for definitions of hydraulic properties and other technical terms used in this chapter.) As

TABLE 2-1 Hydraulic Properties of Aquifers Important for Ground Water Cleanup

Property	Description	Importance for Ground Water Cleanup
Porosity	Volume of pore space relative to the total volume	Pores store water and contaminants
Effective porosity	Interconnected pore space that can transmit fluid	Water and contaminants flow through interconnected pores
Ground water velocity	Rate of fluid movement	Influences the direction and velocity of dissolved contaminant movement
Hydraulic gradient	Elevation and pressure differences that cause fluids to flow	Influences the direction of contaminant movement
Hydraulic conductivity	Ease with which water can move through a formation	Influences the rate at which fluid can be pumped for treatment
Transmissivity	Product of formation thickness and hydraulic conductivity	Influences the rate at which fluid can be pumped for treatment
Storage coefficient	Volume released by pressure changes per unit area during pumping in a confined aquifer	Influences the quantity of fluid that can be obtained by pumping
Specific yield	Fraction of total pore volume released as water by gravity drainage during pumping of an unconfined aquifer	Influences the quantity of fluid that can be obtained by pumping
Specific retention	Fraction of total aquifer volume retained as water above the water table after pumping an unconfined formation	Influences the quantity of contaminant that remains in the subsurface after pumping

an illustration of why hydraulic properties are important in ground water remediation, consider the effect of variations in hydraulic conductivity. The hydraulic conductivity controls the amount of water that can be supplied to a well and therefore reflects the ease with which dissolved contaminants can be removed from the aquifer. The hydraulic conductivity of a sandy aquifer is approximately two orders of magnitude greater than the hydraulic conductivity of a silty sand aquifer (average hydraulic conductivities for these types of materials are 30 meters per day and 0.3 meters per day, respectively). Accordingly, water containing contaminants can be extracted from a sandy aquifer at a rate about 100 times greater than it can be extracted from a silty sand aquifer. Therefore, if the zone of contamination is the same in both aquifers, it will be possible to clean up the sandy aquifer much faster than the silty sand aquifer. However, the ease of cleanup of the clean sand aquifer relative to the silty sand aquifer may be offset by the fact that the zone of contamination will be larger in the clean sand aquifer because it is more permeable. This example illustrates that understanding the aquifer's key hydraulic properties and how they are likely to influence the remediation is essential to predicting the performance of the cleanup system.

Determining the influence of hydraulic properties on remediation is far more difficult in fractured, consolidated rocks than in unconsolidated rocks because the hydraulic properties vary widely with location and therefore depend on the size of the sample of the aquifer being investigated. For example, a small volume of rock obtained from between fractures can have an exceedingly low porosity; on the other hand, a small part of aquifer material primarily from a fracture can have a porosity approaching 100 percent. Therefore, the true values for a reasonably sized portion of the aquifer are between these two extremes. An average value of the hydraulic parameters for such an aquifer is of little use in providing hydrogeologic information required for cleaning up aquifers. Predicting contaminant movement in fractured rock is extremely complex because contaminants will move along the line of least resistance, which is in the fracture and often in a direction that cannot be determined by conventional methods for hydrogeologic investigations. Because of the tendency of contaminants to move through the fractures to locations that are difficult to determine and to access, remediation of fractured rock aquifers poses an extreme technical challenge.

Ground Water Flow

The major influences on ground water flow are precipitation, which recharges aquifers, and gravity, which causes ground water to flow and eventually discharge to springs, rivers, and oceans. As an example, Figure 2-1 shows recharge and discharge in unconsolidated sediments in an idealized and simplified cross section. Water moves from a recharge area at high elevation to a discharge area at low elevation. Water may also move vertically through a series of less permeable layers, known as confining beds, that may separate aquifers at various depths. Figure 2-2 illustrates the complexities of ground water flow paths for fractured, consolidated rocks. Flow paths in fractured rock are often difficult to ascertain because the fractures are not uniformly distributed and may not be interconnected.

The fundamental law describing ground water flow is known as Darcy's Law, which can be expressed as follows:

$$q = -K\, dh/dl$$

In this equation, the term *q* is the volumetric flow rate per unit cross-sectional area of aquifer perpendicular to the direction of flow. The term K is the hydraulic conductivity (see Table 2-1), which is a measure of the ease with which water moves through the aquifer material and which decreases with pore size (just as the flow of water through a pipe decreases with pipe diameter). The term *dh/dl* is the hydraulic gradient (see Table 2-1), which quantifies the pressure and gravity forces that drive flow and which is influenced by aquifer recharge, elevation, and pumping. Darcy's Law states that the rate of ground water flow is determined by the magnitude of the hydraulic gradient and the magnitude of the hydraulic conductivity of the aquifer material.

The Effect of Pumping on Flow

Pumping ground water, as is done with pump-and-treat systems, causes complex perturbations in flow, even at sites with relatively simple hydrogeology. To illustrate this effect, consider a hypothetical site at which water is injected into the aquifer at one well and pumped out of the aquifer at the same rate from a second well. Placement of the wells is critical in determining the flow of water from the recharge well to the discharge well. In the top diagram in Figure 2-3, the wells are placed on a line perpendicular to the direction of ground water flow, and only a small amount of the recharged water (indicated by the stippled area) is removed by the pumping well. In the bottom diagram, the wells are aligned parallel to the direction of ground water flow, and nearly all of the recharged water is pumped out, with almost none moving downgradient. At an actual field site, ground water flow is far more complex than in this simple illustration because the hydraulic properties that describe an aquifer are not uniform. Nevertheless, this example demonstrates the necessity of understanding the flow system before installing a well to remove contaminants or to control the direction of movement of a contaminant plume.

Geochemical Characteristics

Once contaminants enter the subsurface, they become subject to control not only by the aquifer's physical properties but also by a variety of possible geochemical reactions. These reactions may cause the contaminants to change form, sorb to aquifer solids, or form complexes with other chemical species. In addition, geochemical characteristics of the site can influence the operation of aquifer cleanup systems. For example,

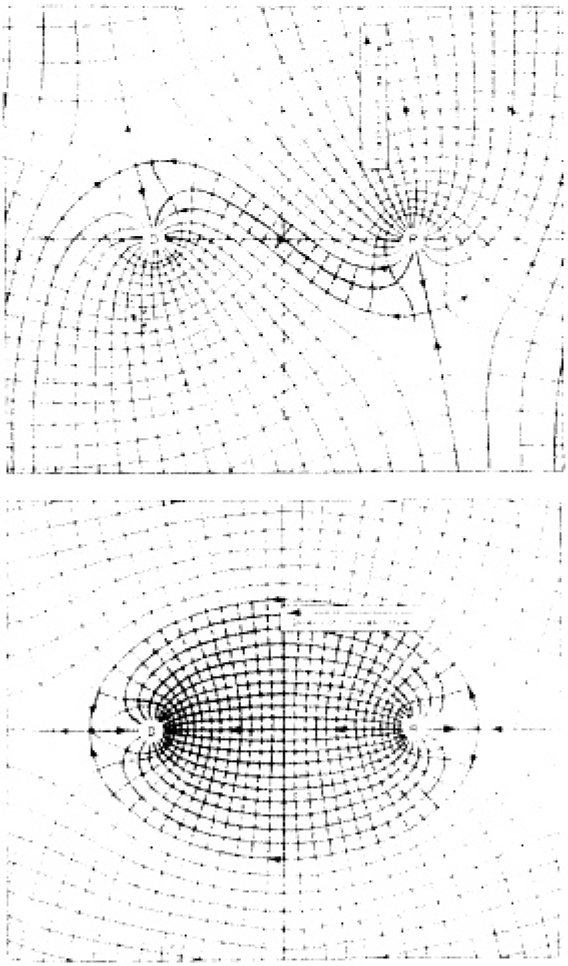


FIGURE 2-3 Diagrams, called flow nets, that illustrate the effect of well placement on the direction and quantity of ground water flow in a homogeneous aquifer with recharge (R) and discharge (D) wells that are at the same depth and are pumping the same amount of water. The solid lines are flow lines, which indicate the pattern of ground water movement. A flow net, by definition, has an equal quantity of water flowing between each pair of flow lines. The dashed lines are lines of equal hydraulic head. Only the water in the stippled areas moves from the recharge well to the discharge well. In the top diagram, the wells are placed in a line perpendicular to the direction of ground water flow, and little recharge water reaches the discharge well. In the bottom diagram, the line from the recharge well to the discharge well is parallel to the direction of ground water flow, and nearly all of the water from the recharge well reaches the discharge well. SOURCE: Da Costa and Bennett, 1960.

Core barrel used to obtain a sample from the subsurface. Courtesy of Rice University, Department of Environmental Science and Engineering.

geochemical characteristics determine whether metals, such as iron, will precipitate when the contaminated water is extracted for treatment. Metal precipitates can clog extraction wells and require installation of special treatment systems, significantly increasing cleanup costs.

The chemical composition of ground water reflects both the mineralogy of the aquifer and the flow path of the water from the point of recharge to the point of discharge. The movement of water and its interaction with soil and rock can be described by the concept of a hydrogeochemical cycle, shown in Figure 2-4. As the figure indicates, the chemistry of the infiltrating water is largely controlled by temperature, precipitation, soil mineralogy, and anthropogenic inputs, including airborne contaminants and chemicals in runoff water. Factors that affect the chemical composition of the water once it infiltrates the subsurface include the mineralogy of the aquifer matrix, the residence time that the water is in contact with the soil and rock, and mixing of ground water with other sources of water or subsurface contaminants. Contaminants and products from microbial activity in the subsurface can also cause important changes in the water chemistry. As shown in Figure 2-4, as water moves through the unsaturated zone the concentrations of solutes increase as soil gases and minerals (which may contain metals such as iron and manganese) dissolve. Ground water has a longer residence time

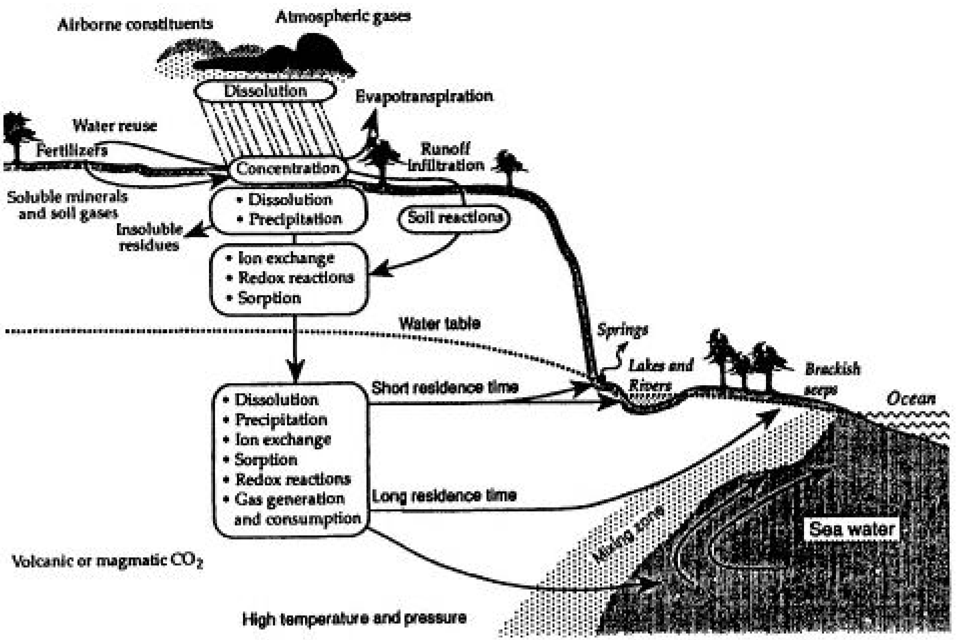


FIGURE 2-4 Schematic showing the hydrogeochemical cycle of water moving through the subsurface. Water begins its path as rainfall, which may contain dissolved matter such as pollutants. Some of this rainfall infiltrates the soil, where the composition of the water changes as soil gases dissolve and as the water reacts chemically with soil components (through ion exchange, redox, sorption, and dissolution reactions). From the soil, the water migrates downward to the water table. Once in the aquifer, the water flows toward discharge points such as springs, lakes, rivers, and the ocean, continuing to change chemically along the way. It then evaporates from these surface bodies and once again begins its path as rainfall.
SOURCE: Modified from Back et al., 1993.

in the deep subsurface than in shallow systems and continues to change in chemical composition as it moves to discharge points in springs, lakes, rivers, estuaries, and oceans. In general, shallow aquifers (2 to 50 meters below land surface) are more vulnerable to ground water quality problems than deep aquifers because most contaminants enter the subsurface via use and disposal near the land surface or leakage from buried storage containers.

Table 2-2 summarizes the many types of geochemical processes that can affect contaminant fate and transport in the subsurface. Many of these reactions occur together or sequentially in contaminated environments (Cherry et al., 1984). For example, the oxidation of organic contaminants to carbon dioxide can be coupled with the reduction of (insoluble) ferric iron oxides to aqueous (soluble) ferrous iron. When sulfide is present, the ferrous iron can precipitate as monosulfide or pyrite. These processes occur within the constraints of thermodynamics and in many cases are mediated by microorganisms.

Biological Characteristics

Microorganisms of many kinds, primarily bacteria but also protozoa and fungi, inhabit subsurface environments (Ghiorse and Wilson, 1988). Microorganisms are important in ground water systems because they consume organic matter, including contaminants, and because they alter the chemical state of the aquifer. Subsurface microorganisms are also extremely important in the development of new technologies that use biological processes to treat contaminated ground water in place rather than having to extract it (see Chapter 4).

The activity of microorganisms in uncontaminated aquifers is often limited by the availability of metabolizable organic carbon, which the organisms require for growth and reproduction. The concentration of natural organic carbon is low in ground water (usually less than 2 mg/liter). Therefore, the presence of degradable organic contaminants in the subsurface generally stimulates microbial growth, although some organic compounds and trace metals inhibit microbial activity.

Two broad classes of bacteria play important roles in the subsurface and in the development of new ground water cleanup technologies: aerobic and anaerobic. Aerobic organisms require oxygen to degrade organic compounds. They transfer electrons from the organic material to oxygen, which is termed the "electron acceptor." The organic material is oxidized and the oxygen is reduced. This process generates energy for the organisms and transforms the organic material to carbon dioxide and new cell mass.

Anaerobic organisms use substances other than oxygen as electron

TABLE 2-2 Geochemical Processes in Subsurface Environments

Process	Definition	Significance in Aquifers	Effect on Contaminants
Dissolution-precipitation	Reactions that dissolve or precipitate solids such as natural minerals	Primary control on the chemical composition of ground water	Can increase or decrease the concentrations of dissolved constituents, including some types of contaminants
Oxidation-reduction	Reactions that add electrons to (reduce) or remove electrons from (oxidize) chemicals, altering their chemical form	Determines the speciation of metals with more than one oxidation state and the possible chemical and biological degradation pathways of organic matter	Can alter contaminant concentration either by direct chemical reactions or by increasing microbial degradation of the contaminant; can dissolve or precipitate metals
Sorption-desorption	Reactions that transfer a substance from the fluid phase (solvent) to the solid phase (sorbent), or vice versa	Affects dissolved concentrations by the attachment and release of constituents on surfaces of aquifer sediment	Sorption can slow the movement of contaminants
Ion exchange	Exchange of ions in clays for ions in solution, with charge balance maintained	Reduces the concentration of one ion and increases the concentration of another	Can remove contaminant ions from solution, particularly when clay is present, and thus slow their removal by pumping
Complexation	Interactions between chemicals in solution that generate combined chemical species, such as ion pairs, complex ions, or chelates	Affects the availability of substances in ground water to participate in reactions	Can alter the concentrations, reactivities, and mobilities of contaminants (especially metals)

acceptors when degrading organic compounds. For example, denitrifying bacteria, which are one common class of anaerobes, use nitrate as an electron acceptor, converting the nitrate to nitrite, nitrous oxide, nitric oxide, or nitrogen gas. Similarly, sulfate-reducing bacteria, a second type of anaerobe, use sulfate as an electron acceptor, converting it to hydrogen sulfide. A third class of anaerobes, the iron reducers, transforms ferric iron (Fe(III)) to ferrous iron (Fe (II)). A fourth class of anaerobes, the methanogens, uses simple carbon-containing compounds such as carbon dioxide or acetate as electron acceptors, producing methane. Each of these classes of organisms can oxidize organic materials to simpler compounds like carbon dioxide, in the process gaining energy for growth and reproduction.

Because electron acceptors are as essential for microbial growth as oxygen is for human growth, the availability of electron acceptors is a major factor that influences the extent of microbial transformation occurring in aquifers and the design of treatment technologies relying on biological processes. Uncontaminated ground water in shallow aquifers is nearly saturated with dissolved oxygen. However, when the oxygen supply is depleted due to microbial consumption of organic matter, it is replenished slowly—by oxygen dissolved in water that recharges the aquifer and to a lesser extent by diffusion from the unsaturated zone. Consequently, alternate electron acceptors play an important role in the subsurface. The most common subsurface electron acceptors other than oxygen are nitrate, sulfate, ferric iron, and inorganic carbon. Electron transfer to oxygen generates more energy for the bacteria than electron transfer to these other electron acceptors. Therefore, theoretically, aerobic organisms will dominate in environments where oxygen is present.

Where a sufficient electron acceptor supply and a large source of metabolizable organic carbon are present, the availability of nutrients such as nitrogen, phosphorus, and to a lesser extent sulfur can limit bacterial growth. The bacteria require these and other elemental nutrients to synthesize new cell matter.

CONTAMINANTS IN GROUND WATER

Once a contaminant enters the subsurface, its fate depends not only on the natural physical, chemical, and biological characteristics at the site but also on the chemical properties of the contaminant. Surveys reveal that a wide range of hazardous substances may be present at hazardous waste sites (NRC, 1991). The most common of these substances are in the following classes: volatile organic compounds (VOCs), toxic inorganic compounds, polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), pesticides, and phthalates. Subsurface migration path ways, mobility, and persistence of contaminants differ greatly between classes and within each class, primarily due to the different chemical natures of the compounds but also due to their modes of release.

Inorganic Compounds

The most frequently reported hazardous substances include 9 inorganic compounds in the top 25 contaminants (see Table 1-1). These inorganics, in order of their frequency of detection in ground water at hazardous waste sites, are lead (Pb), chromium (Cr), zinc (Zn), arsenic (As), cadmium (Cd), manganese (Mn), copper (Cu), barium (Ba), and nickel (Ni). Of this group, Pb, As, and Cd are also ranked among the top ten most hazardous contaminants.

Anthropogenic sources of inorganic compounds include ore mining and smelting, burning of fossil fuels, petrochemical processing, electronic component manufacturing, and industrial plating. Wastes from these processes that were deposited on land or in ponds, wells, or landfills may release inorganic contaminants to the subsurface. In addition, leaking storage tanks that held leaded gasoline may be sources of lead in ground water.

Detection of inorganic compounds at low concentrations at hazardous waste sites can also result from natural weathering processes or sampling procedures rather than from industrial wastes. With the exception of cadmium, metals may occur naturally in aquifer materials and may dissolve by natural weathering processes. In addition, if during sampling the ground water contacts well screens, casings, or pumps constructed of metal, some metal may dissolve in the water. Another source of metals reported in the parts-per-billion range in ground water is suspended sediment that is analyzed in unfiltered water.

The hazard posed by inorganic contaminants depends on the form in which they are present. For example, the toxicity of Cr and As depends on the oxidation state. Cr(VI) is very toxic, whereas Cr(III) is much less so. Similarly, As(III) is more toxic than As(V). Inorganics that form organometallic ions or compounds have increased mobility and therefore present a greater hazard. For example, Pb, As, and Cr can form organometallic ions or compounds. Table 2-3 lists the oxidation states and principal dissolved forms of four hazardous inorganics.

Organic Compounds

Table 2-4 lists representative organic compounds that are prevalent ground water contaminants and representative properties important to remediation efforts. Such organic chemical contaminants typically enter the subsurface as constituents of a liquid phase. This liquid phase may be a dilute aqueous solution, a concentrated leachate, or an organic liquid that is not miscible with water (commonly referred to as a nonaqueous-phase liquid, or NAPL). In addition, the liquid frequently contains mixtures of compounds from various classes, complicating the contaminants' behavior (Department of Energy, 1992).

TABLE 2-3 Characteristics of Toxic Inorganics in Ground Water

Metal	Oxidation State(s)	Principal Dissolved Forms[a]
Lead	Pb(II), Pb(IV)	Pb^{2+} ion Hydroxide complexes[b] Carbonate or sulfate ion pairs[c] Organic (e.g., tetraethyl lead)
Arsenic	As(III), As(V)	Arsenate (As^{5+}) oxyanions Arsenite (As^{3+}) oxyanions Organic (e.g., dimethyl arsenic acid)
Cadmium	Cd(II)	Cd^{2+} ion Carbonate ion pairs Chloride, hydroxide complexes
Chromium	Cr(III), Cr(VI)	Cr^{3+} ion Hydroxide complexes (Cr^{3+}) Chromate, dichromate (Cr^{6+}) oxyanions

[a] From Hem, 1985.

[b] Complex ions are species composed of two or more single ions that are combined (e.g., $Pb(OH)_3$-).

[c] Ion pairs are ions of opposite charge that are adjacent in solution, temporarily forming a pair (e.g., $PbCO_{3(aq)}$). They are weakly bonded relative to complexes.

The characteristics of the "carrier" fluid can greatly influence the migration pathways and persistence of a specific compound. NAPLs, in particular, have been the focus of substantial research and regulatory concern because NAPLs are extremely common and have complicated ground water cleanup at many hazardous waste sites. Contamination by NAPLs occurs in many ways: surface spills; waste injection into subsurface disposal wells; leaking waste disposal lagoons; and leaking drums, pipelines, and storage tanks. As constituents of NAPLs, substantial quantifies of compounds that are only slightly water soluble may travel large distances in the subsurface. VOCs, PCBs, and PAHs usually enter the subsurface as components of NAPLs. Metals also are common constituents of NAPLs; for example, crude oil and solvent wastes from metal plating operations contain metals.

The two most prevalent classes of compounds likely to exist as NAPLs are the chlorinated solvents (such as trichloroethylene and tetra chloroethylene) and petroleum hydrocarbons (including gasoline and fuel oils) (Mercer and Cohen, 1990). Chlorinated solvents are more dense than water and are thus called dense NAPLs, or DNAPLs. Other DNAPLs include coal tars, which contain PAHs, and transformer oil, which may include mixtures of PCBs. Petroleum hydrocarbons are less dense than water and are thus called light NAPLs, or LNAPLs. The mechanics of migration for contaminants vary greatly depending on whether the contaminant is dissolved in water or is carried in an LNAPL or DNAPL.

Collection of a sample from a core of material removed from the subsurface. Courtesy of Rice University, Department of Environmental Science and Engineering.

Compounds having melting points in excess of ambient temperature (approximately 10 to 20°C) may be present as a solid phase and hence immobile in pure organic form; the PAHs listed in Table 2-4 illustrate this behavior. However, such organic solids are likely to dissolve in the liquid organic solvents comprising the NAPL phase, if present.

Mechanics of Migration

Figure 2-5 shows a simplified contamination scenario in which a DNAPL, such as a chlorinated solvent, has been released from a surface

TABLE 2-4 Properties of Representative Organic Ground Water Contaminants

Pollutant	Aqueous Solubility (mg liter^{-1})	Henry's Law Constant (atm m^3 tool^{-1})	K_{ow}	Specific Gravity	Absolute Viscosity (cP)	Melting Point (° C)
Chiorinated hydrocarbons						
Carbon tetrachloride	7.57×10^2	2.41×10^{-2}	4.37×10^2	1.58	0.965	-23
Trichloroethylene	1.10×10^3	9.10×10^{-3}	2.40×10^2	1.47	0.566	-73
Tetrachloroethylene	1.50×10^2	2.59×10^{-2}	3.98×10^2	1.63	0.89	-23
1,2 Dichlorobenzene	1.0×10^2	1.93×10^{-3}	3.98×10^3	1.30	1.32	-17
Fuel hydrocarbons						
Benzene	1.75×10^3	5.59×10^{-3}	1.32×10^2	0.873	0.603	5.5
Toluene	5.35×10^2	6.37×10^{-3}	5.37×10^2	0.862	0.552	-9.5
p-Xylene	1.98×10^2	7.05×10^{-3}	1.41×10^3	0.861	0.644	13
Oxygenated compounds						
Bis-2-ethylhexyl phthalate	2.85×10^{-1}	3.61×10^{-7}	9.50×10^3	1.21	2.14	-50
Phenol	9.3×10^4	4.54×10^{-7}	3.0×101	1.0576	1.24	43
Methyl ethyl ketone	2.56×10^5	4.66×10^{-5}	2.9×10^{-1}	0.80^5	0.40	-86
PAHs						
Benzo[a]pyrene	3.8×10^{-3}	2.4×10^{-6}	1.00×10^6	1.3^5	NA	177
Pyrene	1.30×10^{-1}	5.10×10^{-6}	8.00×10^4	1.27	NA	150
Naphthalene	3.17×10^{-1}	4.60×10^{-4}	1.95×10^3	1.16	NA	80

Pesticides						
Chlordane	5.60×10^{-2}	9.40×10^{-5}	3.00×10^{5}	1.6	NA	103-109
Lindane	7.80×10^{0}	7.80×10^{-6}	7.80×10^{3}	NA	NA	113
Mixtures						
Crude oil	NA	NA	NA	0.70–0.98	8–87	NA
Gasoline	NA	NA	NA	0.73	0.45	NA
JP-1 jet fuel	NA	NA	NA	0.81–0.85	2.05	NA
Coal tar (creosote)	NA	NA	NA	1.05–1.1	1.1–20	NA
PCBs						
Arochlor 1248	5.40×10^{-2}	3.50×10^{-3}	5.62×10^{5}	1.44	212 (38°C)	–7 (approx.)
Arochlor 1260	2.70×10^{-3}	7.10×10^{-3}	1.38×10^{7}	1.57		31 (approx.)

NOTE: Reported values at 20 or 25°C. NA indicates that data are not applicable or not available from the sources used to prepare this table. Viscosity is irrelevant for substances that are solids under ambient conditions, and mixtures melt over a range of temperatures. SOURCES: Lucius et al., 1992; Mercer and Cohen, 1990; Wing and Weaver, 1991; Montgomery and Welkom, 1990; EPA, 1982.

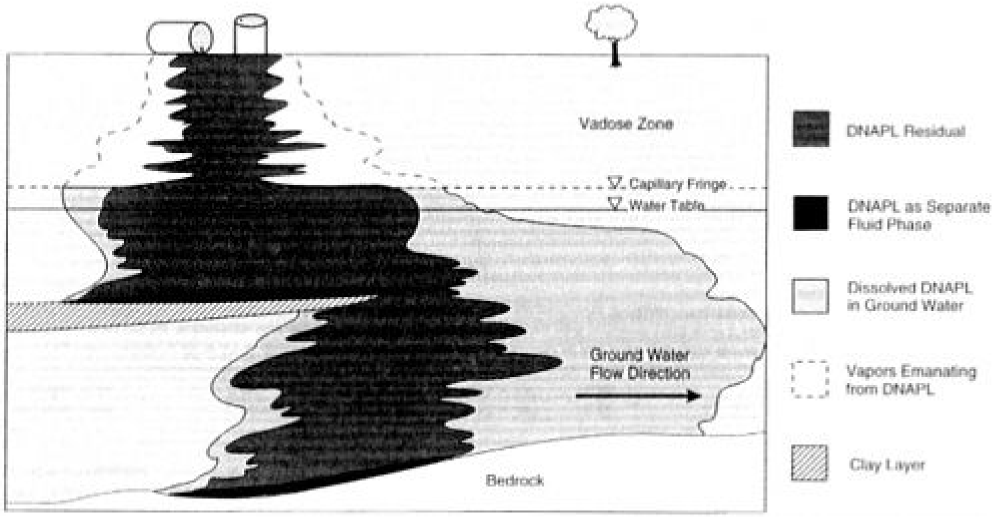


FIGURE 2-5 Conceptual diagram of DNAPL migration through the subsurface. As the diagram indicates, some DNAPL remains as an entrapped residual in the soils (indicated by the dark shading), some migrates as a separate fluid phase (indicated by the black areas), some dissolves in the ground water to create plumes (indicated by the light shading), and some vaporizes into the gas in the soil pores (indicated by white areas).

source. As the chemical enters the subsurface, the liquid may dissolve into the water in the pores, volatilize into the air in the pores, or remain behind in the pore spaces as an entrapped residual. In the unsaturated zone near the ground surface, the organic liquid will move mainly vertically downward with little lateral spreading because gravity forces predominate. The portion that volatilizes, however, will be free to move laterally as an organic vapor within the unsaturated zone, effectively increasing the area of contamination. When the DNAPL reaches the saturated zone (where water completely fills the pore spaces), its downward progress may slow somewhat due to the resistance created by the water. If the spill is sufficient in size, however, it will continue to move vertically downward, displacing the ground water.

In the saturated zone, some of the chemicals from the DNAPL will dissolve in the flowing ground water, forming a contaminant "plume," as illustrated in Figure 2-5. The remainder of the DNAPL will continue to migrate downward, as in the vadose zone leaving behind a trail of residual liquid entrapped in pores. The main body of the DNAPL will continue to move downward until reaching a relatively impermeable stratum, such as the clay layer shown in Figure 2-5. Upon contacting such a layer, the DNAPL may spread laterally, creating a liquid pool. If the impermeable layer is of limited lateral extent, further vertical migration is possible once the DNAPL pool on top of the obstruction extends to the edge. Overall, gravity forces will cause the DNAPL to move predominantly downward, effectively uncoupling its transport from the predominantly horizontal movement of the ground water.

Figure 2-6 shows a second contamination scenario in which an LNAPL, such as a petroleum hydrocarbon, has been released from an underground storage tank. The LNAPL's behavior in the unsaturated zone will be similar to that described above for the DNAPL. When the LNAPL encounters the saturated zone, however, it will spread laterally, forming a "pancake" or "lens" floating at the top of the water table. After its formation, this lens will migrate primarily in the direction of natural ground water flow. If the water table changes due to seasonal fluctuations or pumping, the lens can also spread vertically within the formation, enhancing the area of LNAPL contamination.

The above scenarios illustrate the three most important potential contaminant migration pathways: (1) aqueous-phase transport within the contaminant plume, (2) vapor-phase transport, and (3) transport as a NAPL. The relative importance of each pathway for the transport of a particular contaminant depends on the properties of that substance, as well as the chemical and physical characteristics of the site.

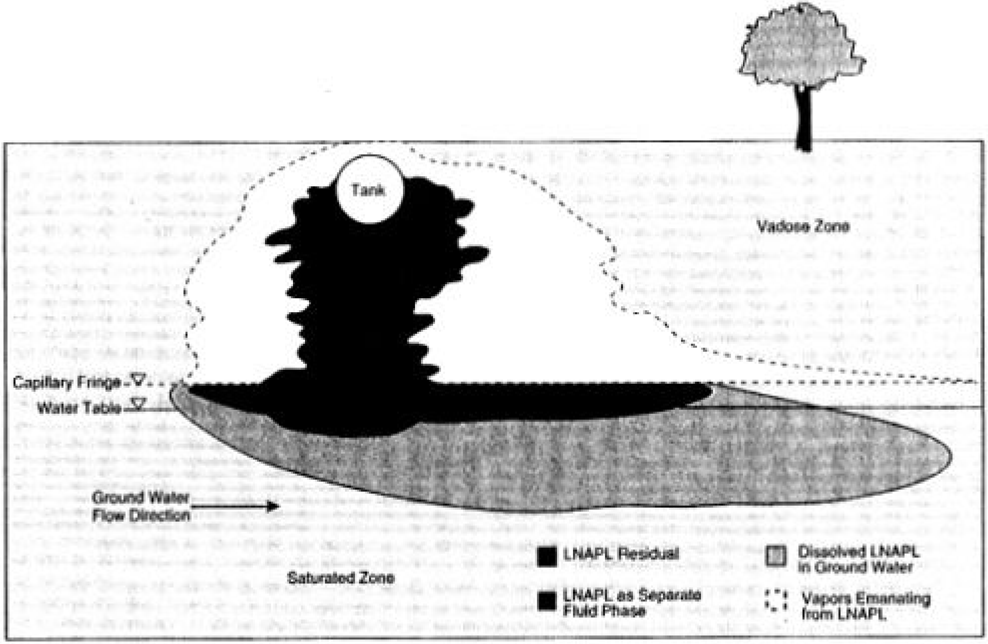


FIGURE 2-6 Conceptual diagram of LNAPL transport through the subsurface. As the diagram indicates, some LNAPL remains entrapped in the soil pores, some remains as a separate fluid phase near the spill source and on top of the water table, some vaporizes into the soil pores, and some dissolves in the ground water to form a plume. SOURCE: Modified from API, 1989.

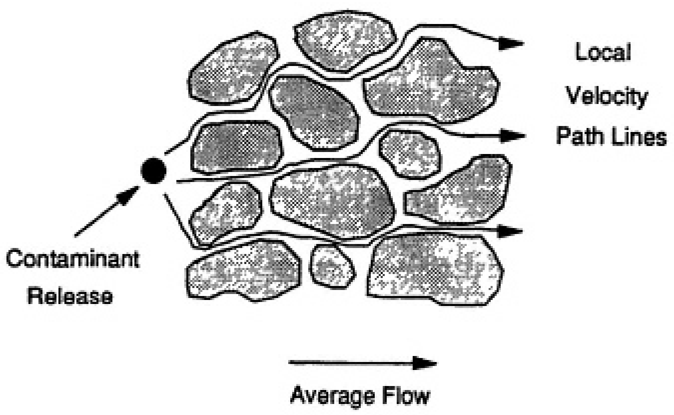
Aqueous-Phase Transport

The mechanics of aqueous-phase contaminant transport differ for the unsaturated and saturated zones. In the unsaturated zone, flows are gravity driven and thus are primarily vertical. In the saturated zone, flows are primarily horizontal. Saturated-zone transport presents perhaps the greatest opportunity for a pollutant to migrate large distances. Natural ground water flow rates, however, are slow in most formations (1 to thousands of meters per year), so this migration will take place over large time scales—months to hundreds or thousands of years, compared to days or weeks in most rivers and streams.

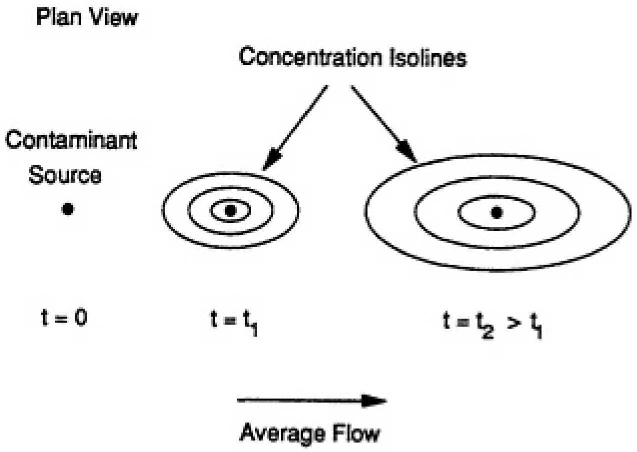
The propensity for a particular contaminant to be transported in the aqueous phase depends primarily on its aqueous solubility. Solubilities of common organic contaminants vary widely (see Table 2-4) and are influenced by hydrophobicity, temperature, salinity, dissolved organic matter, or the presence of multiple organic compounds in solution (cosolvents). The transport behavior of metals in the subsurface is extremely complex. These substances can occur in many forms—as free metals, ions, complexes, ion pairs, or organometallic compounds each of which has distinct properties. The solubility of metals depends primarily on the pH, the presence of complexing ligands, the redox potential of the solution, and the tendency of the metals to precipitate. For example, Pb(II) reaches its highest concentrations when the ground water is acidic and the bicarbonate concentration is low, such that lead carbonate does not precipitate.

Once a compound dissolves in ground water, it Will migrate in the direction of ground water flow. This migration is called "advective flux." As the contaminant moves through a formation, small- and large-scale variations in the flow field caused by the presence of micro- and macroscopic heterogeneities will tend to spread the contaminant. This process, termed "hydrodynamic dispersion," is illustrated in Figure 2-7. In Figure 2-7a, the soil grains (pore-scale heterogeneities) cause the contaminant to spread as it threads its way through the soil pores. In Figure 2-7b, the effect of this spreading is shown at a larger scale, where the point source is observed to spread in the directions parallel and perpendicular to the average ground water flow direction. Larger-scale heterogeneities (for example, zones of differing permeability) also contribute to, and indeed usually dominate, contaminant spreading.

Although advective and dispersive fluxes play the primary role in the migration of a dissolved contaminant, solutes also migrate from regions of high concentration to regions of low concentration by a process called "molecular diffusion." Diffusion is an extremely slow process in



(A) Microscale heterogeneities give rise to contaminant spread.



(B) Macroscale manifestation of microscopic dispersive mechanisms.

FIGURE 2-7 Conceptual diagrams showing how hydrodynamic dispersion can increase contaminant spreading. (A) shows how the water (and associated contaminants) disperses from the average flow direction as it encounters grains of soil. (B) shows the effect of this spreading on the contaminant concentration at a single location over time (indicated by t). At times t_1 and t_2, dispersion has caused the contamination to spread in directions perpendicular and parallel to the average direction of ground water flow.

water, but over large time scales it provides a mechanism for the transfer of contaminants to less permeable zones in the aquifer.

While diffusion and dispersion enhance contaminant spreading, they also lower the concentrations of contaminants. For sources of very small volume, such processes, coupled with natural recharge mechanisms, could potentially reduce contaminant concentrations to acceptable levels at some distance from the source. Unfortunately, because acceptable concentration levels are so small (on the order of parts per billion for many contaminants), the required travel distances for sufficient dilution are generally extremely large.

If a compound has a high aqueous solubility, its presence may change the ground water's density and viscosity. Small density increases—as little as 0.1 percent—may cause the contaminant plume to "sink" (i.e., travel deeper into the aquifer) over large travel distances (Sudicky et al., 1983; Mackay et al., 1986). Large density variations can create gravity flow instabilities. Transport behavior in such systems is a subject of ongoing research (Oostrom et al., 1992).

Vapor-Phase Transport

Contaminants that volatilize into the air contained in soil pores can spread laterally and vertically through the unsaturated zone. Subsequent dissolution into flowing ground water or infiltrating recharge water may then enlarge the zone of ground water contamination (Sleep and Sykes, 1992). A contaminant's tendency to volatilize can be determined from the Henry's Law constant, representative values of which are given in Table 2-4. The Henry's Law constant, which is valid for sparingly soluble nonelectrolytes, relates the aqueous-phase concentration of a chemical to its partial pressure in the gas phase. Contaminants with larger Henry's Law constants have a greater tendency to volatilize.

Volatilized contaminants may migrate within the soil gas via advection or molecular diffusion. Advection may occur due to variations in gas-phase density created by the presence of contaminant vapors. Since gases offer small resistances to flow (low viscosities), transport by advection in the soil gas phase is much more rapid than advective transport in ground water. Similarly, transport by diffusion tends to be much more rapid in the soil gas phase than in the ground water. Free air diffusivities, which describe the relative rates at which contaminants migrate by diffusion in air, are several orders of magnitude larger than free liquid diffusivities: 10^{-2} to 10^{-1} cm^2/s for air, versus 10^{-6} to 10^{-5} cm^2/s for dilute aqueous solutions.

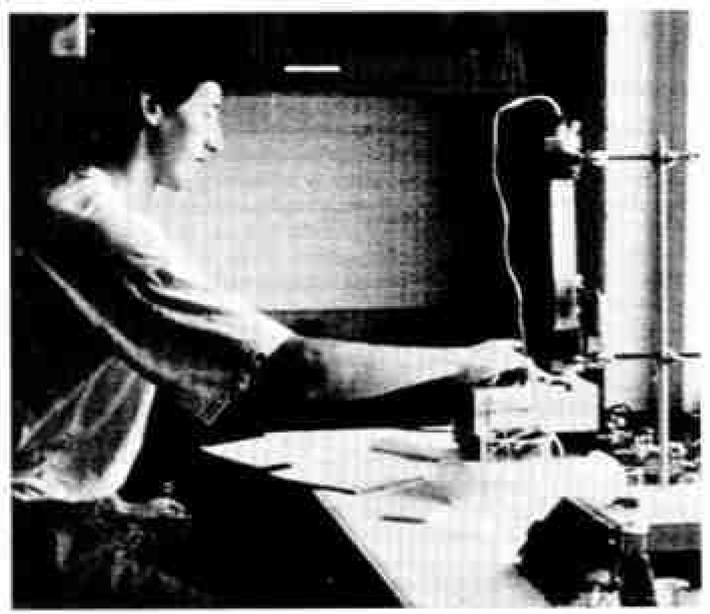
As soil moisture increases, the importance of vapor-phase transport diminishes. An increase in the moisture content reduces the pore space available for migration, decreasing the effective diffusivity and gas-phase permeability. In addition, the partitioning of the organic vapor into this increased aqueous-phase volume further retards vapor-phase migration.

NAPL Transport

Bulk NAPL migration is governed primarily by three fluid properties: density, viscosity, and interfacial tension.

Density determines the contaminant's behavior when the spill encounters the saturated zone. LNAPLs tend to spread laterally at the top of the water table, whereas DNAPLs tend to sink vertically. Table 2-4 shows representative NAPL specific gravities.

Viscosity influences the NAPL's rate of migration. Fluids with lower viscosity migrate more rapidly due to their reduced resistance to flow.



Laboratory experiment to characterize the hydraulics of a column filled with porous material. Courtesy of the Johns Hopkins University, Department of Geography and Environmental Engineering.

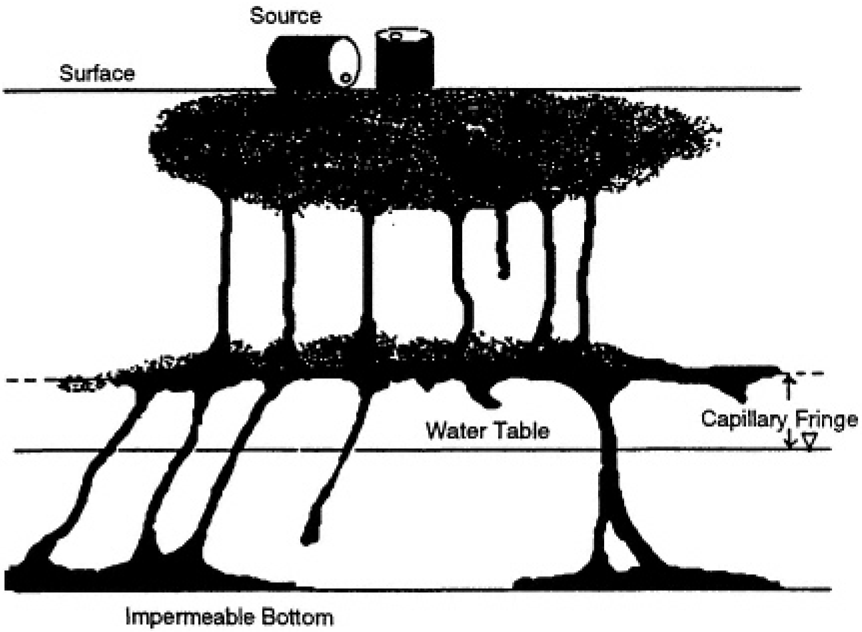


FIGURE 2-8 Enhanced DNAPL migration via viscous fingering. SOURCE: After Schwille, 1988.

Table 2-4 shows that many NAPLs, including some chlorinated solvents and aromatic hydrocarbons, have viscosities smaller than that of water (which is 1.0 centipoise at 20°C). When a denser, less viscous fluid displaces another of lower density and higher viscosity, the process is inherently unstable. Under such circumstances, small perturbations at the displacement front can propagate, creating narrow, preferential pathways of migration for the denser fluid, as shown in Figure 2-8. These pathways are known as "fingers." Fingering can enhance the rate of DNAPL migration. It also makes a spill's location quite difficult to detect because of the small lateral dimensions of the finger.

Interfacial tension gives rise to the capillary forces that control the extent of lateral spreading of a NAPL as it migrates downward. Interfacial tension between two fluids is a measure of the difference in the inter-molecular forces at the interface and the intermolecular forces of the bulk fluids (Adamson, 1982). NAPL-water interfacial tensions are on the order of 20 to 50 dynes/cm (Mercer and Cohen, 1990). The extent and thickness of an LNAPL "pancake" that forms at the water table (see Figure 2-6) decrease and increase, respectively, as the interfacial tension in creases. The existence of interfacial forces can also create a barrier to the movement of NAPLs into fine-pore materials; thus, a downward-migrating DNAPL tends to spread out horizontally when it encounters a low-permeability layer, in a manner similar to that shown at the capillary fringe in Figure 2-6. Interfacial tensions can be affected by pH and dissolved constituents such as natural humic substances that behave as surface-active agents, reducing capillary forces.

Overall, the pathways of NAPL migration are intricate, and the resulting contaminant distribution is highly nonuniform and complex. These complexities greatly complicate the task of locating and removing the contamination.

Mechanisms for Retention

Once contaminants are released to the subsurface, a variety of mechanisms act to retain the contaminants beneath the ground. These mechanisms have two effects: they retard contaminant movement, and they create long-term sources for contaminant elution. The propensity of a specific compound to be retained depends on many factors, including its mode of transport (aqueous, gaseous, NAPL), its chemical behavior, and the chemical and physical properties of the porous medium. Two primary modes of retention are sorption and NAPL entrapment.

Sorption and Ion Exchange

The tendency of a contaminant to sorb to solid materials in the subsurface is governed by a number of molecular interactions of chemical, electrostatic, or physical origin. For metals, sorption is generally caused by the electrostatic affinity of the contaminant for an electrically charged surface, such as that of clay, in the porous matrix. Sorbed metals can remain in aquifers for long time periods and can then be released when the geochemistry of the aquifer changes. Small changes in pH or redox conditions, which may occur during remediation, can have profound effects on the amount of metal that sorbs.

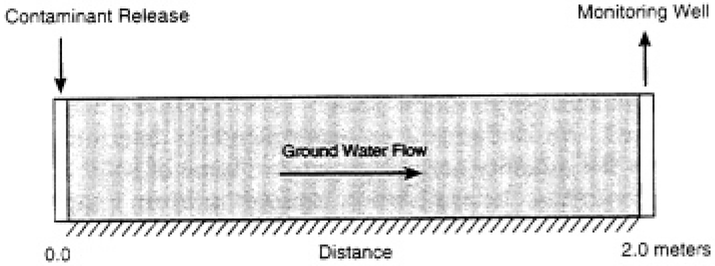
For nonpolar organic contaminants, sorption is a function of the compound's hydrophobicity (its affinity or lack of affinity for dissolving in water). Hydrophobicity may be quantified by the octanol/water partition coefficient (K_{ow}) of a compound, shown in Table 2-4 for representative contaminants. The K_{ow} is the ratio of the concentration of the compound that will dissolve in octanol to its concentration in water when equilibrated between these two phases. In general, the higher the K_{ow} value, the greater the propensity for sorption to organic constituents of the soil. Sorption processes are more complex for soils of very low organic content and for polar and ionic organic solutes.

To estimate the amount of a contaminant that is sorbed to the aquifer solids, mathematical expressions known as sorption isotherms are typically employed. An isotherm is an experimentally determined relationship between the quantity sorbed per unit volume of solid and the concentration in solution. Its application assumes uniform temperature and equilibrium conditions. If the isotherm expression is linear, this implies that the extent of sorption is directly proportional to the dissolved concentration. Over small concentration ranges, a linear isotherm can usually provide a good representation of laboratory data. Over larger ranges of concentration, however, nonlinear expressions are often required.

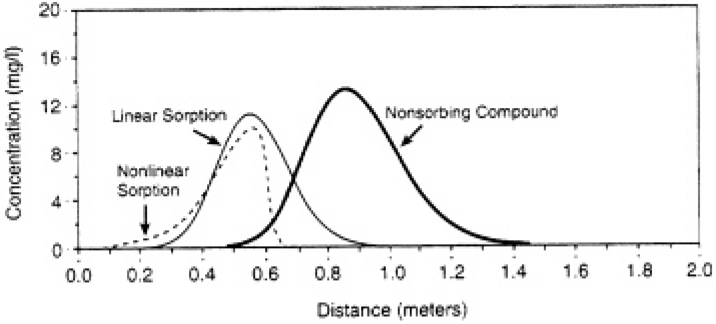
When a contaminant is released to the subsurface, sorption retards its movement with respect to the ground water (compare the nonsorbing compound and linear sorption curves in Figure 2-9a). Nonlinear sorption will not only retard migration but will also increase the spread (or apparent dispersion) of the contaminant. If contaminant concentrations are measured at a monitoring well downstream of the contaminant release site, sorption will tend to reduce concentration levels and cause the contaminant to appear later at the well (see Figure 2-9b). Nonlinear sorption will create a long period of "tailing," during which contaminant concentrations will decrease slowly (Weber et al., 1991). Thus, under nonlinear sorption conditions, the contaminant will be retained much longer in the porous medium, and much larger volumes of water will be required to flush the system.

The total quantity of a contaminant in a unit volume of aquifer relative to that dissolved in the ground water is termed the "retardation factor." Retardation factors depend on contaminant properties (such as K_{ow}) and soil properties (such as organic carbon content). They vary over a wide range, from a value of 1 for nonsorbing compounds such as chloride ions to as large as 100 or more for strongly sorbing compounds such as PCBs in an aquifer with a high organic carbon content. A retardation factor of 1 for chloride indicates that all of the chloride ions are dissolved in the ground water, and a retardation factor of 100 for PCBs indicates that only 1 percent of the PCBs is dissolved in ground water and 99 percent is sorbed to the aquifer solids. If the amount of a chemical sorbed to the aquifer solids is at equilibrium with the concentration in the ground water, the retardation factor is the coefficient by which one must divide the average ground water velocity to obtain the velocity of the sorbed chemical.

The degree to which equilibrium sorption is a valid assumption is a question that has important implications for remediation. If sorbed contaminants do not equilibrate with the adjacent pore water, then the dura



(a) Concentration Distribution at Four Days



(b) Concentration Evolution at Monitoring Well

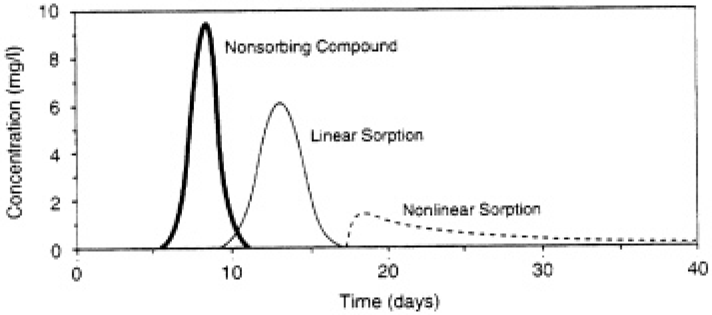


FIGURE 2-9 Influence of sorption on contaminant transport. A contaminant is released at a concentration of 20 mg/liter over a short time period (i.e., in a pulse release); (a) illustrates the concentration profile as a function of distance from the release point four days after release for nonsorbing and sorbing solutes, while (b) illustrates the time evolution of the concentration measured 2 meters downstream of the release point for sorbing and nonsorbing solutes. As shown in (a), sorption slows movement of the contaminant toward the monitoring well. As shown in (b), nonlinear sorption creates a long period of "tailing," during which the contaminant concentration decreases slowly at the well.

tion of cleanup may be extended substantially by the slow desorption. A number of investigations have suggested that sorption processes may exhibit nonequilibrium behavior under natural field conditions (Brusseau and Rao, 1989). Such behavior could be due to the kinetics of the sorption reaction, the mineralogical composition of the formation, or the slow diffusion of contaminants into less accessible pores within the solid materials. Whatever the underlying mechanism, nonequilibrium sorption impedes the release of sorbed contaminants, extending the duration of remediation.

NAPL Entrapment

As a NAPL migrates through the subsurface, small globules become trapped within porous materials by capillary forces. This entrapped NAPL is frequently quantified as the residual saturation (s_r): the volumetric ratio of entrapped contaminant to the total pore volume. Entrapment occurs when capillary forces are large enough to overcome the viscous and gravitational or buoyancy forces that would otherwise cause continued contaminant movement. Residual saturation is thus a function of pore geometry, NAPL properties (including interfacial tension, viscosity, and density), ground water flow velocity, and porous medium wettability. Values of s_r measured in field-scale and laboratory experiments are typically in the range of 10 to 35 percent in water-saturated, unconsolidated media, with levels as high as 50 percent in materials of low permeability (Conrad et al., 1987; Schwille, 1988). In unsaturated media, residual saturation tends to be 50 to 75 percent smaller (Wilson et al., 1990) due to the reduction in capillary forces in this zone. Graded materials with a wide distribution of particle sizes (and, consequently, pore sizes) tend to entrap more contaminants.

Due to the strength of the capillary forces holding it in place, the entrapped NAPL cannot be mobilized by ground water flow under typical operating conditions for pump-and-treat systems (Darcy velocities in the range of 0.01 to 50 meters per day) (Powers et al., 1991). Thus, contaminants present as residual saturation contamination will be physically removed only by dissolution or volatilization to the ground water or gas phases, respectively. Because NAPLs typically have low aqueous solubilities, removal of entrapped NAPL contaminants by pump-and-treat systems will be a very slow process.

Degradation Reactions

Contaminants can be transformed into other compounds, ionic species, or elemental forms by both microbial and chemical processes in the subsurface. Degradation rates for organic compounds vary by several orders of magnitude for both microbial and abiotic reactions, even for compounds with similar structures. Thus, to predict the behavior of contaminants in aquifers, reaction rates need to be known for each compound of interest under environmental conditions specific to the aquifer. Contaminants usually degrade by sequences of reactions that occur under different environmental conditions. In some cases, these reactions may terminate before producing stable, harmless end products, leaving hazardous intermediate byproducts. The term "degradation" usually refers to complete transformation all the way to stable, harmless end products, whereas the term "transformation" refers to partial degradation.

Microbial Transformations

Microbial transformations of many organic compounds have been documented in numerous laboratory investigations. In aquifers, however, the possibility of these laboratory-tested reactions occurring depends on hydrologic and geochemical conditions and on the availability of electron acceptors, nutrients, metabolizable carbon, and bacteria capable of mediating the transformations. Some compounds degrade only under aerobic or anaerobic conditions, some under either condition, and others not at all. Table 2-5 lists susceptibility to biodegradation by various classes of bacteria (discussed earlier in this chapter) for five organic contaminants frequently found at hazardous waste sites. For most of these compounds, degradation by aerobic bacteria is faster than degradation by the other types of bacteria. However, the subsurface oxygen supply is often limited, and therefore the activity of the other types of bacteria shown in Table 2-5 often determines the extent of degradation of organic compounds in the anoxic part of a contaminant plume. The estimated half-lives for biodegradation of six monoaromatic hydrocarbons at five methanogenic field sites ranged from 0.05 to 3.6 years (Barker and Wilson, 1992).

Microbial populations may need to adapt before they are able to degrade certain man-made contaminants. The adaptation time may be required for microorganisms to multiply to a significant biomass or to mutate so that they can use the organic contaminant. Organic compounds known to be degradable can at first resist degradation, later disappearing in short time periods after the microbial biomass acclimates. Such a case explained the sudden disappearance of 1,2-dichlorobenzene in a sand and gravel aquifer in a field test reported by Roberts et al. (1986). It is important to realize that while organisms can adapt to most organic contaminants, adaptation may require a long time period. In addition, some

TABLE 2-5 Microbial Degradation of Selected Organic Compounds

Type of Bacteria	Benzene	Toluene	Naphthalene	Dichloro-benzenes	Trichloro-ethylene	Methyl-phenols	Pentachloro-phenol
Aerobic	++	++	++	++	+	++	+
Denitrifying	+	++	+	-	+	++	-
Iron reducing	-	++	-	-	-	++	-
Sulfate reducing	+	++	-	-	+	++	-
Methanogenic	+	++	-	-	+	++	+

NOTE: -, not demonstrated unequivocally; +, demonstrated, effectiveness in field uncertain; ++ many observations, confirmed in laboratory and supported by field evidence.

contaminants, such as mercury, inhibit microbial growth when the concentration is sufficiently high.

Abiotic Transformations

At some contaminated sites, abiotic chemical reactions (i.e., reactions not caused by microbial activity) can have an important influence on the fate of contaminants. Abiotic reactions can either convert the contaminant to another type of hazardous compound or eliminate it. Transformation rates generally proceed faster by microbial than by abiotic processes, but some abiotic reactions can be fast enough to influence the fate of contaminants in aquifers.

One of the most commonly observed ground water contaminants, 1,1-dichloroethene (see Table 1-1), is formed as the result of an abiotic reaction. This chemical is not widely used. Its prevalence at contaminated sites is due to the abiotic transformation of 1,1,1-trichloroethane, a common solvent, by elimination. Studies have indicated that the half-life of 1,1,1-trichloroethane is between about 3 and 19 years (Vogel and McCarty, 1987).

An important abiotic reaction that can detoxify contaminants is substitution of other groups for halogens. For example, in hydrolysis reactions, a hydroxyl group can replace a halogen to form an alcohol and a hydrogen halide. The half lives of hydrolysis reactions for nine halogenated methanes containing bromide or chloride at concentrations typical for fresh-water systems were 0.05 to 7,000 years (at 25°C and a pH of 7); the median rate was 274 years (Mabey and Mill, 1978). A 1,000-fold reduction in contaminant concentration at this median rate would require 3,000 years. Thus, except for a few compounds, hydrolysis of halogenated hydrocarbons is too slow to be significant in remediation programs.

SPATIAL VARIABILITY

The subsurface is inherently heterogeneous. At the microscale, aquifers contain a mixture of multiple phases—solid, liquid, and gas—characterized by complex geometry. At larger scales, natural geologic processes that occurred during the formation of the aquifer and subsequent chemical, physical, and biological processes result in multiple levels of heterogeneity. The impact of such heterogeneities on contaminant migration and aquifer remediation cannot be overemphasized. Heterogeneities result in the transport of contaminants to places where they are difficult to locate and remove, and they cause the accumulation of contaminants in zones that subsequently become long-term sources of pollution.

Physical Heterogeneity

At the microscale, an aquifer may be composed of aggregates of materials that have large pore spaces between the aggregates but small pore spaces within the aggregates. The presence of such aggregates can substantially affect contaminant transport. Dissolved contaminants will tend to migrate via molecular diffusion into the small pores within these aggregates (often referred to as immobile zones). Once present within the aggregates, these compounds will serve as a long-term source of pollution, as they slowly diffuse from the pores when the contaminant concentration in the mobile ground water is reduced (Van Genuchten and Wierenga, 1976; Rao et al., 1980). Such mobile-immobile zone mass transfer processes mimic the behavior described above for sorption. Both processes tend to create a persistent contaminant release mechanism, interfering with attempts to flush contaminants out of the aquifer.

Microscale heterogeneities can also influence NAPL migration and entrapment. Recent studies have revealed that grain size variability can affect the entrapment and subsequent dissolution of organic globules (Powers et al., 1992). Nonuniform media tend to impede the dissolution of entrapped NAPLs more than uniform materials of the same average grain size. As with sorption and diffusion from aggregates, this slowing of the dissolution process further enhances the persistence of the contaminants underground.

Larger-scale heterogeneities also pose complications. For example, in sand and gravel aquifers, deposits of silt and clay are common. Because water moves more slowly through silt and clay than through sand and gravel, silt and clay layers can significantly change ground water and contaminant movement from what would occur in a sand and gravel aquifer without silt and clay deposits. Heterogeneities can cause wide variability in hydraulic properties such as hydraulic conductivity. For example, in a detailed investigation of a so-called "homogeneous" sand and gravel aquifer at a scale of approximately 1,000 m^3, the hydraulic conductivity varied between 0.001 and 0.021 cm/s (Sudicky, 1986). The geologic features that controlled the variability were at a scale of a few centimeters to tens of centimeters vertically and one to a few meters horizontally. These changes in hydraulic properties enhance the dispersion of a dissolved contaminant as it travels over large distances, increasing the contaminant spread. Due to the presence of large-scale heterogeneities, the spreading of dissolved contaminants at the field scale is generally much greater than would be predicted by employing laboratory-scale dispersion information (Anderson, 1979). Accurate prediction of contaminant transport at a specific site thus requires a detailed (on the scale of 10 to 100 cm) description of aquifer hydraulic properties. As an exam

Laboratory model of the transport of a DNAPL contaminant through an aquifer with varying permeability; note the DNAPL pools above the low-permeability zones (the horizontal discs). Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

ple, Figure 2-10 illustrates the complexity of a bromide plume produced by a tracer test conducted in a relatively uniform sand and gravel aquifer in Cape Cod, Massachusetts. The complexity of the plume, as determined from 650 multilevel samplers, reflects the sensitivity of transport to spatial variations in hydraulic properties even in simple subsurface environments.

The presence of low-permeability zones or lenses can cause rate-limited mass transfer behavior similar to that observed in aggregated soils. Over time, solutes will diffuse into such strata. These zones thus function alternately as sinks and then sources of solute mass for the bulk ground water (Valocchi, 1988; Gilham et al., 1984). The large amounts of time required for compounds to diffuse out of these low-permeability strata can add considerably to the time and volume of water required to flush out contaminants (Wilson, 1992).

The presence of low-permeability lenses will also influence NAPL migration. For materials with sufficiently small pores, NAPL phases cannot displace the water in the pores and therefore cannot penetrate the pores. These strata therefore act as capillary barriers to NAPL flow, inducing lateral spreading, irregular migration pathways, and "pooling" of the NAPL (see Figures 2-5 and 2-6). Such pools may be extremely difficult to locate. In addition, ground water makes minimal contact with these NAPL pools, thus causing flushing to be an ineffective method for recovering the organic liquid.

Heterogeneities can also create preferential pathways for NAPL migration, greatly enhancing travel distance and limiting lateral spreading. NAPLs have been observed to preferentially flow along fine-scale surfaces between subsurface layers (Kueper et al., 1993). In addition, small-scale permeability variations can trigger the onset of viscous fingering in an inherently unstable flow regime. Subsurface macropores, created by plant roots or chemical weathering, and formation joints and fractures can serve as preferential pathways. In addition to enhancing the contaminant transport rate, such pathways may permit the NAPL to penetrate otherwise impermeable strata and facilitate the transport of contaminants between formations. Preferential flow paths tend to create highly variable distributions of NAPL in the subsurface. Under such conditions, locating contaminants is a formidable task, making contaminant removal through excavation infeasible and posing great difficulties for contaminant containment.

Chemical Heterogeneity

Variable chemical composition within a formation may also affect contaminant transport over a range of scales. At the pore scale, a vari

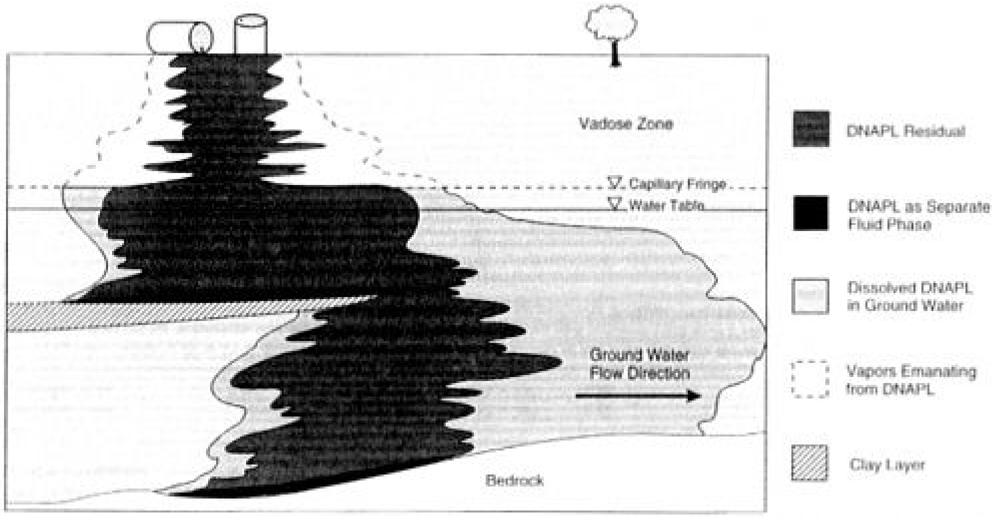


FIGURE 2-10 The complexity of a plume created by a bromide ion solution in a sand and gravel aquifer in Cape Cod, Massachusetts. SOURCE: LeBlanc et al., 1991.

able mineral composition will create a complex environment in which many sorption mechanisms may coexist (Weber et al., 1992) and behavior is not easily quantified. At a larger scale, spatial variability in organic carbon content or formation mineralogy will tend to produce zones of high contaminant retention. Some theoretical studies suggest that spatial variability of chemical factors controlling sorption can enhance contaminant dispersion (Garabedian, 1987; Valocchi, 1989). Relatively little is known, however, about the degree to which sorption characteristics vary and are correlated with variations in hydraulic conductivity (Sudicky and Huyakorn, 1991). Variable mineral composition and organic carbon content may also affect NAPL entrapment mechanisms, possibly creating zones of entrapped NAPL that are less accessible to flowing ground water.

Source Variability

In addition to physical and chemical variability, variability in the composition and distribution of the contaminant source also affects contaminant behavior in the subsurface. Contaminants rarely enter the subsurface individually. Thus, an understanding of the behavior of mixtures is critical to predicting contaminant migration and retention. Unfortunately, the composition of the contaminant source is usually imprecisely known. For NAPLs, properties such as density, viscosity, solubility, and interfacial tension depend on composition. For example, chlorinated solvents ordinarily enter the subsurface as DNAPLs, which tend to sink below the water table, but they may also enter as minor components of a hydrocarbon mixture constituting an LNAPL, which tends to spread laterally at the water table. As components of a NAPL mixture dissolve or volatilize over time, the NAPL properties change, a process termed "weathering." Very little information is available pertaining to the weathering of chemical mixtures of interest in aquifer remediation.

The presence of multiple dissolved contaminants creates competition for sorption sites. In severely contaminated systems, the properties of dissolved contaminants will also be influenced by the presence of cosolvents. The effect of multiple solutes and cosolvents on sorption phenomena seriously complicates the task of characterizing contaminant distribution and transport (Weber et al., 1991; Nkedi-Kizza et al., 1985; Rao et al., 1990).

The magnitude, temporal evolution, and spatial distribution of the source of contamination greatly influence the transport and retention of pollutants. These factors, however, are unknown at many sites. Temporal fluctuations in contaminant release will create zones of high concentration within a plume, although such zones tend to flatten over large travel distances due to natural dissipative mechanisms. The size of the spill may influence the amount of contamination that ultimately reaches the aquifer. For example, if a spill is small, it may never reach the saturated zone due to residual entrapment of the contaminant within the unsaturated zone. The spatial distribution of the original source of contamination may affect the extent of aquifer contamination. For example, DNAPLs will tend to remain localized within a small horizontal cross-sectional region because these chemicals have no tendency to spread laterally until they encounter a stratum of low permeability.

In the majority of cases it is useful to separate the contamination conceptually into two parts: (1) the plume of dissolved contaminant and (2) contaminant source areas, which include the potentially substantial amounts of contaminant in precipitated or NAPL form. As Chapter 3 will explain, the plume can be contained and its size decreased by pumping. The sources of contamination are generally much more difficult to control and remove; they will often extend over a considerable volume, and no adequate methods are available for locating all of them. Removal of contaminant sources by pumping may require years or centuries, depending on factors such as the solubility of the contaminant in water, the size of the sources and their distribution, and the flow pattern of the aquifer.

RESEARCH NEEDS FOR IMPROVING UNDERSTANDING OF THE CONTAMINATED SUBSURFACE

This chapter has documented that the subsurface environment even in its uncontaminated condition—is a complex system that scientists do not fully understand. Advances in knowledge about subsurface processes are essential for improving ground water contamination assessments and cleanup technologies. These advances are needed in three broad areas: subsurface characteristics, contaminant transport and distribution, and reaction pathways and rates. The greatest progress will be made if site cleanups are accompanied by investigations aimed at identifying the critical conditions and processes controlling contaminant behavior, while gathering data helpful for optimizing performance of the cleanup system.

Subsurface Characteristics

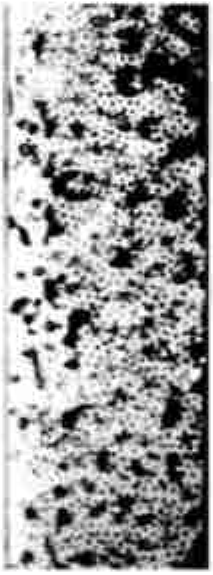
This chapter has documented that hydrogeologic investigations of contaminated environments must provide both fine resolution and complete coverage of the contaminated area. Heterogeneities ranging from the microscale to the macroscale can have profound effects on transport of contaminants and performance of cleanup systems. Errors in predicting subsurface characteristics—and hence the performance of cleanup systems—frequently result from the inability to obtain representative samples at both sufficiently small and large scales. Improvements in subsurface sampling methods especially in noninvasive methods that do not jeopardize the integrity of the site with extensive drilling—would significantly advance the ability to design ground water cleanup systems and to predict the fate of contaminants. Research is needed to answer the following questions:

- How can sampling methods be improved to ensure that the samples are representative?
- What parameters—physical, chemical, and biological—must be included in the site characterization program for formulation of realistic cleanup objectives and optimization of the treatment system?
- How can the variability of aquifer properties be characterized over a sufficient range of scales—millimeters to kilometers—to understand the effect of variability on contaminant transport and cleanup system performance?
- What level of characterization is needed to support decisionmaking at the various stages of remedial investigation and design?
- Can the variability of aquifer properties be assessed adequately with statistical information developed from common geologic environments?
- How can the costs of sampling methods be reduced to allow more extensive sampling at sites?
- What new ideas and techniques can contribute to development of a reliable three-dimensional map of subsurface geology and ground water flow patterns at a site?

Contaminant Distribution and Transport

Considerable progress has been made in recent years in developing the ability to predict the distribution and transport of contaminants in the subsurface. For example, a greater understanding now exists pertaining to the coupling of permeability variations and dispersive contaminant transport. Similarly, the fundamental physical phenomena governing NAPL migration and entrapment have been identified in laboratory studies under simple, well-defined conditions. However, much still needs to be learned regarding contaminant behavior in complex natural systems. Most investigations of contaminant fate in the subsurface have been carried out under ideal conditions such as in homogeneous aquifers with single contaminants. As this chapter has emphasized, however, the subsurface is neither chemically, biologically, nor physically homogeneous. Unfortunately, relatively little is understood about the impact of heterogeneities on processes that control the fate and transport of contaminants, including sorption, abiotic and biotic reactions, and residual entrapment and dissolution. More information is needed about the behavior of contaminants at a fundamental level in nonideal systems to answer the following questions:

- How can the full range of contaminants and other organic compounds in the ground water—not just those targeted in the monitoring plan—be determined?
- What critical parameters and properties govern transport of contaminants in various types of complex subsurface systems?



Trapped globules of NAPL in a laboratory column containing a porous medium (glass beads). Courtesy of Rice University, Department of Environmental Science and Engineering.

- How can the relationships between these critical parameters and properties and the transport of contaminants be quantified?
- How can these properties be measured, or how can they be inferred from more easily quantifiable media properties?
- How can detection methods for NAPLs or other concentrated sources of contamination be improved to provide more detailed characterization of the distribution of contaminant mass?
- How can data from sampling and pumping wells be used to locate contaminant sources more precisely?
- How can site-specific data best be incorporated into mathematical models for predicting contaminant transport?

Reaction Pathways and Rates

This chapter has documented that a variety of chemical and biological reactions influence the fate of contaminants in the subsurface. Time scales for ground water transport are generally large enough—on the order of many years—that even exceedingly slow reactions can register an impact. For this reason, classes of reactions of minimal importance in other environments can significantly affect the fate of ground water contaminants. Furthermore, the large fluid-solid interfacial area typical of aquifers increases the occurrence of reactions mediated by mineral constituents and microorganisms on the solid surfaces.

The heterogeneity of subsurface conditions greatly complicates understanding of contaminant reactions. Because of the diversity of geochemical conditions, expressed as compositional gradients from the molecular scale to the macroscale, a bewildering variety of reaction behavior can occur. Furthermore, the study of subsurface reaction rates poses severe methodological problems, especially when working with natural aquifer solids of diverse composition. Special precautions are necessary to define and control the experimental system sufficiently so that reaction rates can be measured while at the same time preserving the connection to the real environment. It is not surprising that researchers have been reluctant to take up this challenge and that knowledge is often sparse regarding the reaction mechanisms and pathways that may determine the fate of ground water contaminants. The fundamental study of such reaction systems is relatively new, and if pursued may open new vistas for in situ ground water cleanup. Research is needed to address the following questions:

- What are the critical chemical and biological reactions affecting contaminants in various types of subsurface environments?
- How can rates of these reactions be quantified, and how do they

depend on geochemical conditions and the presence of particular microorganisms?

- How can reaction rates measured in the laboratory be extrapolated to the field?
- Are naturally occurring microorganisms able to achieve desired biotransformations, or must specially cultured organisms be introduced?
- How can the subsurface microorganisms be assayed to enable prediction of biochemical transformations?
- To what extent do specific chemical or biochemical reactions depend on geochemical conditions such as pH, redox state, and mineralogy?
- To what extent do particular reactions modify geochemical conditions —pH, redox state, and surface composition—thus promoting or inhibiting other reactions?
- For localized contaminant sources, what chemical treatments could destroy or solubilize contaminants, particularly NAPLs?
- How can reaction rate information best be incorporated into mathematical models for predicting contaminant fate?

CONCLUSIONS

Based on consideration of the properties of the subsurface environment and contaminant behavior in the subsurface, the committee reached the following conclusions:

- **Theoretically, it is possible to clean up contaminated ground water, subject to constraints imposed by the principles of mass and energy conservation, thermodynamics, and kinetics.** However, practical limitations arising from the uneven distribution of contaminants, subsurface complexity, and the inherently slow rate of ground water movement severely restrict decontamination efforts.
- **Subsurface environments have complexities and heterogeneities that make them inherently difficult to decontaminate.** The complexity of the subsurface and the difficulty of characterizing it contribute in large measure to the problems experienced in ground water cleanup documented in the following chapters. While some generalizations are possible, each site has a character of its own and must be studied carefully to enable effective remediation.
- **Contaminants found at hazardous waste sites are diverse in nature, manifesting a wide range of properties that may complicate remediation.** Contaminants that are present as separate liquid phases, sorbed strongly to aquifer soil and rock, or precipitated as solids constitute a large reservoir that is difficult to remove. Immiscible liquid contami

nants (NAPLs) especially increase the complexity of remediation because they migrate into places inaccessible to extraction by hydraulic forces.

- **Ground water contamination problems may become increasingly complex with the passage of time because of the potential for contaminants to migrate and accumulate in less accessible zones.** Measures to remove contaminants from zones where the release occurred and to contain contaminants that cannot be removed should be taken as soon as possible after the contamination occurs.
- **Transport and transformations in the subsurface occur relatively slowly, at time scales as long as years, decades, and centuries.** All of those concerned with ground water remediation—scientists and technologists, as well as decisionmakers and the public—must recognize that ground water cleanup requires patience and perseverance to an extent considerably greater than for surface water cleanup. Expectations of quick and easy solutions are illusory.

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3

Performance of Conventional Pump-and-Treat Systems

Between 1982 and 1992, 73 percent of the cleanup agreements at Superfund sites where ground water is contaminated specified the use of pump-and-treat technology (Kelly, 1994). At most of these sites, the cleanup goal is to restore the aquifer so that the water extracted from it will be suitable for drinking without further treatment. Yet, within the past few years, studies of pump-and-treat systems have indicated that drinking water standards may be essentially impossible to achieve in a reasonable time frame at certain sites (Keely, 1989; Mackay and Cherry, 1989; EPA, 1989a; Mercer et al., 1990; Doty and Travis, 1991; Travis and Doty, 1990). This chapter presents the Committee on Ground Water Cleanup Alternatives' assessment of how well existing pump-and-treat systems have performed and whether it is reasonable to expect that they can achieve drinking water standards.

The analysis presented in this chapter is based on a review of 77 sites where pump-and-treat systems have been studied and the committee members' own extensive experience with ground water cleanup. Appendix A shows the sites the committee evaluated and summarizes the performance of pump-and-treat systems at each site. At 69 of the 77 sites, the pump-and-treat systems have not yet reached cleanup goals, as indicated in Appendix A. However, the committee also found eight sites where pump-and-treat systems have apparently achieved cleanup goals.

Throughout this chapter are brief case studies of sites where goals have been reached and those where they have not. Although the chapter highlights many success stories, the committee wishes to emphasize that these successes are rare, as is evident in Appendix A. The committee also wishes to emphasize that whether a cleanup is labeled a success or a failure depends in part on the stringency of the cleanup goal. The success or failure of a cleanup should not be viewed as a simple "yes" or "no" but instead should be evaluated according to a continuum of possible results, from unequivocal failure to reduction in exposure to contaminants to unequivocal success, as shown in Table 3-1.

TABLE 3-1 Continuum of Possible Results for Pump-and-Treat Systems

Result	Explanation
Unequivocal failure	Fails to contain subsurface sources of contamination and to clean up the plume of dissolved contaminants emanating from source areas
Prevention of additional exposure to contamination	Contains subsurface sources of contamination and prevents the plume of dissolved contaminants from increasing in size
Reduction of additional exposure and significant shrinkage of the area affected by the contamination	Contains subsurface sources of contamination and possibly reduces the amount of contaminant mass in source areas; cleans up part or all of the plume of dissolved contaminants to healthbased standards
Unequivocal success	Fully removes sources of contamination and cleans up the plume of dissolved contaminants to health-based standards

HOW PUMP-AND-TREAT SYSTEMS WORK

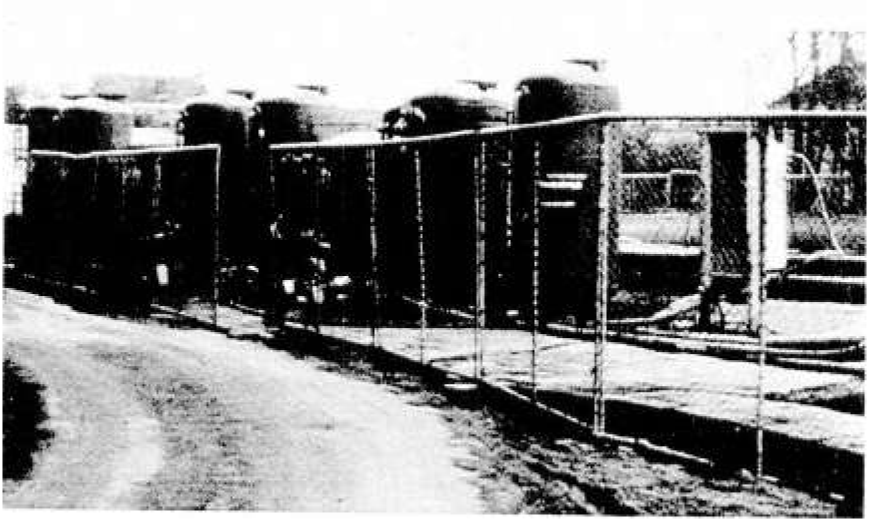
Conventional pump-and-treat systems are based on a theoretically very simple concept: contaminated ground water is extracted from the subsurface, and the extracted water is replaced with clean water. The clean water comes either from areas immediately adjacent to the contaminated zone or from water injected into the subsurface as part of the pump-and-treat process. (See Figure 1-1 in Chapter 1 for an example of a pump-and-treat system.)

Occasionally, the extracted water is discharged directly into a surface water body, such as a stream. Direct discharge is acceptable where the surface water standards allow higher contaminant levels than do the ground water standards and where the contaminant concentration in the extracted ground water is low enough that surface water standards will not be exceeded. More often, however, the extracted water requires treat ment. The extracted water may be treated using any of a number of methods that have been well tested for removing contaminants from drinking water and industrial and municipal wastewater. For example, air strippers can remove volatile contaminants, granular activated carbon can remove dissolved organic contaminants, and biological systems can remove biodegradable contaminants. Once treated, the water may be discharged to a surface water body or reinjected underground. Reinjection can improve the system's efficiency and reduce cleanup time by speeding the flow of water and contaminants to the extraction wells.

Pump-and-treat systems can be designed for two very different goals: containment, to prevent the contaminant from spreading, and restoration, to remove the contaminant. In pump-and-treat systems designed for containment, the extraction rate is generally established as the minimum rate sufficient to prevent enlargement of the contaminated zone. In pump-and-treat systems designed for restoration, the pumping rate is generally established to be much larger than that required for containment so that clean water will flush through the contaminated zone at an expedited rate. Because of their reduced pumping requirements, pump-and-treat systems designed for containment are much less costly to operate than pump-and-treat systems designed for restoration. In all other fundamental ways, the two types of systems are identical. However, pump-and-treat systems designed for restoration face a much greater technical challenge than those designed for containment. Even when these systems extract contaminated water and replace it with clean water, undissolved contaminants may remain underground. The remaining contaminants will dissolve slowly over time, making complete restoration of the ground water impossible until all of the contaminants can be removed

PREVIOUS STUDIES OF PUMP-AND-TREAT SYSTEMS

Before 1989, the limitations of pump-and-treat systems were not fully appreciated. No large-scale studies of the effectiveness of pump-and-treat systems were available because most of the systems were so new that their long-term performance could not be assessed. In 1989, however, the Environmental Protection Agency (EPA) released a study of pump-and-treat systems that caused concern in the regulatory community and among businesses paying for the cleanups. After a detailed review of 19 sites where pump-and-treat systems were operating, the EPA determined that at none of these sites had the aquifers been restored to drinking water standards (EPA, 1989a,b,c). In 1991, the EPA reassessed the data from these 19 sites and reviewed 5 additional sites. The agency found one site of the 24 where cleanup goals were apparently reached (EPA, 1992a,b). However, no follow-up monitoring was performed at the site to confirm the cleanup, and agency personnel have questioned the existing site data (Sutter and Glass, 1992).



Components of a pump-and-treat system at a former coal gas plant: pumped water is filtered through the activated carbon units shown here. Courtesy of the Johns Hopkins University, Department of Geography and Environmental Engineering.

After the EPA studies, others conducted their own investigations. Researchers at the Oak Ridge National Laboratory reexamined data from 12 of the EPA sites and evaluated 4 additional sites (Doty and Travis, 1991). Like the EPA researchers, the Oak Ridge investigators concluded that pump-and-treat systems had not restored the aquifers to drinking water standards at any of the sites. More recently, the American Petroleum Institute (API) released a study of 13 sites not included in the EPA or Oak Ridge studies (API, 1993). The API's results were more promising: the study identified five sites, all gasoline stations, where pump-and-treat systems have reached cleanup goals. In a fourth study, researchers representing the California Regional Water Quality Board reviewed the records of 37 pump-and-treat systems at semiconductor manufacturing sites in California's Santa Clara Valley (Bartow and Davenport, 1992). Like the API study, this study yielded results somewhat more promising than previous studies: the researchers found two sites where pump-and-treat systems have reduced concentrations to below health-based standards for all of the contaminants; they identified an additional eight sites where the pump-and-treat systems have reached health-based cleanup levels for some but not all contaminants.

A common limitation of all the studies of pump-and-treat systems is that at most sites, systems have been operating for too short a time period to allow a final assessment of their effectiveness. The average starting year of all the systems in the EPA, Oak Ridge, API, and California Water Quality Control Board studies was 1985, which means these studies were based on only about five to seven years' worth of data, on average. A second problem with the studies is that for many of the early pump-and-treat systems, the designers did not fully appreciate the complexity of the subsurface and thus did not consider it in the system plans. For these systems, separating system success or failure from inadequate design is difficult. A third problem is that at many sites, surface sources of contamination such as heavily contaminated soils remain in place, raising questions about whether the inability to reach cleanup goals is due to continued leaching from these sources. As a consequence of these limitations, existing studies do not rule out the possibility that, given more time, optimal designs, and removal of surface sources of contamination, a larger number of pump-and-treat systems could reach cleanup goals.

Amidst the uncertainty raised by the recent studies, some analysts have suggested that pumping and treating may be a wasted effort (Travis and Doty, 1990). Such critics question whether, given the poor record in meeting health-based cleanup goals, pump-and-treat systems are worth operating. These critics emphasize the enormous cost of pumping and treating large volumes of ground water over long time periods. On the other hand, others view the technology more favorably, contending that pump-and-treat systems can significantly reduce the risks of exposure to ground water contamination by removing contaminant mass and by containing the plume to keep it from points of water use, even if they cannot return all of the aquifer to near-pristine conditions.

FEASIBILITY OF CLEANUP WITH PUMP-AND-TREAT SYSTEMS

The effectiveness of pump-and-treat systems depends strongly on hydrogeologic and contaminant properties. As the complexity of the hydrogeologic conditions and the contaminants increases, the likelihood that the pump-and-treat system will meet stringent cleanup goals decreases.

Table 3-2, developed by the committee, provides a framework for assessing the complexity of cleaning up contaminated ground water. In the table, the complexity of ground water cleanup increases with the complexity of contaminant chemistry, from left to right. The complexity

TABLE 3-2 Relative Ease of Cleaning Up of Contaminated Aquifers as a Function of Contaminant Chemistry and Hydrogeology

	Contaminant Chemistry					
Hydrogeology	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved	Strongly Sorbed, Dissolved[a] (degrades/ volatilizes)	Strongly Sorbed, Dissolved[a]	Separate Phase LNAPL	Separate Phase DNAPL
Homogeneous, single layer	1[b]	1-2	2	2-3	2-3	3
Homogeneous, multiple layers	1	1-2	2	2-3	2-3	3
Heterogeneous, single layer	2	2	3	3	3	4
Heterogeneous, multiple layers	2	2	3	3	3	4
Fractured	3	3	3	3	4	4

[a] "Strongly sorbed" generally indicates contaminants for which the retardation coefficient is greater than 10. A retardation coefficient of 10 indicates that at any given time, 10 percent of the contaminant is dissolved in the water and 90 percent is sorbed to the aquifer solids.

[b] Relative ease of cleanup, where 1 is easiest and 4 is most difficult.

of cleanup also increases with hydrogeologic complexity, from top to bottom. Conditions categorized as 1, shown in the upper left portion of the table, represent those that will be easiest to remediate. Conditions categorized as 4, shown in the lower right portion of the table, will pose the greatest technical challenge.

Influence of Contaminant Chemistry and Site Geology

As Table 3-2 shows, two types of contaminant characteristics can complicate ground water cleanup. The first characteristic is the tendency of the contaminant (organic or inorganic) to sorb to solid materials. As explained in detail in Chapter 2, chemical compounds dissolved in ground water interact with the solid media in the subsurface. As a result, at any given time, some of the chemical compound is dissolved in the ground water and some is attached to the solid media. Pump-and-treat systems can remove only dissolved contaminants. When a portion of the contaminant mass remains sorbed to solid media, it is possible that cleanup standards will not be met because the sorbed contaminants will desorb too slowly to be entirely removed but quickly enough to contaminate the clean ground water.

The second contaminant characteristic complicating cleanup is the tendency for certain organic contaminants to remain undissolved as a nonaqueous phase. As explained in Chapter 2, these phases may be organic chemicals present as light nonaqueous-phase liquids (LNAPLs) that tend to float on the water table, such as gasoline, or as dense non-aqueous-phase liquids (DNAPLs) that tend to sink, such as chlorinated solvents. Contaminants dissolve slowly from these nonaqueous-phase liquids (NAPLs) into the passing ground water. As a result, it is likely that cleanup standards will not be met when NAPLs are present.

As Table 3-2 shows, two types of contaminant characteristics can facilitate cleanup. As indicated in Chapter 2, certain chemicals degrade and/or volatilize. These processes may aid in cleanup when the processes occur naturally or when the remediation system takes advantage of them. For example, many LNAPLs are petroleum chemicals that degrade (when dissolved from the LNAPL) and/or volatilize. These processes, along with the fact that the LNAPLs usually rest above the water table, facilitate cleanup when a pump-and-treat system is combined with other technologies such as soil vapor extraction or bioventing (see Chapter 4).

In addition to contaminant characteristics, Table 3-2 shows three types of geologic characteristics that can complicate cleanup: multiple layers, heterogeneities, and fractured rock. When such geologic features are present, different regions of the contaminated zone will flush at different rates, with high-permeability zones cleaned up first. Attainment of cleanup standards will often be determined by how quickly the lower permeability zones flush. Furthermore, as explained in Chapter 2, heterogeneous regions with low permeability and regions with fractured rock can store significant quantities of contaminants that the bulk of the ground water cannot reach. Chemical transfer from these regions is slow and is controlled by diffusion. Regardless of the amount of contaminated water extracted, as long as significant diffusion occurs out of the low-permeability zones, it is possible that ground water cleanup standards will not be met.

Geologic complexities and the presence of sorbed or nonaqueous-phase contaminants may affect the outcome of pumping and treating by causing progress toward cleanup to tail off above the cleanup goal. When the pump-and-treat system begins operation, contaminant concentrations may drop very rapidly, but after continued operation this rapid progress may cease at a level significantly above the cleanup goal. At such sites, there is no doubt that additional progress is still being made toward remediation, because the contaminant mass left in the aquifer is finite, and the pump-and-treat system continues to remove mass. In addition, the leveling effect often is observed only at some of the wells, near contaminant sources, while at other wells contaminant concentrations may continue decreasing. However, at wells where the concentration has leveled, continued progress toward reducing the concentration will be very slow, and the "final" stages of remediation may proceed for a very long time, as shown in Figure 3-1.

Geologic and chemical complexities may also affect the result of pumping and treating by causing regrowth of the contaminant plume when pumps are turned off, even after the cleanup goal has been reached. Plume regrowth may occur when nonaqueous-phase contaminants that were not extracted with the pump-and-treat system dissolve in the clean water. It may also occur when contaminants in zones of low permeability that were not flushed with the pump-and-treat system diffuse into the clean water.

Influence of the Quantity and Duration of Contamination

In addition to the geologic and chemical characteristics depicted in Table 3-2, two other factors are very important in determining the difficulty of cleanup: (1) the mass of contaminant released and (2) the length of time the contaminant remained in the subsurface before cleanup. The easiest sites to remediate are those at which only a small mass of chemi cal has been released in a small area and pumping and treating begin soon after the release.

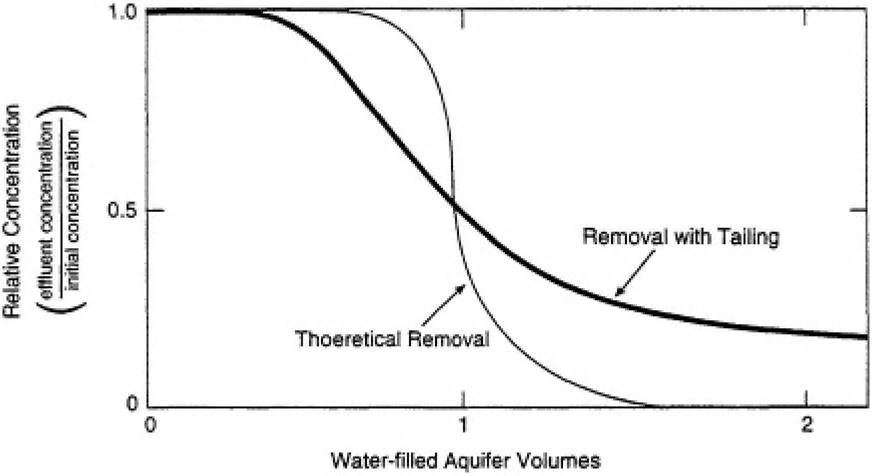


FIGURE 3-1 The effect of tailing on cleanup time. The "theoretical removal" curve shows the number of aquifer volumes of ground water that must be pumped to remove the contamination, assuming all of it dissolves readily. The "removal with tailing" curve shows the number of aquifer volumes of ground water that must be pumped to remove the contamination when significant undissolved sources of contamination are present. Examples of such sources include contaminants present as pools of NAPLs and metals that have precipitated. SOURCE: Mercer et al., 1990.

The length of time required for remediation generally increases with the amount of contaminant mass and the size of the source area. The size of the source influences cleanup time not only because larger quantities of contamination require more time to remove but also because the larger the source, the more difficult it is to identify and characterize the impact on ground water. The sites reviewed in Appendix A span a wide spectrum of source sizes and complexities. For example, at the Varian Associates site in Santa Clara, California, approximately 40 to 80 liters of 1,1,1-trichloroethane were lost in a one-time spill in 1984, whereas at the Aerojet site in Sacramento, California, potentially more than 4 million liters of chlorinated organic solvents were released at more than 100 source areas scattered about a 30-square-kilometer site starting in the early 1950s.

For contaminants that resist degradation, the length of time for remediation increases with the length of time between the contaminant release and the start of remediation, because some processes that control ground water migration, such as diffusion, are time dependent. On the other hand, for contaminants that degrade to nontoxic products by chemical or biological processes, remediation may become easier as the time between the release and the start of remediation increases. Sites with ground water contamination range from coal gas generating facilities where releases occurred more than a century ago to service stations with ruptured underground storage tanks that are addressed within days of the release. Table 3-2 assumes that a "medium" amount of contaminant has resided in the subsurface for a "medium" length of time.

Cleanup of crude oil from a burst pipeline near Bemidji, Minnesota. The equivalent of 8,000 barrels of oil was removed directly, but 2,500 barrels remained in the subsurface, forming a plume of contamination in the ground water. Courtesy of Hans-Olaf Pfannkuch, University of Minnesota.

CATEGORIZING SITES FOR CLEANUP

Provided certain qualifications are kept in mind, the categories in Table 3-2 can provide a preliminary indication of the difficulty of clean ing up a particular site. The table does not encompass all of the factors that make ground water cleanup a complex task. As indicated above, it does not consider chemical mass released and duration of contamination. In addition, it does not consider cleanup goals, which influence whether the cleanup is perceived as a success or failure. Nevertheless, the categories in Table 3-2 are useful as subjective criteria for evaluating sites.

Categorizing a site according to Table 3-2 requires information about the following site characteristics:

1. site stratigraphy (i.e., a description of the geological layers),
2. permeability of the layer(s),
3. structural geology (especially information about fractures),
4. types of chemicals in the subsurface,
5. properties of chemicals in the subsurface, and
6. estimates of the distribution of chemicals in the subsurface, including estimates of the potential or actual presence of LNAPLs or DNAPLs.

Determining the appropriate row in Table 3-2 requires an assessment of whether the site hydrogeology is homogeneous, heterogeneous, or fractured, which can be determined by analyzing the first three types of information (stratigraphy, permeability, and structural geology). The ideal hydrogeologic environment for pump-and-treat systems is one that is a single layer with a hydraulic conductivity greater than about 10^{-5} cm/s (Mercer et al., 1990). Determining the appropriate column in Table 3-2 requires a judgment about the likely contaminant behavior in the subsurface, which requires the above types of information about the contaminants (types, properties, and distribution), as well as information about the composition of the solid media comprising the aquifer. For example, the retardation coefficient, which depends on properties of the contaminant and the solid media, indicates whether or not the contaminant will sorb strongly. In general, pump-and-treat systems are best suited to recover mobile chemicals that have retardation coefficients less than 10, which in general means that at any given time at least 10 percent of the contaminant in the plume is dissolved in the ground water (see Chapter 2). Relatively volatile organic compounds, indicated in the first and third columns of Table 3-2, have high vapor pressures and Henry's Law constants greater than 10^{-3} atm-m^3/mole (EPA, 1990). Degradation, also shown in the first and third columns, is both chemical and site specific. As explained in Chapter 2, a wide variety of compounds—from gasoline and other fuels to chlorinated solvents—are potentially biodegradable, but whether they will degrade in the field depends on site conditions (especially on the presence of electron acceptors and other compounds necessary to support microbial activity).

As an example of how this information can be used to categorize sites, a plume containing a contaminant with a retardation coefficient greater than 10 would belong in the fourth column under the contaminant chemistry heading of Table 3-2 because it would have a strong tendency to sorb. If the site geology is heterogeneous, then according to the table the site would be assigned a category of 3. The committee used this process to categorize the sites in Appendix A and to evaluate the feasibility of ground water cleanup under different types of site conditions.

Cleanup of Sites in Category 1

At sites with conditions in category 1 in Table 3-2, well-designed pump-and-treat systems generally should be able to restore the ground water to health-based standards in reasonable periods of time. These sites have uniform geologic characteristics and contaminants that are fully dissolved. Such ideal site conditions are rare. For example, of the 77 sites listed in Appendix A, only 2 are in category 1; the pump-and-treat system reached cleanup goals at one of these sites, a service station reviewed in the API study (API, 1993). At this site, the initial total concentration of the gasoline components benzene, toluene, ethylbenzene, and xylene (BTEX) was 1,021 parts per billion (ppb). After five years of pumping, the BTEX concentration was below the detection limit. This is a relatively small site and thus design and operation of the cleanup system were much simpler than at the more complex sites typical of the Super-fund program. The treatment system consisted of one extraction well operating at an estimated average rate of 95 liters per minute; it removed approximately 19 kg of contaminants in total. In addition to the smaller size of the site, another factor that may have aided the cleanup is the biodegradability of the contaminants. Numerous researchers have demonstrated that under the right conditions, BTEX is degradable even without human intervention (National Research Council, 1993). When this report was prepared, operators at this service station had applied to shut down the pump-and-treat system and commence post-remediation monitoring.

Cleanup of Sites in Category 2

Cleanup of sites in category 2 also is possible but is subject to greater uncertainties than cleanup of sites in category 1. Of the 77 sites in Appendix A, 12 sites are in category 2 and 2 sites are on the borderline between categories 2 and 3. Cleanup goals have been achieved at four of these sites. At these four sites, some or all of the contaminants were biodegradable compounds such as BTEX, ketones, and alcohols. Conse quently, it is possible that some of the contamination was removed by biodegradation rather than by pumping and treating. It is also possible that at some sites, cleanup goals will be achieved in the future with continued pumping and treating.

Table 3-2 indicates two broad types of sites in category 2: (1) sites with contaminants that are fully dissolved and therefore amenable to extraction but with geologic heterogeneities that interfere with contaminant extraction and (2) sites with homogeneous geologic conditions that facilitate ground water extraction but with contaminants that sorb to solid materials, interfering with their extraction. An example of a category 2 site is the service station described in Box 3-1. This site is similar to the category 1 service station described above, except that the site contains geologic heterogeneities. At this site, three years of pumping reduced the BTEX concentration below regulatory standards in monitoring wells. The company ceased pumping in May 1991; one-and-a-half years later, the last set of available monitoring data indicated that contaminant concentrations remained below regulatory levels.

In the cases where cleanup goals have apparently been achieved at category 2 sites, it is possible that some contamination may remain—either in low permeability zones that were not adequately flushed by the pump-and-treat system or sorbed to solid materials in the aquifer. It is uncertain whether such lingering contaminants will dissolve in the ground water in sufficient quantities that, at some future date, contaminant concentrations will again exceed regulatory levels. An example of such a situation is the tire manufacturing plant described in Box 3-2, which was contaminated with chlorinated solvents and BTEX. At this site, regulators have approved shutdown of the pump-and-treat system because cleanup goals have been achieved in all 25 extraction wells. However, monitoring well data show that a small contaminant "hot spot" remains. It is uncertain whether contaminants remaining in the soils in the hot spot may spread and create a risk at some future date.

Cleanup of Sites in Category 3

Complete cleanup of sites in category 3 is possible but is subject to significant uncertainties. Partial cleanup may be a more realistic scenario for many such sites. For example, 19 of the sites in Appendix A are in category 3, 2 sites are on the borderline between categories 2 and 3, and 8 sites are on the borderline between categories 3 and 4; cleanup goals have been achieved at only 3 of these 29 sites. All three sites were gas stations contaminated with BTEX, some of which may have biodegraded.

Four types of sites have category 3: (1) sites with fractured bedrock and dissolved or sorbing contaminants, (2) sites with sorbed contami

BOX 3-1 COMPLETE RESTORATION OF GROUND WATER CONTAMINATED WITH GASOLINE—SERVICE STATION, UNIDENTIFIED LOCATION

This example illustrates the ability of a pump-and-treat system to completely restore a site in category 2 according to Table 3-2 when the source of contamination is removed rapidly and the pump-and-treat system begins operating soon after the contaminant release. This site fits category 2 because the contaminants were primarily mobile and dissolved (although some LNAPLs were initially present) and the geology is heterogeneous. The contaminants—components of gasoline—are readily biodegradable (National Research Council, 1993), a property that may have aided the cleanup.

At this service station, gasoline spilled when the installation of a monitoring well resulted in the puncturing of a 38,000-liter (10,000-galion) underground fuel tank. The puncture caused the release of an undetermined amount of gasoline into the soil surrounding the tank. After the tank was emptied, an emergency response was initiated immediately, and 83,000 liters (22,000 gallons) of ground water mixed with gasoline were pumped from an excavated pit and hauled away for disposal. Within days, a monitoring well system was installed to delineate the contaminant plume and to provide information for designing the pump-and-treat system. The contaminated aquifer was composed of dense silty fine sand with zones of calcareous semiconsolidated sandstone. A single extraction well was put into operation approximately eight months after the spill.

Prior to pumping, the maximum concentrations of the chemical components of gasoline that had dissolved in the ground water were as follows: benzene, 3,600 ppb; toluene, 4,030 ppb; ethyl benzene, 730 ppb; xylene, 5,300 ppb; and methyl tertiary butyl ether, 6,700 ppb. After one year, the pump-and-treat system had reduced all of these concentrations in the extraction well to below regulatory standards. After three years, the system had reduced the concentrations below regulatory standards in all monitoring wells. In all but one well, contaminant concentrations were below levels detectable with standard analytical methods.

The company has ceased pumping at this site, and the concentrations in all the monitoring wells remain below cleanup levels. Mobile LNAPLs were never detected in any of the wells, probably because most of the LNAPL was removed during the emergency response. This case illustrates the potential for successful application of pump-and-treat systems under favorable conditions and the value of rapid action.

REFERENCE: API, 1993.

nants and heterogeneous geology, (3) sites with separate-phase LNAPLs and homogeneous or heterogeneous geology, and (4) sites with DNAPLs and homogeneous geology. At sites with fractured bedrock, removing contaminants from the fractures is difficult because of problems in circulating water through these regions. At sites with sorbed contaminants and heterogeneous geology, tion and diffusion rates. At sites with LNAPLs and DNAPLs, cleanup cannot be achieved unless the NAPLs are removed. Because ground water extraction is not generally efficient at cleaning up NAPLs, some other remedial action may be necessary. NAPLs that float on the water table may be partially removed by direct pumping. DNAPLs that have migrated below the water table may also be partially removed by direct pumping, but locating them is much more difficult than locating LNAPLs. NAPLs that are not removed or contained can cause regrowth of the contaminant plume, even after the pump-and-treat system has apparently reached cleanup goals. For example, at the Dayton, New Jersey, computer manufacturing facility described in Box 3-3, the pump-and-treat

BOX 3-2 RESTORATION OF GROUND WATER CONTAMINATED WITH SOLVENTS—SALINAS, CALIFORNIA

This case illustrates the ability of a pump-and-treat system to reduce the size of a large contaminant plume to health-based levels. However, it also illustrates that even where cleanup goals have apparently been achieved, some contamination may remain. This site fits category 2 in Table 3-2 because the contaminants were dissolved and the geology is heterogeneous, with multiple layers.

Firestone Tire and Rubber Company operated a tire manufacturing plant at this site, near Salinas, California, from 1963 until 1980. As part of the Resource Conservation and Recovery Act requirements for closing the storage area at the facility, Firestone was required to conduct environmental investigations, which began in 1983. The investigations revealed a range of contaminants in on- and off-site wells, the most significant of which were 1,1-dichloroethane (DCA), 1,1-dichloroethene (DCE), and 1,1,1-trichloroethane (TCA). Historical records indicated that TCA was the solvent most commonly used at the site; the other two compounds were produced by chemical and biological degradation of the TCA.

The investigations traced the sources of contamination to soil near the plant buildings. Firestone subsequently excavated 4,800 tonnes of soil from this area, disposed of it at a hazardous waste landfill, and backfilled the excavated area with clean material. Although TCA is a chlorinated solvent that may enter the subsurface as a DNAPL (see Box 3-3), in this case there was no evidence that significant quantities of the contaminant had migrated below the water table in DNAPL form. The potential DNAPL sources were excavated with the soil. The excavation of source areas and the absence of DNAPLs in the ground water helped facilitate cleanup.

The aquifer system beneath the site is made up of three interconnected zones: shallow (approximately 30 meters deep), intermediate (30 to 40 meters below ground surface), and deep (four subzones 60, 90, 120, and 150 meters deep). The zones are separated by clay and silt layers of varying thicknesses that are locally discontinuous. Only the deep water-bearing zones are used extensively.

The subsurface geology acted as a series of steps that forced contaminated ground water into the intermediate and deeper zones as it flowed away from the system initially succeeded in reducing contaminant concentrations below regulatory standards, but the plume reemerged when the pump-and-treat system was turned off. Investigators attributed the regrowth of the plume to NAPLs that had not been removed or accounted for when the pump-and-treat system was designed.

Although full restoration is unlikely for many sites in category 3 except over extremely long time periods, cleanup of the majority of the plume is possible at these sites. For example, at the site described in Box 3-3, the pump-and-treat system eliminated the dissolved plume in six years, and the cleanup might have lasted if a containment system had been installed around the contaminant source areas before the pump-

site. The initial plumes were 900 meters long and 300 meters wide in the shallow aquifer. 120 meters long and 30 meters wide in the intermediate aquifer, and 2,000 meters long and 500 meters wide in the deep aquifer. However, although contaminants were present in the deep aquifer, risk assessments showed that the contaminant levels in this aquifer were below those requiring regulatory action: contaminant levels in the deep aquifer were below the maximum permissible levels allowed under the Safe Drinking Water Act, and the combined cancer risk from the contaminants was below 10^{-6}. Therefore, the pump-and-treat system was designed to clean up only the shallow and intermediate aquifers and to prevent additional contamination from spreading to the deeper aquifers.

Ground water extraction began in 1986 in the shallow aquifer and in 1989 in the intermediate aquifer, with a total combined pumping rate between 2,100 and 2,800 liters per minute. By June 1992, health-based cleanup standards had been achieved in all 25 of the extraction wells. However, in a small "hot spot" between extraction wells, samples from monitoring wells showed levels of DCE above the drinking water standard of 6 µg/liter. Consultants at the site have hypothesized that the hot spot is located in a zone where, due to the placement of the extraction wells, there was no ground water flow while the pump-and-treat system was operating. Despite the presence of the hot spot, regulators allowed shutdown of the pump-and-treat system in November 1992 under the condition that monitoring would continue until June 1994. After pumping stopped, DCE concentrations increased at the not spot from 18 µg/liter to approximately 50 µg/liter but then returned to a level of approximately 20 µg/liter.

During the remediation at this site, the pump-and-treat system removed 97 kg of DCE, 72 kg of TCA, and 33 kg of DCA. This is a relatively small quantity, making cleanup at this site less difficult than at some other sites.

REFERENCES: International Technology Corporation, 1989; Smedes et al., 1993; R. Leonard Allen, International Technology Corporation, personal communication, 1994; Edwin Wing, International Technology Corporation, personal communication, 1994.

and-treat system was shut down. At such sites, the part of the plume that does not contain nonaqueous phases or other significant contaminant sources in many cases can be cleaned up relatively rapidly, and the aquifer will remain clean as long as source areas are contained. Containment can be accomplished through physical barriers or by continued pumping around the source zone at a rate just sufficient to prevent contaminant migration.

Cleanup of Sites in Category 4

Cleanup of sites in category 4 to health-based standards is extremely unlikely, although in most cases containing the contamination and shrinking the contaminated area is possible at these sites. Sites in category 4 have either LNAPLs in fractured rock aquifers or DNAPLs in heteroge

BOX 3-3 THE REEMERGENCE OF A CONTAMINANT PLUME AFTER CLEANUP—DAYTON, NEW JERSEY

This case illustrates how contaminant plumes can reemerge after an apparently successful cleanup when sources of contamination are left in place. This site is in category 3 according to Table 3-2 because it contains DNAPLs and because the geology is homogeneous.

In 1977, routine monitoring at a municipal drinking water supply well near Dayton, New Jersey, revealed contamination by chlorinated solvents, primarily TCA and perchloroethylene (PCE). Investigators from the New Jersey Department of Environmental Protection (NJDEP) traced the source of contamination to a nearby IBM plant that had manufactured ink ribbons for printers and punch cards for computer data. They determined that tanks used to store TCA and PCE had leaked, eventually contaminating the ground water.

IBM removed the storage tanks that were the suspected source of contamination and began cleaning up the ground water with a pump-and-treat system in 1978. The company installed 14 extraction wells and 9 injection wells and evaluated the performance of the system at more than 100 monitoring wells. In 1980, IBM and the NJDEP reached an agreement that the company would continue pumping and treating until it could demonstrate that further treatment would not significantly reduce contaminant concentrations.

By 1984, the pump-and-treat system had nearly eliminated the contaminant plume. Levels of TCA and PCE were undetectable at most monitoring wells near the drinking water supply well. Near where the chemical storage tanks had been located, concentrations of both PCE and TCA were well below 100 µg/liter at all but one well, down from maximum concentrations of 12,000 µg/liter for TCA and 8,000 µg/liter for PCE before treatment. Consultants for both IBM and South Brunswick Township, which operated the drinking water well, agreed that further pumping and treating would not yield substantial reductions in contaminant levels. The NJDEP agreed that IBM could cease treatment in 1984, with contin neous or fractured rock aquifers. Removal of NAPLs from fractured rock and heterogeneous regions poses the most extreme of technical challenges because of the difficulty of circulating water through these regions and the difficulty of dissolving NAPLs. Of the 34 sites in category 4 and the 8 sites on the borderline between categories 3 and 4 in Appendix A, none have been fully cleaned up.

Although full restoration is not possible with existing technology for sites in category 4, varying degrees of cleanup may be possible at some of these sites. One example of such a site is the semiconductor manufacturing facility described in Box 3-4, where the pump-and-treat system eliminated the plume of dissolved contaminants. The contamination remaining at this site is confined to a source zone within a bentonite-slurry wall; the areal extent of this source zone is small compared to the original area of the dissolved plume. In effect, the dissolved plume at this site fit

ued monitoring to ensure that contaminant concentrations did not rise above 100 µg/liter off site.

After the pump-and-treat system was shut down, monitoring wells indicated gradual increases in contaminant concentrations and a reemergence of the contaminant plume. IBM's consultants warned the NJDEP in 1987 that within a year, contaminant concentrations would exceed the 100-µg/liter action level. By 1990, contaminant concentrations in some monitoring wells were higher than they had been before cleanup began in 1978. The NJDEP agreed that IBM should restart a modified version of the original pump-and-treat system. The new system operates fewer wells than the originate the goal is to prevent off-site contaminant migration and, as the plume shrinks, ultimately reduce pumping to a rate just sufficient to contain contamination within the source area. Pumping will likely continue at this site indefinitely.

Researchers at the site concluded that the contaminant plume reemerged because of the presence of NAPLs in the soil and ground water near the contaminant source area. Although the researchers never observed the NAPLs directly, the very high concentrations of TCA and PCE present in the ground water before cleanup, as well as the site history and the known characteristics of TCA and PCE, indicate that undissolved sources of these chemicals are trapped in the subsurface.

Although this case shows that contaminant concentrations can rebound if contaminant sources are not removed or contained, ironically it also demonstrates that pump-and-treat technology can work for cleaning up dissolved contamination. The pump-and-treat system at this site nearly eliminated the contaminant plume, and the cleanup would have been a long-term success if a containment system had been installed around the contaminant source area.

REFERENCES: Robertson, 1992; Stipp, 1991; EPA, 1989b.

category 2 (and therefore cleanup was possible), while the source zone fits category 4 (and therefore contamination remains). Another example of such a site is the abandoned quarry described in Box 3-5. Here, the pump-and-treat system has successfully isolated the contaminant source zones (in fractured rock) and has prevented further discharge of dissolved contaminants to the Schuylkill River, which interconnects with the aquifer.

Despite such relative successes, it is important to realize that at some sites hydrogeologic conditions may prevent isolation of contaminant source areas. For example, at the computer manufacturing facility described in Box 3-6, an extensive pump-and-treat system consisting of 14 wells has been unable to contain contaminant source areas. At this site the pump-and-treat system has effectively stabilized the plume of dis

BOX 3-4 CLEANUP OF DISSOLVED CONTAMINANTS AND ISOLATION OF THE CONTAMINANT SOURCE—SAN JOSE, CALIFORNIA

This example illustrates the ability of pump-and-treat systems to meet cleanup standards in part of the contaminated zone if the contaminant source is isolated and prevented from continuously regenerating the dissolved plume. This site fits category 4 according to Table 3-2 because it contains DNAPLs in a heterogeneous geologic setting.

In 1981, Fairchild Semiconductor Corporation discovered a rupture in a waste solvent tank at its San Jose, California, manufacturing facility. The company initiated a ground water investigation, which identified contamination on site. Off site sampling then revealed that one large municipal water supply well and five private wells were contaminated.

The company began plume delineation efforts immediately, ultimately installing 124 monitoring wells. The plume was located in a complex hydrogeologic setting composed of stratified alluvial sand and gravel deposits. Silt and day layers separated the sands and gravels into separate water-bearing zones (the shallowest called aquifer A the next B, and so on). Investigations established that the plume was 1,700 meters long and 300 meters wide, the majority of which was off site, downgradient of the area in which it was generated by dissolution of contaminants from the solvent tank. The primary contaminant was TCA, with lesser concentrations of DCE and Freon 113. The waste solvent tank rupture is itself almost conclusive evidence that DNAPL chemicals were released to the subsurface. In addition, the very high TCA concentrations—above the aqueous solubility in samples from the A aquifer and at 93 percent of solubility in the B aquifer—further support the conclusion that DNAPL had penetrated into the subsurface.

The pump-and-treat system was initially designed for full aquifer restoration. The company installed 11 extraction wells to contain both the source area and solved contaminants, but because uncontained contaminant sources remain, the plume has not decreased in size.

When planning an approach for remediating a site, it is extremely important to recognize from the outset the presence of complexities such as those indicated in category 4. Failure to account for these complex conditions can result in the establishment of unrealistic cleanup goals. For example, at the waste lagoon site described in Box 3-7, the government planned that the site would be cleaned up to drinking water standards within five years. However, after four years of pumping it became clear that drinking water standards could not be attained within the foreseeable future because the aquifer contained DNAPLs trapped in fractured bedrock.

the dissolved plume. The system attained full hydraulic containment in 1982. In 1985, the company constructed a bentonite slurry wall around the entire plant to isolate the source area. Subsequently, contaminant concentrations in the off-site plume (outside the slurry wall) dropped to below drinking water standards. In 1991, the company shut down the pumping system for the off-site plume.

Analyses of monitoring data indicate that the pump-and-treat system removed approximately the amount of dissolved mass that was estimated to be within the plume initially (1,400 kg) but that approximately 12 times the initially contaminated volume of water was removed during this time. These findings suggest that (1) the extraction system was not perfectly efficient, resulting in extraction of uncontaminated ground water from outside the plume boundaries, and/or (2) the contaminated area needed to be flushed several times to remove the mass that was present within the plume, perhaps because of contaminant sorption to aquifer soils or because of diffusion into clay lenses. However, the fact that the pump-and-treat system removed an amount of contaminant mass approximately equal to that present in the dissolved phase initially suggests that very little of the contaminant mass was strongly sorbed.

This case illustrates that under some circumstances, pump-and-treat systems may clean up the plume of dissolved contaminants. It appears that cleanup was possible in this case primarily because the company isolated the source area from contact with the flowing ground water and secondarily because sorption of the contaminants was slight or negligible. The company is attempting to clean up the source area with a combination of excavation and vapor extraction. Because it is unlikely that the slurry wall is uniformly impermeable, pumping from within the slurry wall (to maintain an inward hydraulic gradient) must continue until the source area is remediated to ensure that no contaminants will escape and regenerate the plume.

REFERENCES: Harman et al., 1993; EPA 1989b.

BOX 3-5 CONTAINMENT OF DNAPLS IN FRACTURED ROCK—KING OF PRUSSIA, PENNSYLVANIA

This example illustrates the use of a pump-and-treat system to contain contaminated ground water at a site where restoration was deemed infeasible because of the presence of DNAPLs in a fractured bedrock aquifer, conditions in category 4 according to Table 3-2.

This site, known as Tyson's Dump, is an abandoned sandstone quarry located 25 km northwest of central Philadelphia. The site is located just south of the Schuylkill River, which is a major river that is approximately 600 meters wide in the vicinity of the site, flowing from west to east. The site was used for the disposal of various septic and chemical wastes from 1969 to 1973. Large quantities of 1,2,3-trichloropropane, a DNAPL with a density of 1.4 g/cm^3, were disposed of in the quarry. Prior to site remediation, this chemical was found in water samples collected at downstream local water supply intakes.

The Tyson's Dump site is underlain by a thin veneer of colluvium, fill, and floodplain deposits that overlie sandstone siltstone members of the Stockton Formation. The beds in the Stockton Formation dip to the north-northwest, under the Schuylkill River, at approximately 12 degrees. Ground water flow is primarily along bedding plane fractures and partings and high-angle joints, as is illustrated in Figure 3-2. Shallow bedrock ground water flow is toward the Schuylkill River both from the south side of the river in the vicinity of the Tyson's Dump site and from the north side of the river.

A zone of ground water contamination, characterized primarily by 1,2,3-trichloropropane, extends from the quarry northward to the river and under the river to the north bank of the river. The primary mode of transport for the 1,2,3-trichloropropane was transport as a DNAPL phase downdip along bedding plane fractures from the quarry to under the river. Dissolution of the DNAPL has created an extensive dissolved plume. The extent and depth of the DNAPL under the river has led all parties involved with the site to conclude that the DNAPL cannot be effectively recovered and that the DNAPL will continue to act as a source of dissolved contaminants in ground water. As a result, the cleanup remedy for the site is a containment system that prevents further discharge of dissolved contaminants to the Schuylkill River. The initial ground water containment system began operation in 1988. Operation of this initial system has apparently significantly reduced the amount of contaminants discharging to the Schuylkill River, as 1,2,3-trichloropropane is not currently detected at the water supply intakes at a detection limit of 0.5 μg/liter.

REFERENCE: EPA 1992b.

Appropriate Uses for Pump-and-Treat Systems

In summary, the committee found that there is a spectrum of possible uses for pump-and-treat systems, depending on site conditions. At relatively simple sites, pump-and-treat systems may be able to restore the ground water to health-based standards. At more complex sites,

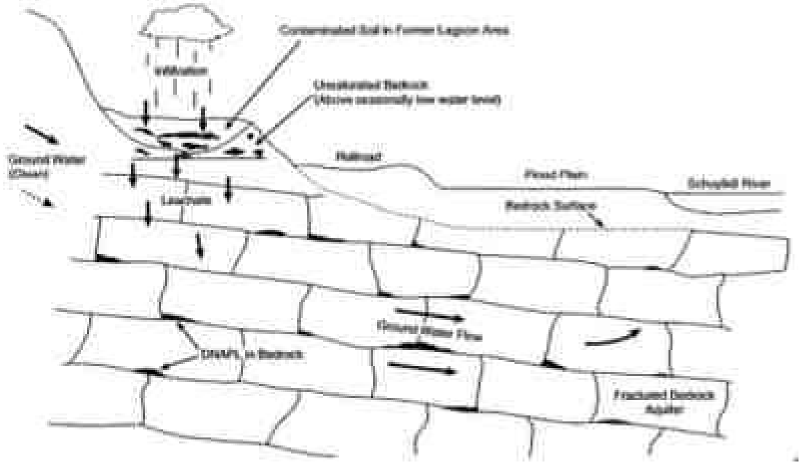


FIGURE 3-2
Hydrogeology and contaminant migration at the Tyson's Dump site (see Box 3-5).
SOURCE: EPA, 1992b.

BOX 3-6 CONTAMINANT STABILIZATION WITH A PUMP-AND-TREAT SYSTEM—SAN JOSE, CALIFORNIA

This example illustrates a situation in which a pump-and-treat system prevented further contaminant migration but was unable to shrink the plume of dissolved contaminants. Because of its heterogeneous geology and the presence of DNAPLs, this site matches category 4 in Table 3-2. The primary reasons that plume shrinkage was not achieved appear to be the very high ground water flow rates at this site coupled with the fact that the system was not effective in isolating contaminant source areas.

IBM Corporation discovered ground water contamination at this facility during audits at all of its manufacturing plants after discovering a contamination problem at a different site. The sources of contamination appear to be what would previously have been considered minor spillage of chemicals during routine filling of underground storage tanks. During site investigations IBM removed all tanks and tested all tanks and pipes for leakage. The company found no tank leaks but did identify one leaking pipe.

Site investigations began in 1978 immediately after discovery of the problem. The primary contaminants of concern are TCA DCE, and Freon 113. The subsurface is composed of a complex interlayered assemblage of sand and gravel units and less permeable units of silts and days. The sand and gravel aquifers are not completely isolated from one another because there are discontinuities in the less permeable layers that separate them vertically. The contaminant plume is on the order of 4,000 meters long and 460 meters wide. The plume volume prior to the commencement of pumping and treating was estimated to be 2 million m^3, containing a total dissolved mass of contaminants on the order of 130 kg. The pump-and-treat system began operating in 1983. Between 1983 and 1986, 12 extraction wells were put in operation; 8 of the wells were designed to prevent further migration of contaminants (to hydraulically isolate the source). Two additional wells were put in operation in 1990, one to aid in source containment and the other to aid in dissolved plume control and removal. Based on the monitoring data, the system does not yet appear to have hydraulically isolated the source area, possibly in part because of the very high natural ground water flow rates (3 meters per day) and in part because of extreme heterogeneity of the subsurface.

Although to date approximately 18 times the estimated initial contaminated water volume has been extracted, there has been little change in the areal extent of the plume. Peak concentrations in the plume have been reduced somewhat, but not dramatically. The mass of contaminants removed is almost four times what site investigators initially estimated was present in dissolved form. This latter fact suggests that significant contaminant mass continues to be released to the ground water, this mass may have sorbed to the aquifer media and may be present in subsurface DNAPL sources. It does not appear that operation of the existing pump-and-treat system will result in restoration of the aquifer to the cleanup criteria in the foreseeable future. The inability of the pump-and-treat system to shrink the plume is likely due to the very high ground water flow rates, which act to spread the plume, and to geologic heterogeneity, which has prevented isolation of the contaminant source areas. It is conceivable that a different configuration of wells and pumping schedules could have improved performance, but it is not evident how the information required to design an improved system could be gained with reasonable effort in such a complex hydrogeologic environment.

REFERENCES: Harman et al., 1993; EPA 1989b.

BOX 3-7 PUMPING AND TREATING A DNAPL SITE—VILLE MERCIER, PROVINCE OF QUEBEC

This example illustrates how not realizing the full complexity of a site can result in unrealistic cleanup goals. Because of the presence of DNAPL in fractured rock, this site fits category 4 in Table 3-2.

The lagoons at this site, in the Municipality of Ville Mercier, Province of Quebec, were used for industrial waste disposal between 1968 and 1972. Before 1972, the lagoons had been mined, leaving sand and gravel pits overlaying a glacial till and fractured bedrock aquifer. Ground water contamination was recognized as early as 1971. A variety of chemicals have subsequently been identified in the subsurface, but the most prevalent is DCA which accounts for approximately 42 percent by weight of the organic compounds present.

In 1984 the government of Quebec established a system of three wells to pump contaminated ground water and built a water treatment plant about 300 meters south of the former lagoons to treat the pumped water. The government intended that this pump-and-treat system would remove essentially all the contamination from overburden and bedrock and restore these aquifers to drinking water use within five years.

By about 1988, after four years of pumping, it became obvious that ground water pumping would not restore the shallow and deeper aquifers within any practical period of time. During approximately four years of pumping and removal of 6 billion liters of ground water, the initially very high concentrations of DCA were reduced by dilution as less contaminated and uncontaminated ground water was drawn toward the wells. However, health-based cleanup goals were not reached, and many experts have agreed that they will not be reached in the foreseeable future because of the presence of DNAPLs (Mercier Remediation Panel, 1993; Martel, 1988; Jackson et al., 1991).

According to Martel (1988), DNAPL from the lagoons penetrated downward through the ground water in the sand and gravel formation. Some of the DNAPL pooled on top of a low-permeability basal till. In some locations, the till formed a barrier and prevented the movement of DNAPL through the fractured porous bedrock. However, because the till is sloped and rests erratically on bedrock, the DNAPL continued to move down the slope and eventually penetrated into the fractures in the bedrock. Likewise, Pakdel et al. (1990) determined that the widespread occurrence of volatile hydrocarbons in ground water at the site is generally the result of lateral movement of LNAPL and downward penetration of DNAPL from the lagoons. Along its downward path, the DNAPL left behind residual ganglia in pores and fractures. Martel estimated the lifetime of this residual at several decades to centuries (Martel, 1988).

Without removing the subsurface DNAPL sources, which can persist for decades to centuries, ground water contamination cannot be eliminated from this site. Although excavation can be used to remove some of the DNAPL from the soils above the water table, this is not true for the saturated zone below 5 to 10 meters. Unfortunately, there are currently no remedial methods available for completely removing DNAPL sources below the water table. Because of the residual DNAPLs at this site, Martel concluded that "ground water withdrawal from [the Ville Mercier] aquifer is not a suitable solution." Martel further noted that the pump-and-treat system "is actually a confinement measure preventing the propagation of contaminants rather than a restoration measure."

REFERENCES: Jackson et al., 1991; Martel, 1988; Mercier Remediation Panel, 1993; Pakdel et al., 1990.

pump-and-treat systems may clean up the dissolved portion of the contaminant plume, while either a pump-and-treat system or other method contains the remaining contamination. At the most complex sites, cleanup to health-based standards may be impossible, and contaminant containment may be the only feasible option.

It is important to recognize that contaminated sites may consist of areas with varying degrees of complexity. For example, a site may contain a contaminant source area that should be categorized as 4 according to Table 3-2 and is therefore extremely difficult or impossible to clean up. However, the same site may have a dissolved plume in which cleanup is possible. Similarly, a contaminated site may have areas with relatively homogeneous geology, in which cleanup is possible, and areas where the geology is more complex. Thus, in choosing remediation alternatives for a given site, it may be necessary to view the site as having several different components, each of which should be approached with a different remediation scheme.

It is also important to recognize that at sites where pump-and-treat systems have achieved cleanup goals, the long-term effectiveness of the cleanup may still be uncertain, and the site may require continued monitoring. Although the ground water may test clean at the wells, it is possible that secondary sources of contamination remain in undiscovered non-aqueous phases or zones of low permeability. Continued monitoring at these sites is necessary to establish that the cleanups are permanent.

CLEANUP TIMES FOR PUMP-AND-TREAT SYSTEMS

Under Superfund and other ground water cleanup laws, the goal is not only to return ground water to a usable condition, but also to do so in a reasonable time frame. Consequently, an important consideration in evaluating the effectiveness of pump-and treat systems is not only whether they can work, but also how long cleanup will take. Time is one factor that regulatory agencies may consider in determining whether cleanup is technically feasible. For example, a recent EPA guidance document specifying factors for determining whether ground water cleanup is technically impracticable states that "very long restoration timeframes (e.g., longer than 100 years) may be indicative of hydrogeologic or contaminant-related constraints to remediation" (EPA, 1993).

Like performance capability, cleanup time varies widely with site conditions. Theoretical cleanup times range from years to centuries or more, depending on contaminant and geologic characteristics. Furthermore, the scientific community has not agreed on the best methods for estimating cleanup times under complex geologic and chemical condi tions. The models and equations used for time estimates are subject to continuing scientific investigation and controversy. A long time is required for cleanup at most sites, as is demonstrated by the large number of pump-and-treat systems currently in operation and the very few systems that have attained cleanup goals.

Predicting the time required to clean up contaminated ground water would be relatively straightforward if the volume of water that required extraction was equal to the volume of contaminated ground water. For example, if one assumes as representative conditions a contaminated site that is 4 hectares (10 acres), with an aquifer that is 17 meters thick and that has a porosity of 30 percent, then a total of 200 million liters of water are contaminated, and a simple computation shows the cleanup time:

Volume of contaminated water

$$\begin{aligned}&= 4 \text{ hectares} \times 10^4 \frac{\text{m}^2}{\text{hectare}} \times 17 \text{ meters aquifer material}\\ &\quad \times 10^3 \text{ liters/m}^3 \times 0.3\\ &= 2 \times 10^8 \text{ liters.}\end{aligned}$$

With a pumping rate of 380 liters per minute, the time required to pump the equivalent of the volume of contaminated water is one year:

$$\frac{2 \times 10^8 \text{ liters}}{380 \text{ liters/min}} \times \frac{1 \text{ day}}{1440 \text{ min}} \times \frac{1 \text{ yr}}{365 \text{ days}} = 1 \text{ year}.$$

Unfortunately, this will not be the cleanup time in a real aquifer system. The volume of water that must be extracted will be generally much larger than the volume of contaminated ground water, for many of the same reasons that the performance of pump-and-treat systems varies.

Processes That Affect Cleanup Time

Five primary processes in the subsurface explain why the volume of water that must be extracted to clean up an aquifer is greater than the volume of contaminated ground water:

1. *Mixing of clean ground water and contaminated ground water:* All pump-and-treat systems will cause some mixing of clean and contaminated ground water during extraction. Mixing increases the volume of water that needs to be extracted. In practice, most systems are not designed to minimize mixing; as a result, significant mixing of clean and contaminated ground water often occurs.

Excavation of a contaminant source area at a former coal gas plant. Courtesy of the Johns Hopkins University, Department of Geography and Environmental Engineering.

2. *Geologic heterogeneities*: Geologic heterogeneities, such as at sites in categories 2 through 4 in Table 3-2, can increase cleanup times, just as they increase the difficulty of reaching health-based cleanup goals. The cleanup time is often determined by how fast the lower-permeability zones flush. In addition, in regions where there is almost no ground water flow, the cleanup time may be determined by the rate of contaminant diffusion from the low-permeability zones, which is an extremely slow process.

3. *Nonaqueous phases*: NAPLs, such as at sites in categories 3 and 4 in Table 3-2, can slow cleanup, just as they interfere with reaching health-based cleanup goals. At sites with NAPLs, the cleanup time for pump-and-treat systems will be a function of how quickly these liquids dissolve.
4. *Sorbed contaminants*: Sorbed contaminants, as at sites in categories 2 and 3, can slow cleanup. At sites with sorbed contaminants, the cleanup time will depend on how quickly the contaminants desorb, which depends on contaminant solubility and the organic carbon content of the soils.
5. *Leachate from remaining contaminant sources*: When the original source of contamination or contaminated soils near the original source remain, it is obvious that a pump-and-treat system will be unable to attain cleanup standards. Nevertheless, at many sites listed in Appendix A, it is likely that chemicals are still migrating to the water table beneath the original source areas, prolonging the cleanup.

In contrast to these five processes, which all work to increase the volume of water that must be extracted to attain a cleanup standard, there are processes that work to decrease the volume of water that must be extracted. These processes are biological, chemical, and physical phenomena that cause the chemicals to degrade or volatilize (see Chapter 2). For many of the most common ground water contaminants, these processes are not very important. However, for some important ground water contaminants, such as gasoline-derived contaminants and chlorinated phenoxy pesticides, degradation processes are a dominant factor in determining the time required to reach cleanup goals.

Methods for Estimating Cleanup Times

A convenient way to view the problem of estimating cleanup time is to consider the number of pore volumes that must be pumped from the contaminated zone to attain the cleanup goals. One pore volume equals the amount of water stored in the contaminated portion of the aquifer. The number of pore volumes required for cleanup (in other words, the number of times the contaminated region must be flushed) will be a function of the cleanup standard, the initial contaminant concentrations, and the five processes listed above. The 1988 EPA document *Guidance on Remedial Actions for Contaminated Ground Water at Superfund Sites* describes two approaches for estimating ground water cleanup times that are implicitly based on the number of pore volumes: the "batch flushing model" and the "continuous flushing model" (EPA, 1988). These two ap proaches consider only the processes described in items 1 and 4 listed above (i.e, mixing and sorption).

The two approaches described in the EPA guidance document address the situation in which clean water is circulated through a region that initially contains contaminated ground water. The approaches assume simple advective displacement of the contaminated water, thus neglecting dispersive transport. The approaches further assume that the contaminant concentration in the influent water is always zero as the water enters the contaminated region but that it adjusts instantly to a concentration in equilibrium with the remaining sorbed contaminant mass after the water enters the contaminated region.

In the two EPA approaches, the assumed mechanism of contaminant removal is the same: clean water enters the contaminated region; contaminant mass is transferred from the soils to the water; water is removed and with it the dissolved contaminants; and the process is repeated. Thus, the two approaches are based on the same physical assumptions. Because both approaches assume instantaneous equilibrium between the sorbed and dissolved phases, if properly formulated they should give the same results except for numerical error. In this sense, the distinction between the "batch flush" and "continuous flush" methods described in the EPA's guidance document is misleading.

The EPA batch flush model represents an explicit finite-difference approximation of the solution to the governing differential equation. This approximation is relatively difficult to use and is subject to numerical errors. The exact solution to the governing differential equation, which is relatively simple to apply, is the following expression for the number of pore volumes, P_V, required to reach the cleanup concentration, C_{wt}, in ground water:

$$PV = -R \ln \frac{C_{wt}}{C_{wo}}$$

where R is the retardation factor and C_{wo} is the initial contaminant concentration in the ground water. The derivation of this equation and the finite-difference approximation is described by Zheng et al. (1992).

The batch flush model is a useful approach for estimating cleanup times in a simple aquifer system with chemicals for which interaction with the solid matrix can be represented by linear sorption. For example, this approach was used for estimating cleanup times at the Lone Pine, New Jersey, Superfund site, which has a relatively simple aquifer system and dissolved chlorinated solvents (Zheng et al., 1991). The selected remedy at this site had an estimated cleanup time of 165 years.

In general, the batch flush model will underestimate cleanup time because it does not account for the processes described above in items 2, 3, and 5 (i.e., heterogeneities, NAPLs, and leachate from the original source of contamination). In addition, if the interaction between the dissolved chemical and the chemical attached to the solid media is not represented by linear sorption, as is the case for most inorganic compounds, the batch flush model will tend to underestimate cleanup time. For example, Stephanatos et al. (1991) contend that the use of linear sorption models may introduce errors that underestimate cleanup times. They recommend estimating sorption effects with site-specific leaching tests or the EPA's Organic Leachate Model.[1] Stephanatos et al. found that for an iron-arsenic compound at the Whitmoyer Laboratories Superfund site, the effect of sorption as estimated from soil leaching tests is nonlinear. A linear sorption model predicted a cleanup time of 160 years, but the nonlinear model estimated a time of 50,000 years.

Detailed, computer-based models that include all the major processes affecting contaminant flow are available for estimating cleanup times (see, for example, Zheng et al., 1992; National Research Council, 1990; EPA, 1985). However, given budget and time constraints typical for hazardous waste investigations, the site-specific data necessary to run such models are rarely collected. Even in research settings, collecting all the necessary data is difficult. As a result, these types of models have been used to estimate cleanup times at only a limited number of sites. In addition, even when these models have been used, they have most often been used only to describe processes represented by the batch flush model and have overlooked the other important influences on cleanup time.

The following examples illustrate the effects of items 2 and 3—heterogeneities and NAPLs—on aquifer cleanup times. These examples, although simple, demonstrate processes that significantly increase ground water cleanup times at many, if not most, sites. The effect of item 5—leachate from contaminant source areas—is not included in the following discussion because it is axiomatic that cleanup goals will not be achieved if significant quantities of contaminants continually enter the aquifer from surface source areas.

Example 1: The Effect of Heterogeneities on Cleanup Time

The effect of geologic heterogeneities on ground water cleanup times can be illustrated by considering an aquifer comprised of sands and clay lenses and contaminated with trichloroethene. If the aquifer has been contaminated for a long time, it is reasonable to assume that contaminant concentrations in the ground water prior to cleanup will be the same in the sand portions of the aquifer and the clay lenses. Concentrations in the sand portions of the aquifer will decrease rapidly after the start of cleanup because advection, which is rapid, will be the dominant process controlling contaminant migration. However, concentrations in the clay lenses will decrease slowly because the dominant process controlling contaminant migration out of the lenses is molecular diffusion, which is very slow.

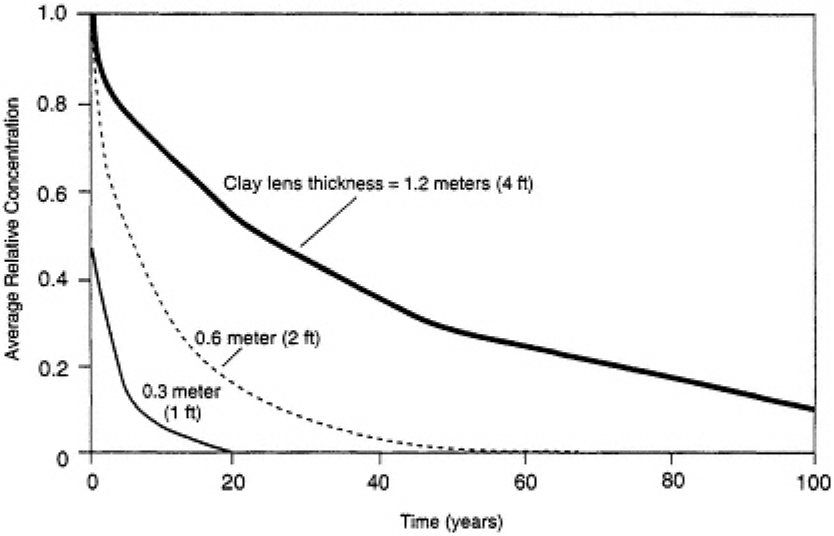


FIGURE 3-3 Changes in average relative trichloroethene concentration in clay lenses of varying thicknesses as a function of time. This figure shows that the time required for contaminants to diffuse out of clay lenses can be considerably long and can substantially prolong the cleanup effort.

Figure 3-3 shows the estimated time required to reduce the average concentration of trichloroethene in clay lenses with thicknesses of 0.3, 0.6, and 1.2 meters to various average relative concentration levels for this hypothetical example.[2] In a clay lens with a thickness of 0.6 meters, approximately 6 years will be required to reduce the average concentration to 50 percent of the initial concentration, and approximately 25 years will be required to reduce the average concentration to 10 percent of the initial concentration. The time required to reduce the concentration to 10 percent of the initial concentration will be 0.25 years at a thickness of 6 cm, 6 years at a thickness of 30 cm, and 100 years at a thickness of 1.2 meters. This example demonstrates that clay lenses can provide a long-term source of contamination to permeable portions of an aquifer and thus can significantly increase the cleanup time.

Example 2: The Effect of Residual Napls on Cleanup Time

The effect of residual NAPLs on cleanup times can be illustrated by considering an aquifer composed of fine-grained sands with a residual trichloroethene content of 30 liters/m^3 (a volumetric NAPL content of about 3 percent). The concentration of trichloroethene in the ground water in this aquifer volume will be a function of the size of the residual NAPL globules and the kinetics of globule dissolution. Using theoretical calculations, it is possible to show that dissolving all of the trichloroethene in the volume will require 122 years.[3] However, the theoretical calculations oversimplify the actual dissolution process. The concentration of trichloroethene in the ground water will change as the residual trichloroethene globules dissolve. As the globules dissolve, their size and surface area will decrease, and the dissolution rate will be lower. As a result, the actual time required to completely dissolve residual NAPLs in this example may be significantly longer than 122 years.

Example 3: The Effect of Dnapl Pools on Cleanup Time

Dissolution of DNAPL from a pool that has migrated to the base of an aquifer will occur at a much slower rate than dissolution of residual NAPL globules because significant dissolution occurs only at the top of the pool. As an example, consider a 10-meter-long trichloroethene pool in a sandy aquifer. Figure 3-4 shows the time required to reduce the thickness of the DNAPL pool by 1 cm at ground water velocities in the range of 0.01 to 1 meter per day for transverse dispersivities of 0.1, 0.01, and 0.001 meters.[4] (The transverse dispersivity, a property of the aquifer medium, describes the amount of dispersion occurring in a direction perpendicular to the ground water flow direction.) These ranges of ground water velocities and dispersivities are representative of those found in most aquifers. At a ground water velocity of 0.03 meters per day, about 4 years will be required to remove a centimeter from the surface of the DNAPL pool with a transverse dispersivity of 0.1 meter, about 10 years with a dispersivity of 0.01 meter, and about 30 years with a dispersivity of 0.001 meter. Actual dissolution rates are likely to be slower than those shown on Figure 3-4 because of site-specific limitations to trichloroethene dissolution that are not considered in the calculations. These limitations may include microscale irregularities on the DNAPL pool and/or the presence of microlayers such as films or microorganisms at the interface between the DNAPL and the water.

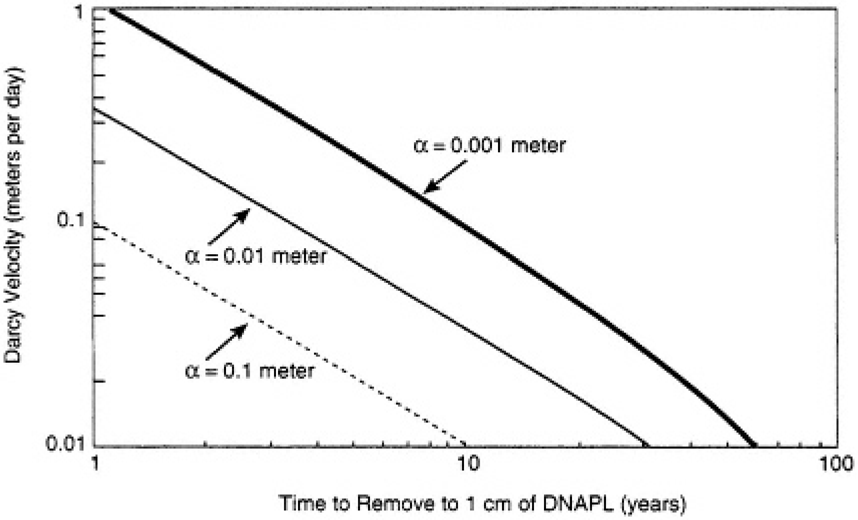


FIGURE 3-4 Calculated time to remove 1 cm from a DNAPL pool as a function of ground water velocity for various transverse dispersivities (a). (Transverse dispersivity describes the tendency for contaminants to diffuse in a direction perpendicular to the direction of ground water flow.) This figure shows that dissolution of DNAPL pools is an extremely slow process.

Determining Technical Impracticability Based on Cleanup Time

When regulators are deciding whether to consider ground water cleanup technically impracticable because the predicted cleanup time is long, they should evaluate cleanup time *and* the number of pore volumes required to attain cleanup, rather than cleanup time alone. Cleanup time is a function of both the number of pore volumes pumped per year and the number of pore volumes required for cleanup. The former can be controlled by design of the cleanup system, while the latter is a function of the ground water system. When cleanup time alone is the criterion for determining technical infeasibility, there may be an incentive to design pump-and-treat systems that minimize the number of pore volumes extracted per year. (There are legitimate technical reasons for pumping at low rates. For example, some system designs may minimize pore volumes extracted per year in order to maximize mass recovery when diffusion processes dominate.) No good criterion has yet been developed for deciding what number of pore volumes would constitute technical infeasibility; the number will probably be site specific. In addition, when considering what cleanup time constitutes infeasibility, it is important to realize that continued pumping over long time periods will remove additional contaminant mass and will therefore likely reduce risk, even though cleanup goals may not be achieved.

The committee reviewed data for the 24 sites described in the EPA study of pump-and-treat systems (EPA, 1992a,b) to obtain a rough estimate of the number of pore volumes per year that were being extracted at the sites in the study. These estimates, which are based on the extraction rates, plume areas, and plume thicknesses reported in the study, are listed in Table 3-3. At 13 of the 24 sites, the estimated extraction rate is less than one pore volume per year. Attainment of cleanup criteria at most sites under the most favorable of circumstances can be expected to take decades with extraction rates of less than one pore volume per year. The sites in the EPA study where the cleanup criteria were met in the dissolved part of plume, Fairchild San Jose (see Box 3-4) and IBM Dayton (see Box 3-3), are sites where extraction rates exceed one pore volume per year. At the two sites with the highest extraction rates, Ponders Corner and Site A, the cleanup criteria have not yet been attained, even though the extraction systems at both sites have operated for a number of years. The lack of attainment of cleanup standards at both sites can be explained by continued leaching of chemicals from source materials above the water table; in addition, it is possible that NAPLs may be present in the source areas at both sites. Some of the sites with very small extraction rates in terms of pore volumes per year are those where the pump-and-treat systems are designed only for containment and not for restoration.

Currently, data indicating the number of pore volumes pumped are not reported at most sites. Nevertheless, the time required for a pump-and-treat system to extract one pore volume of ground water from the contaminated zone is a fundamental system parameter that should be documented for all pump-and-treat systems. Assessments of ground water cleanup time should include estimates of the number of pore volumes that must be extracted to attain cleanup goals. The models described above are generally the most appropriate means for making these calculations, keeping in mind that specifying appropriate parameters for some of the important contaminant transport processes may be difficult, and the uncertainty in specifying the appropriate parameters may result in underestimated cleanup times.

IMPROVING SYSTEM PERFORMANCE THROUGH PROCESS MONITORING

This chapter has documented that how well a pump-and-treat system will perform and how long it will take are uncertain at the outset of cleanup and vary widely with site conditions. As a consequence, the

TABLE 3-3 Pore Volumes Pumped per Year at 24 Sites

		Plume Dimension				
Site Name	Extraction Rate (liters/min)	Area (ha)	Thickness (meters)	Pore Volumes (per year)	Years to Pump 20 Pore Volumes	Year Pumping Started
Amphenol	980	3.6	30	1.55	13	1987
Black & Decker	38	4.5	12	0.12	164	1988
Des Moines	4,900	53	15	1.08	19	1987
DuPont Mobile	680	15	9	0.85	24	1985
Emerson Electric	110	1.2	15	1.08	19	1984
Fairchild San Jose	15,000	30	55	1.59	13	1982
General Mills	1,500	45	15	0.38	52	1985
GenRad	150	4.0	6	1.08	19	1987
Gilson Road	1,100	6.5	34	0.92	22	1981
Harris	1,200	24	27	0.31	65	1984
IBM Dayton	3,800	24	24	1.12	18	1978
IBM San Jose	23,000	310	76	0.17	118	1982
Lathrop	2,300	310	58	0.02	907	1982
Mid-South Wood Products	160	6.0	52	0.09	228	1985
Nichols Engineering	250	0.8	30	1.75	11	1988
Olin	24,000	97	24	1.74	12	1974
Ponders Corner	7,800	9.3	24	5.84	3	1984
Savannah River	2,100	420	46	0.02	1045	1985
Site A	140	0.3	6	14.59	1	1988
Tyson's Dump	450	26	110	0.03	735	1988
Utah Power and Light	760	3.6	53	0.68	29	1985
Verona Well Field	9,100	51	37	0.86	23	1984
Ville Mercier	2,800	3,100	24	0.01	3015	1983
Western Processing	830	5.7	20	1.30	15	1988

operation of pump-and-treat systems should be viewed as a long-term project, in which the system's design is modified in response to improved understanding of the site. In effect, operation of the pump-and-treat system should become part of a continued site characterization process. Continued monitoring of the system is essential to determine the performance of the original design and to predict and subsequently assess the improvement in performance that might result from modifications made during operation.

What To Monitor

The parameters to be monitored and the necessary frequency of monitoring vary from one situation to the next, but generally the minimum requirements for both are established by the lead regulatory agency. Typically, the following types of monitoring data are necessary to track performance of the cleanup system:

- **water levels or piezometric heads at numerous sampling points throughout and around the contaminated zone** to allow estimation of water flow directions and the portion of the aquifer that the extraction system is controlling;
- **contaminant concentrations in ground water at numerous sampling points throughout and around the contaminated zone** to allow estimation of the areal and vertical extent of contamination and the remaining dissolved contaminant mass;
- **contaminant concentrations in the extracted ground water** to assess progress toward the cleanup goal and to estimate the cumulative mass of contaminants removed from the aquifer;
- **contaminant concentrations in the treatment system effluent** to assess performance of the treatment system and compliance with discharge requirements;
- **flow rates from the extraction wells and through the treatment** system to confirm that the system is operating to specifications; and
- **other operational parameters**, such as line pressures, that indicate proper operation or incipient failure of pumps and filters or rising water levels in injection wells that may signal clogging.

Given, as described throughout this report, that contaminated sites often have lingering subsurface sources of contamination, it would be advantageous to monitor the decrease or change in distribution of contaminant mass within source zones. Unfortunately, the tools currently available for source monitoring have not proven to meet the need or, in some cases, have been realized as potentially worsening the contamination problem. There is a great need for reliable, accurate techniques for source mass monitoring, and several promising techniques are now under research and development.

Modifying Existing Pump-and-Treat Systems

Monitoring data may be used to assess performance of a pump-and-treat system by determining progress toward six general end points, which will vary with the site:

1. elimination of contaminant migration beyond the extraction system,
2. decrease in the size of the contaminated area,
3. decrease in the contaminant concentration in the extracted ground water,
4. decrease in the contaminant concentration remaining within the aquifer,
5. increase in the cumulative mass of contaminants extracted from the subsurface, and
6. minimization of the volume of water extracted for containment (and therefore the costs of treatment and disposal).

If progress toward any of these objectives does not meet expectations, modification of the system's design or operation should be considered (or may be required). This iterative process will lead to a remedial program that changes over time, with the twin purposes of meeting remedial objectives and minimizing costs.

For example, if the initial design does not meet the first goal, plume capture, the system may be modified by installing additional wells and/or by increasing the pumping rates in existing wells. The optimal modification should be predictable given the additional insight gained from head or water level data collected during initial system operation. Subsequent monitoring should show whether the modifications were adequate or whether the system will require further tuning.

If progress toward goals 2 through 5, which indicate successful contaminant removal, is considerably slower than expected, then one or more assumptions used in the original system design are incorrect. Such disappointing progress may result because of the unanticipated discovery of the types of geologic and chemical complications discussed earlier in this chapter and shown in Table 3-2. Monitoring may provide insight about the most important of these complications. For example, researchers conducting field tests at the Rocky Mountain Arsenal cleanup site learned from multilevel monitoring that variations in hydraulic conductivity within the aquifer were an important cause of the unanticipated tailing of contaminant concentrations above cleanup goals after pumping and treating (Mackay and Thorbjarnarson, 1990). The consultants work

Drilling rig used to install wells at a contaminated site. Courtesy of Rice University, Department of Environmental Science and Engineering.

ing at this site had assumed, in essence, that the site belonged in category 2 according to Table 3-2 when in fact it was more appropriately categorized as 3 due to heterogeneities.

Where monitoring reveals especially complex conditions (as in categories 3 and 4 in Table 3-2) and the tailing of contaminant concentrations at an asymptote, there may be a need to adjust the system design and to reevaluate the remedial objective and projected cleanup time. In such cases, as discussed earlier in this chapter, the most realistic remedial objective might be plume capture. Continued monitoring will be necessary to confirm that the plume is completely contained and to determine whether changes in extraction rates and/or locations would conserve money and/or water.

In the ideal case that progress in cleaning up the dissolved plume is initially relatively rapid or is enabled by source isolation, particularly for sites in category 1 or 2 in Table 3-2, subsequent monitoring is likely to reveal that portions of the aquifer have been cleaned adequately as remediation proceeds. In such cases, one or more of the extraction wells may no longer be removing significant amounts of contaminants. As monitoring confirms this situation, some of the wells may be shut down, or the extraction rate in some or all of the wells may be adjusted (some decreased and perhaps some increased, depending on the interactions between the wells). The goal of these adjustments is to minimize remaining costs while continuing the progress toward achieving cleanup goals.

If the remediation has apparently reached the original cleanup goals or a relaxed cleanup criterion has been agreed upon, active remediation may cease. However, as illustrated graphically by the Dayton, New Jersey, case discussed in Box 3-3, monitoring should continue well beyond the time of active remediation. The goal is to ensure that residual contamination is not sufficient to cause the reestablishment of a contaminant plume. If monitoring reveals significant contamination, then new alternatives for remediation or isolation of the contamination will have to be evaluated.

RESEARCH NEEDS FOR IMPROVING THE PERFORMANCE OF PUMP-AND TREAT SYSTEMS

Much of the research needed to design better pump-and-treat systems exists (although this research has not all been transferred to practitioners in the field). Current research focuses on new technologies to couple with pump-and-treat systems and is discussed in Chapter 4. The key problems requiring further research to improve the performance of conventional pump-and-treat systems are all related to developing better methods for site characterization. Especially important is research to address the following questions:

- How can NAPLs, especially DNAPLs, be better characterized in the subsurface?
- How can partitioning of chemicals between the aqueous phase and NAPL and sorbed phases be more accurately quantified?
- How can this information be used to more accurately estimate cleanup times?

CONCLUSIONS

Based on a review of the case studies listed in Appendix A and the experience of committee members, the committee reached the following conclusions about the performance of pump-and-treat systems:

- **At some sites with simple geology and dissolved contaminants, pump-and-treat systems appear to be capable of cleaning up ground water to health-based standards in a relatively short time**. Such simple sites are the exception rather than the rule. Nevertheless, the committee found examples of sites where pump-and-treat systems achieved health-based cleanup goals for one or more contaminants. At such sites, it is important to recognize that continued monitoring is necessary to verify the long-term effectiveness of the cleanup. Contaminants may remain attached to solid materials or stored in nonaqueous phases in the subsurface even when ground water from monitoring wells meets regulatory standards.
- **At many of the sites where pump-and-treat systems have attained cleanup goals, the contaminants of concern are readily biodegradable** . Pump-and-treat systems have achieved health-based goals at sites contaminated with gasoline, sites where contaminants are fully dissolved, and sites with both dissolved and LNAPL plumes (where the source has been removed) in shallow aquifers. The success of pump-and-treat systems at these sites may in part be due to biodegradation processes that convert contaminants to nontoxic products.
- **The chemical nature of contaminants can prevent pump-and-treat systems from restoring aquifers to health-based standards in a relatively short time**. Pump-and-treat systems cannot restore aquifers except over very long time periods (hundreds or thousands of years) where NAPL contaminants remain unless the NAPLs are contained or removed. For contaminants that strongly sorb to solid materials in the subsurface, cleanup times using pump-and-treat systems may also be very long.
- **The geologic conditions of the site can prevent pump-and-treat systems from restoring aquifers to health-based standards in a relatively short time**. Clay lenses and other heterogeneities, fractured bedrock, and zones of low hydraulic conductivity can trap contaminants and prevent the large-scale water circulation necessary for effective flushing of the subsurface.
- **At sites where complete aquifer restoration to health-based standards is impossible or impractical due to the chemical nature of the contaminants or geologic complexity, pump-and-treat systems can prevent the contamination from spreading and can clean up or shrink the**

dissolved portion of the contaminant plume. Pump-and-treat systems can prevent contaminant migration by establishing a hydraulic barrier around the site. They can shrink the contaminant plume by pumping out contaminated water, which is then replaced at the outer edges of the plume with clean water. These accomplishments reduce the risk posed by the contamination by minimizing the area affected by the contamination.

- **Cleanup times for pump-and-treat systems vary widely depending on site conditions and pumping rates**. For small sites with simple geology and dissolved contaminants, cleanup times may be relatively short, on the order of years. The presence of geologic heterogeneities, nonaqueous-phase contaminants, sorbed contaminants, and contaminant sources above the water table can extend cleanup times by anywhere from a few years to thousands of years and can make predicting the time highly uncertain. Because cleanup time also depends on the pumping rate (which system operators can control), evaluations of cleanup time should consider the number of pore volumes of ground water that must be extracted to achieve cleanup, in addition to the estimated cleanup time.
- **The operation of pump-and-treat systems should be viewed as a long-term project, in which the system's design is modified in response to improved understanding of the site**. Because of the complexity of the contaminated subsurface, the performance of a pump-and-treat system will always be uncertain until the system is tested by beginning the cleanup. Monitoring provides the information necessary to optimize the system's performance and ultimately determine whether it will be able to reach cleanup goals.

NOTES

1. See 51 Fed. Reg. 21,653, June 13, 1986; 51 Fed. Reg. 27,062, July 29, 1986; 51 Fed. Reg. 41,088, November 13, 1986.

2. To prepare Figure 3-3, the committee assumed that the areal extent of the clay lenses is such that contaminant flow out of lenses is essentially one-dimensional and can be described by Fick's law:

$$J_x = -D_e \frac{\partial C}{\partial x}$$

where .J_x is the contaminant flux from the clay lens, D_e is the porous media molecular diffusion coefficient, and C is the concentration of the contaminant in the clay lens. (The porous media diffusion coefficient is a function of the water molecular diffusion coefficient for the contaminant corrected for the porosity and the tortuosity of the day lens.) The committee further assumed that the relative concentration of the trichloroethene in the clay lens is one (unit concentration) as a result of the long period of contamination, while the trichloroethene concentration in the sands is zero because the pump-and-treat system has removed the contaminant from the water stored in the sand portion of the aquifer. Using these initial and boundary conditions, the committee followed a solution method for Fick's law similar to that described by Carslaw and Jaeger (1959) for heat flow from a solid bounded by parallel planes. The committee assumed that the porosity of the clay lens is 0.35, the retardation factor for trichloroethene in the clay lens is 2, and the water molecular diffusion coefficient for trichloroethene is 8.3×10^{-6} cm^2/s, which results in a porous media molecular diffusion coefficient of 1×10^{-6} cm^2/s.

3. For this example, the committee based its computations on a 1 m^3 volume of aquifer and used the following assumptions: (1) a porosity of 0.3, (2) a ground water flow rate of 0.03 meters per day (typical of conditions in fine-grained sands), (3) a dissolved trichloroethene concentration equal to 10 percent of the aqueous solubility of this compound (a value consistent with field observations but less than that indicated by theoretical calculations) (Hunt et al., 1988), and (4) a random distribution of the trichloroethene globules. The density of trichloroethene is 1.47 g/cm^3, and its water solubility is about 1,100 mg/liter. With these assumptions and trichloroethene properties, the following calculations show the time required to dissolve the trichloroethene globules:

Total contaminant mass	=30 liter/m$^{3 \times 1 \text{ m}}$3 × 1.47 g/cm3 × (100 cm/m)3 × 10-3 m3/liter
	=44,100 g
Concentration of dissolved trichloroetherne	=10% × 1,100 mg/liter
	=110 rag/liter
Mass flux through 1-m^2 area	=0.03 meter/day × 1 m$^{2 \times 1}$10 mg/liter × 10-3 g/mg × 103 liter/m3 × 0.3
	=0.99 g/day
Time required to dissolve residual trichloroethene	=44,100 g/(0.99 g/day)
	=122 years

4. The rate at which the trichloroethene dissolves from the pool was estimated from the following equation, which is based on Hunt et al. (1988, 1989):

$$T = \frac{V_x Y C_s}{L \rho n} \left[\frac{1 - e^{-\omega^2}}{\omega \sqrt{\pi}} + \operatorname{erfc}(\omega) \right]$$

where

$$\omega = \frac{Y}{\left((\alpha_t V_x + D_e) L / V_x \right)^{.5}}$$

T is the thickness of DNAPL removed per unit time; V_x is the ground water velocity; *Y* is the aquifer thickness; C_s is the water solubility of the DNAPL; *L* is the length of the DNAPL pool in the direction of ground water flow; erfc is the complementary error function; is the DNAPL density; *n* is porosity; $_t$ is the transverse dispersivity (which describes dispersion normal to the ground water flow direction); and D_e is the porous media molecular diffusion coefficient. For a given DNAPL pool geometry, the rate of dissolution in most aquifers is a function primarily of the ground water velocity and the transverse dispersion length. For this example, the committee assumed that the aquifer has a porosity of 0.35, a thickness of 5 meters, and a bulk molecular diffusion coefficient of 1×10^{-6} cm^2/s.

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4

Capabilities of Enhanced Pump-and-Treat and Alternative Technologies

Given the limited capabilities of conventional pump-and-treat systems and the large number of contaminated sites, a substantial market exists for innovative ground water cleanup technologies. However, use of innovative technologies has not been as extensive as might be expected, considering the potential size of the market. For example, while conventional pump-and-treat systems were selected for use at 73 percent of Superfund sites with ground water contamination through fiscal year 1992, at the remaining 27 percent of sites the most common "remedies" were not innovative technologies but nontreatment measures such as providing alternative water supplies, aquifer use restrictions, and wellhead treatment (Kelly, 1994; K. Lovelace, Environmental Protection Agency, unpublished data, 1992). Furthermore, technologies that treat ground water in place rather than extracting it were specified as remedies at fewer than 2 percent of Superfund sites (Kelly, 1994).

This chapter evaluates the capabilities of innovative subsurface cleanup technologies and reviews why application of these technologies has been limited. Included in addition to reviews of technologies that treat ground water below the water table are reviews of technologies that treat soils above the water table, because ground water cleanup cannot be achieved if contaminants from the overlying soil continue to migrate downward. While the Environmental Protection Agency (EPA) defines innovative technologies as those for which limited or no cost and effi ciency data exist, this report groups all technologies other than conventional pump-and-treat systems under the heading "innovative." It is important to note that some of the technologies reviewed in this chapter are gaining wider use. However, the increasing use of newer technologies applies mainly to soil above the water table. The most striking example of this desired technical evolution is the increased use of soil vapor extraction systems, which have now become a leading cleanup technology for soil (Kovalick, 1993). For cleaning up petroleum hydrocarbons, in situ bioremediation is also becoming increasingly common. Despite the increasing use of these two technologies, application of innovative technologies for cleaning up ground water remains rare.

In this chapter, the committee has divided innovative technologies into two categories: enhanced pump-and-treat systems and alternative technologies. Enhanced pump-and-treat systems all involve, to some extent, the pumping of fluids such as water, water solutions, or air and thus will face some of the same difficulties as conventional pump-and-treat systems; the advantage of these enhanced systems is their potential to significantly increase the rate at which contaminant mass can be removed from the subsurface. Alternative technologies do not involve continuous pumping.

For each of these technologies, the importance of thorough site characterization and field tests prior to implementation and of process monitoring after implementation cannot be overstated. Because of the lack of performance data for most of the technologies reviewed here, the uncertainty associated with these methods is proportionately greater than the uncertainty associated with conventional pump-and-treat systems. Thorough characterization of the site's geologic and chemical characteristics, field tests of the remediation method, and continual monitoring of the full-scale system are all essential steps for minimizing uncertainties. For innovative technologies even more than for conventional pump-and-treat systems, an observational approach to remediation—in which the design of the system evolves as information on field performance is collected—is a requirement for effective cleanup.

ENHANCED PUMP-AND TREAT SYSTEMS

Conventional pump-and-treat systems extract relatively large volumes of water with relatively low contaminant concentrations. Because of geologic complexity and slow rates of contaminant desorption and dissolution, these systems must displace many pore volumes of aquifer water to flush out contaminants, as explained in Chapter 3. Conventional pump-and-treat systems thus are inherently inefficient for removing contaminants from the subsurface. Many technologies currently being developed or tested are designed to enhance the efficiency of pump-and-treat systems. Some of these technologies reduce the ultimate burden on the pump-and-treat system by removing from the soil contaminants that would otherwise migrate to the ground water or by removing volatile contaminants from the soil and ground water. Other innovative technologies improve the efficiency of contaminant extraction by increasing the amount of contaminant removed with each volume of pumped water. Another group of innovative technologies pumps minimal amounts of fluids to stimulate treatment of contaminants in place, either biologically or chemically, rather than requiring contaminant extraction and surface treatment. All of these technologies have in common the requirement to pump fluids through the subsurface, meaning that to varying degrees the geologic and chemical conditions that impose limitations on conventional pump-and-treat systems also present problems for these innovations.

The committee has divided enhancements to pump-and-treat systems into two categories: demonstrated technologies and technologies in development.

Demonstrated Technologies

The following technologies are all close to being accepted or are already accepted for site cleanups. They have been tested in laboratory-scale batch and column studies, in controlled field experiments, and in large-scale site trials. Data collection and analysis are comprehensive.

Soil Vapor Extraction

Description

Soil vapor extraction (SVE) is one of the few innovative technologies that has gained wide use. The technology extracts organic contaminants (primarily from the unsaturated zone) by flushing with air. Air flow is induced by applying a vacuum at a sealed wellhead or with blowers. Where the air stream contacts contaminants—which may be present as a nonaqueous-phase liquid (NAPL), dissolved in water in the soil pores, or associated with the soil—mass transfer to the air can occur, with subsequent transport of the air and contaminants to the surface. An incidental effect of SVE is that by increasing the subsurface oxygen supply, it can promote biodegradation of contaminants by aerobic microbes, although standard SVE systems are not specifically designed for this purpose.[1]

As shown in Figure 4-1, an SVE system usually consists of one or more extraction wells, vacuum pumps or air blowers, and a treatment system for the extracted vapors. In some cases, the ground is covered with an impermeable cap to improve system performance by controlling the direction of air flow and ensuring total capture of the extracted vapors. SVE also has been called soil venting, subsurface venting, in situ soil air stripping, and vacuum extraction. (For detailed descriptions of SVE systems, see Hutzler et al., 1989, and American Academy of Environmental Engineers, 1994.)

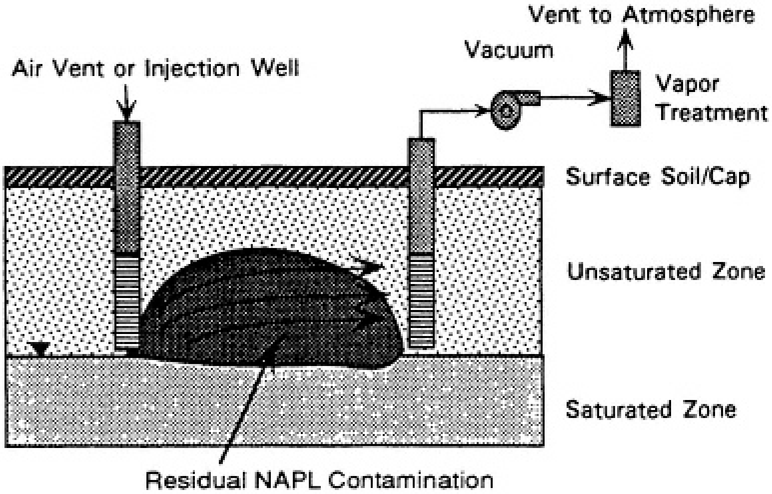
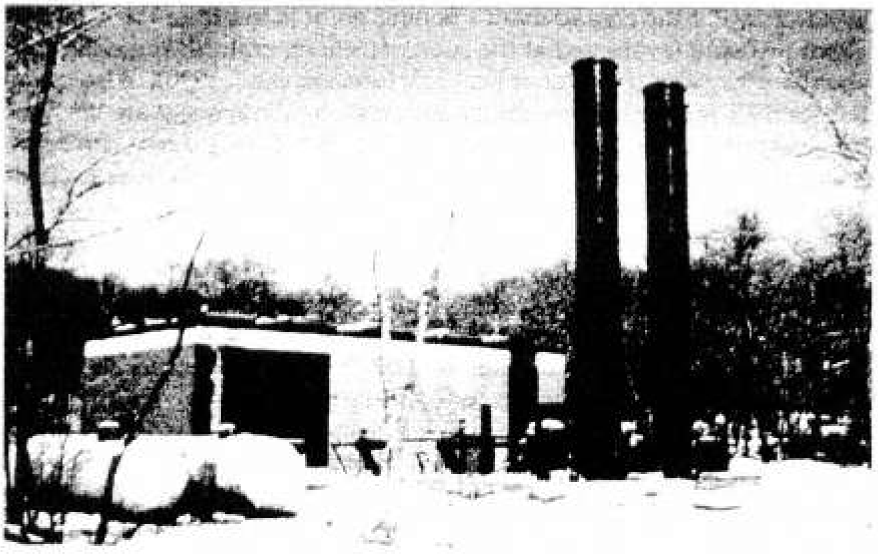


FIGURE 4-1 Process diagram for soil vapor extraction.

Application

SVE has proven effective for removing substantial quantifies of certain volatile organic contaminants from the unsaturated zone at a variety of sites in the United States and abroad. Numerous Records of Decision at Superfund sites have specified SVE as the technology of choice for unsaturated zone cleanup. The technique has also been extensively used for cleanups at gas stations and other sites where large quantities of volatile organic compounds have leaked from underground storage tanks. Although SVE also can remove contaminants from dewatered portions of the saturated zone, in which the water table has been purposely lowered through pumping, its use for this purpose has not been as extensive as for unsaturated zone treatment.

Conceptually, contaminant removal efficiency for SVE systems depends on the physical state of the contaminant. When present as a NAPL, contaminants will transfer from the pure liquid phase to the air via evaporation. If contaminants are adsorbed on or in the soil, then transfer must occur within the soil to the air-soil interface, with subsequent trans fer to the air stream. Finally, if the contaminants are dissolved in water in the soil pores, mass transfer must occur through the water-air interface. The rate of extraction thus depends in part on the efficiency of each of these molecular-scale mass transfer processes.



Vapor extraction facility that treats highly concentrated gasoline vapors from a large free-product plume. Courtesy of Peter Gerbasi, Roux Associates, Inc., Islandia, New York.

Based on this conceptual model, it is apparent that the efficiency of SVE depends strongly on contaminant and soil properties. Contaminant properties include vapor pressure, Henry's Law constant, hydrophobicity (usually quantified with the octanol-water partition coefficient), and diffusion characteristics. Soil properties include stratigraphy (for example, size distribution, permeability, and porosity), organic carbon content, mineralogy, and moisture.

The design of the SVE system also influences contaminant extraction efficiency. Principal design variables include the number of extraction wells, the rate of air flow (level of vacuum applied or rate of air injection), and the depth and length of the screened zone. Especially important to consider is the vapor flow path relative to the contaminant location. If the air stream bypasses zones of low permeability, the slow process of diffusion will dominate, making contaminant removal extremely slow.

As a rough rule of thumb for feasibility assessment, SVE is likely to be successful if the contaminant's boiling point is less than 150°C or if its vapor pressure (evaluated at the subsurface temperature) is greater than about 5×10^{-4} atm (Hutzler et al., 1989; Johnson et al., 1990). Also essential for SVE is a soil permeability sufficient to allow adequate air flow. Typically, if the soil's permeability to air is less than 1 darcy (10^{-16} m^2), flow rates may be too low to achieve successful removal in reasonable time frames. Because of the complex interrelationships among all the factors that influence SVE, the effectiveness of SVE should be evaluated carefully on a site-by-site basis.

Reviews of SVE systems in the United States show successful recovery of volatile organic compounds from the subsurface down to a depth of over 60 meters (see, for example, Hutzler et al., 1989; Buscheck and Peargin, 1991). Most of these systems addressed contaminant removal from the unsaturated zone rather than from dewatered portions of the saturated zone. Air flow rates ranged from 0.3 up to approximately 100 standard cubic meters per minute, with applied vacuums ranging from 0.0067 arm (5 mm of Hg) to 0.3 atm (230 mm of Hg). Unfortunately, the efficiency of the systems in terms of contaminant recovery was not reported. Typically, concentrations of volatile compounds in the extracted air stream decreased rapidly with time and approached asymptotic values similar to those seen in ground water pump-and-treat systems. Average removal rates for sites reviewed by Hutzler exhibited a narrow range: from 0.005 to 0.01 kg of contaminant per m^3 of air extracted. Due to the apparent lack of detailed field investigations, a detailed assessment of SVE performance under controlled field conditions is needed.

Limitations

Flushing the subsurface with air, either injected or induced, is subject to the same limitations as flushing with water. The air stream is unlikely to flush zones of low permeability, which can contain significant quantities of contamination. In addition, SVE must overcome mass transfer limitations that inhibit the desorption of strongly adsorbed contaminants or contaminants that have penetrated the microstructure of the aquifer materials. Thus, all of the factors that inhibit release of contaminants during traditional pumping and treating also limit the performance of air flushing systems.

Advantages

A major advantage of air flushing versus water flushing is the higher fluid flow rates possible with air—provided that the soil permeability allows sufficient volumetric flow rates. Large numbers of pore volumes of air can be flushed through the subsurface in a short time, which permits recovery of a significant mass of released contaminants. Whether this increased flushing is sufficient to remove contaminants to acceptable levels is highly site specific.

SVE appears very promising for enhancing contaminant removal from dewatered sections of the saturated zone, although the degree to which this technology can remove contaminant sources has yet to be thoroughly evaluated. It is probable that SVE will be more successful at sites with light NAPLs (LNAPLs) than at sites with dense NAPLs (DNAPLs) because LNAPLs tend to remain above the water table, where they are more accessible, whereas DNAPLs tend to sink.

In Situ Bioremediation—Hydrocarbons

Description

In situ bioremediation systems stimulate subsurface microorganisms, primarily bacteria, to biodegrade contaminants. When given the proper stimuli, microorganisms can transform the contaminants to innocuous mineral end products, such as carbon dioxide and water. As explained in Chapter 2, the necessary stimuli for microbial growth in aquifers are oxygen or other electron acceptors (such as nitrate or sulfate) and nutrients (such as nitrogen and phosphorus). Typical in situ bioremediation systems therefore perfuse electron acceptors and nutrients through the contaminated region, as shown in Figure 4-2.

In situ bioremediation near the land surface can be achieved by using infiltration galleries that allow water amended with nutrients and electron acceptors to percolate through the soil. When contamination is deeper, in situ bioremediation systems inject the amended water through

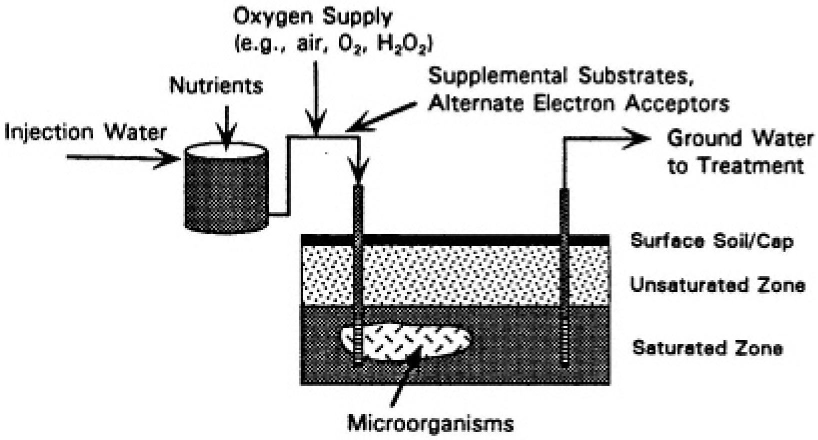


FIGURE 4-2 Process diagram for in situ bioremediation.

wells. As shown in Figure 4-2, some in situ bioremediation systems use extraction and injection wells in combination to control the flow of electron acceptors and nutrients and to hydraulically isolate the contaminated area.

The most common electron acceptor for the full-scale in situ bioremediation systems used today is oxygen, although in the future other electron acceptors (such as nitrate) may become more common. In situ bioremediation systems typically supply oxygen by bubbling air or pure oxygen into the injection water or by dosing the water with hydrogen peroxide. Alternately, they may supply oxygen by injecting air directly into the ground water, with nutrients added through injection wells or infiltration galleries.

Application

In situ bioremediation has been well established as a successful method for treating soil and ground water contaminated with certain types of hydrocarbons, primarily petroleum products and derivatives. In situ bioremediation was first successfully demonstrated for cleaning up subsurface petroleum hydrocarbons at a Sun Oil pipeline leak in Ambler, Pennsylvania, in 1972 (Lee and Ward, 1985). Since then, the technique has been used to clean up subsurface spills of refinery wastes, crude oil, and fuels. It has also been used to treat other easily biodegraded organic contaminants such as phenols, cresols, acetone, and cellulosic wastes. Although in situ bioremediation of other types of or-garlic contaminants, such as chlorinated solvents, is possible, the technology has not yet been demonstrated for these other applications.

Before an in situ bioremediation project is initiated, a specific microbial enhancement feasibility study and a general hydrogeologic site investigation are essential. The microbial study will help determine the types and amounts of substances required to stimulate optimum contaminant degradation. Site-specific geology and geochemistry also should be considered in project design. These parameters affect nutrient and electron acceptor availability, which may be hindered by sorption to the soils or reactions with naturally occurring subsurface chemicals.

Limitations

Like conventional pump-and-treat systems, in situ bioremediation systems are limited by geologic heterogeneities such as low-permeability zones, except the problem is reversed. For pump-and-treat systems, geologic heterogeneities limit the ability to extract contaminants, whereas for in situ bioremediation, geologic heterogeneities interfere with the ability to inject the necessary electron acceptors and nutrients. Adequate concentrations of electron acceptors and nutrients must be available to the bacteria throughout the contaminated zone to stimulate growth; delivery of these growth-stimulating materials to zones of low permeability is difficult.

Mass transfer limitations that slow the dissolution of sorbed or NAPL contaminants and create problems for conventional pump-and-treat systems also interfere with in situ bioremediation. Microorganisms with the metabolic capability to degrade a contaminant will not do so if the contaminant is unavailable to the cell because it is contained in a NAPL or sorbed to subsurface particles. Slow dissolution from NAPLs and slow desorption from soils decrease the biodegradation rate, thereby increasing the cleanup time and the amount of chemicals that must be added to sustain microbial activity. Since there is currently no scientific consensus on what factors affect bioavailability or how bioavailability ultimately affects bioremediation, contaminant bioavailability must be considered on both a site- and a compound-specific basis.

Toxicity of contaminants to the microorganisms may also limit in situ bioremediation. Many contaminants are toxic to bacteria at high concentrations. For example, concentrations within a NAPL pool are likely to be toxic and restrict bioremediation to the periphery of the NAPL zone. Fortunately, the soluble concentrations of hydrocarbons normally observed at field sites are well below the toxic range.

Another limitation of in situ bioremediation is the requirement for a minimum contaminant concentration to maintain the microbial population and to induce the enzymes necessary for degradation. The existence of such a concentration threshold means that, theoretically, there is a minimum concentration below which no further bioremediation will occur. This minimum may exceed cleanup goals, particularly for heavier hydrocarbons. In studies of hydrocarbon biodegradation, minimum concentrations have ranged from 1 μg/liter to 1 mg/liter.

An additional limitation is the difficulty of delivering sufficient oxygen to the microorganisms because of oxygen's low water solubility. Injecting air directly into the ground water, rather than applying it in dissolved form in the nutrient-amended water, is one approach used to improve oxygen delivery.

Advantages

In situ bioremediation has four unique advantages over conventional pump-and-treat systems. First, while pump-and-treat systems extract contaminants to the surface for disposal or treatment elsewhere, in situ bioremediation treats contaminants in place and can convert them to innocuous products (such as carbon dioxide and water). As a result, in situ bioremediation reduces the requirement for surface treatment and disposal of the recovered water and minimizes the contaminant exposure hazard. Second, pumping requirements are likely to be lower for in situ bioremediation than for conventional pump-and-treat systems. The wa ter circulation requirements for delivering growth-stimulating materials to the subsurface are much lower than the requirements for attempting to flush out contaminants with a pump-and-treat system. Third, in situ bioremediation may be faster than conventional methods. Bioremediation at the periphery of a NAPL pool or on surfaces where contaminants are sorbed decreases the contaminant concentration near these remaining sources, increasing the dissolution rate. In addition, microbially mediated chemical transformations are generally faster than the same reactions in the absence of microorganisms. Fourth, certain microorganisms are able to move toward regions of higher contaminant concentration through a process known as chemotaxis, helping to expand the zone of biodegradation and eventually achieve complete treatment (Bosma et al., 1988)

Bioventing

Description

Bioventing is in situ bioremediation of the unsaturated zone. Like soil vapor extraction, bioventing involves inducing air movement through the unsaturated soil. However, the main purpose of bioventing is not to extract volatile contaminants but to enhance aerobic biodegradation of contaminants by supplying oxygen to soil microbes. Air flow requirements are therefore much lower for bioventing systems than for soil vapor extraction systems. Inorganic nutrients also may be added, if necessary.

As shown in Figure 4-3, the components of a bioventing system resemble those of a soil vapor extraction system, with the addition of a mechanism for nutrient delivery. Bioventing systems use air recovery wells either alone or with air injection wells. Since they are designed to promote biodegradation rather than physical removal of vapors, air recovery wells are located at the periphery of the contaminated area, and air flow rates are kept at the minimum rate required to deliver oxygen.

Application

Bioventing is used primarily for petroleum hydrocarbons and some chlorinated solvents. The technology is particularly useful in cases where excavation of the site is impractical, such as under buildings, where underground utilities are present, or where the contaminated soils are deep. Because bioventing requires air flow, it is more easily applied to permeable soils such as sand than to clays. Soil moisture levels are also an important parameter. Although biodegradation rates improve with high moisture levels, high soil moisture inhibits air movement.

Limitations

Where the natural nutrient supply is insufficient, nutrient addition can be problematic, especially at capped sites with low-perme

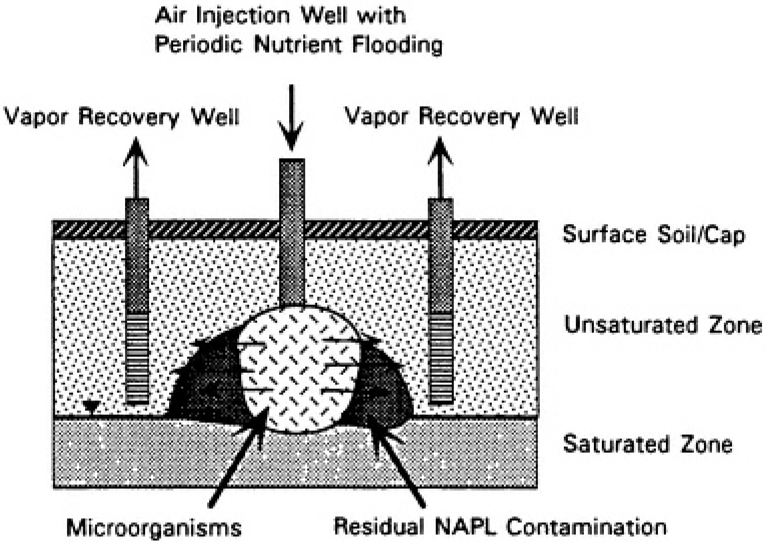


FIGURE 4-3 Process diagram for bioventing.

ability soils. Bioventing systems add nutrients in aqueous solution. The added liquid affects soil moisture content and, consequently, may inhibit air movement. The change in soil moisture can also affect the load-bearing capacity of the soil—an important consideration when treating soil under or near a building. In addition, flushing nutrients through the soil may transport contaminants from the unsaturated into the saturated zone. Researchers have investigated the possibility of using gaseous ammonia as a nitrogen source to eliminate these problems, but this method has not been very successful. To avoid causing unintended contaminant migration, before nutrients are added, the air circulation system can be operated for a period of time to biodegrade and/or physically remove the most mobile contaminants.

Another limitation of bioventing systems is that they may cause air quality problems if large quantities of volatile contaminants are vented to the atmosphere. Off-gas treatment may be necessary to meet local regulatory discharge limits.

Bioventing systems are also limited by the same factors mentioned for SVE. Significant masses of contaminants may remain in zones of low permeability or in the microstructure of aquifer materials, even after bioventing.

Advantages

As for SVE, an advantage of bioventing is the greater ease of circulating air compared to circulating water. Soil permeability to air is two to three orders of magnitude greater than its permeability to water (Wilson and Ward, 1987). Furthermore, oxygen can be transported more easily in air than in water: at 15° C, air can transport 280 mg O_2/liter, versus only 10 mg O_2/liter for water sparged with air and 40 mg O_2/liter for water sparged with pure oxygen. It is therefore possible to move relatively large amounts of oxygen with a bioventing system, even through soils with moderate to low permeabilities.

Technologies in Development

The following technologies are in the investigation and development stage. They have been tested in the laboratory, in controlled field experiments, and in some cases at a limited number of sites. However, they lack adequately documented cost and performance data. More controlled field studies and large-scale site trials are necessary to generate reliable performance data.

Pulsed and Variable Pumping

Description

The simplest enhancements to conventional pump-and-treat systems are pulsed and variable pumping. These methods intermittently slow or stop pumping to allow the contaminant concentration to build up, with the goal of increasing the mass of contaminant removed per unit volume of water pumped. Variable pumping differs from pulsed pump-Lug in that the pumping rate cannot be diminished to zero because hydraulic control of the plume is required.

As discussed in Chapter 3, pump-and-treat systems treat only dissolved contaminants. In conventional systems, the subsurface flow rates induced by pumping may be too rapid to allow enough time for sorbed or trapped chemicals to enter the bulk ground water for extraction. Pulsed and variable pumping allow more contact time between the moving water and residual contaminants that are sorbed, contained in NAPLs, or trapped in low-permeability zones. The increased contact time permits the system to approach chemical equilibrium, increasing desorption, dissolution, and diffusion.

Application

Pulsed and variable pumping have application for sites with large areas of residual contamination spread through the saturated zone and for sites with pools of separate-phase organic liquids. The key design criteria are the duration of the cycle of maximum pumping and the duration of the cycle during which the pumping rate will be slowed or stopped. Like conventional systems, pulsed systems are most effective in homogeneous zones with high hydraulic conductivities (greater than about 10^{-5} cm/s). Pulsed pumping can work in heterogeneous, less permeable rocks, but with far longer projected cleanup times.

Limitations

Like conventional pump-and-treat systems, pulsed pumping systems are effective only in zones with sufficient permeability to sustain pumping. In addition, cleanup times may be long—presumably longer than for conventional pump-and-treat systems—because of the reduced extraction rate. Therefore, pulsed pumping may decrease the time efficiency of cleanup.

Advantages

Pulsed pumping may reduce total pumping requirements and costs, although its effectiveness is currently being debated and needs to be evaluated on a case-by-case basis.

In Situ Bioremediation—Chlorinated Solvents

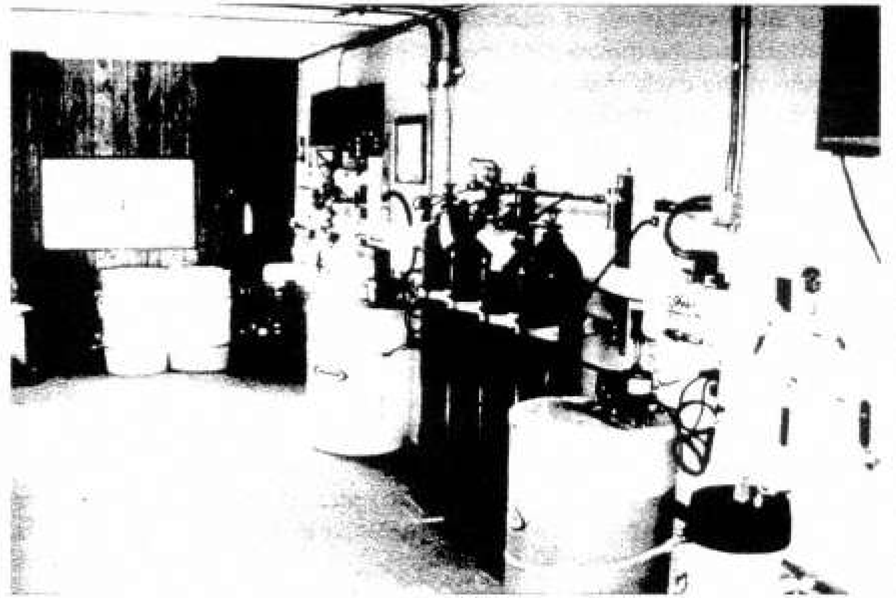
Description

The physical components of in situ bioremediation systems for chlorinated solvent removal are the same as those for hydrocarbon removal: these systems use pumps, wells, and injection galleries to circulate materials through the subsurface to stimulate bacterial growth (see Figure 4-2). However, the metabolic processes for chlorinated solvent degradation are more complex than those for hydrocarbon degradation. Therefore, in situ bioremediation of chlorinated solvents often requires circulation not only of electron acceptors and elemental nutrients, but also of other growth-stimulating materials specific to the metabolic process by which the contaminants are degraded.

Application

Laboratory- and pilot-scale studies, along with a limited number of field tests, have documented two metabolic pathways for chlorinated solvent destruction. Each of these pathways requires different environmental conditions to proceed.

The first possible metabolic pathway is biodegradation by bacteria known as methanotrophs under aerobic conditions (i.e., in the presence of oxygen). Transformation by methanotrophs does not appear effective for compounds such as carbon tetrachloride and perchloroethylene that are fully substituted with chlorine atoms. However, research has shown that methanotrophic bacteria can transform chlorinated compounds such as trichloroethylene while using methane as their primary energy source



Equipment used to deliver nutrients and electron acceptors in an in situ bioremediation system. Courtesy of Ground Water Services, Houston, Texas.

(Haber et al., 1983; Wilson and Wilson, 1985). In the process of consuming the methane, the bacteria produce an enzyme, methane-monooxygenase, that incidentally transforms the chlorinated compound. Therefore, stimulating methanotrophic bacteria to transform chlorinated solvents requires adding methane to the site, in addition to oxygen and nutrients.

Methanotrophs have been tested for controlling chlorinated solvents at a limited number of field research sites. Semprini et al. (1990) alternately injected about 20 mg/liter methane and 32 mg/liter oxygen into a test plot at the Moffett Naval Air Station in Mountain View, California, to stimulate methanotrophs and evenly distribute their growth in the aquifer. They observed the following amounts of biodegradation by the active methanotrophs with fluid residence times of one to two days: trichloroethylene, 20 to 30 percent; cis-1,2-dichloroethylene, 45 to 55 percent; trans-1,2-dichloroethylene, 80 to 90 percent; and vinyl chloride, 90 to 95 percent. The same approach—injecting methane for in situ stimulation of methanotrophs to degrade chlorinated solvents—was employed in St. Joseph, Michigan, with equally promising results (McCarty et al., 1991).

The second possible metabolic pathway for chlorinated solvent destruction is biodegradation by a consortium of bacteria under anaerobic conditions (i.e., in the absence of oxygen). Anaerobic biotransformation of chlorinated solvents has been widely observed in field studies (Roberts et al., 1982), in laboratory experiments using continuous-flow fixed-film reactors (Bouwer and McCarty, 1983; Vogel and McCarty, 1987; Bouwer and Wright, 1988), and in aquifer microcosms (Wilson et al., 1986). The initial step in the anaerobic biotransformation is generally reductive dechlorination. In reductive dechlorination, the chlorinated compound becomes an electron acceptor, and microbially catalyzed reactions replace a chlorine atom on the compound with a hydrogen atom. For reductive dechlorination to proceed, an electron donor, such as a low-molecular-weight organic compound (lactate, acetate, methanol, glucose, or toluene) or hydrogen (H_2), must be available to provide reducing equivalents. Consequently, in situ bioremediation using reductive dechlorination requires the addition of an electron donor, in addition to nutrients.

Sometimes, reductive dechlorination is incomplete, and compounds that are less chlorinated than the original contaminant but still hazardous accumulate in the system. Commonly observed intermediates include vinyl chloride, chloroform, and various isomers of dichloroethene and dichloroethane. However, although some observers have reported the buildup of such intermediates, recent work has demonstrated that complete reductive dechlorination of trichloroethylene and perchloroethylene to ethene or ethane is possible under anaerobic conditions (DiStefano et al., 1991; De Bruin et al., 1992). Ethene and ethane are innocuous and are easily degraded by aerobic microbes. Consequently, complete detoxification of chlorinated solvents appears possible under certain anaerobic conditions.

Limitations

All of the limitations that apply to in situ bioremediation of hydrocarbons also apply to in situ bioremediation of chlorinated solvents. In situ bioremediation of chlorinated solvents also has limitations that are not factors in hydrocarbon bioremediation. Probably the major obstacle to using anaerobic processes is the possibility that hazardous intermediates will accumulate. A second limitation is the possibility of undesirable water quality changes. As conditions switch from oxic to anoxic, iron and manganese may dissolve. These metals cause taste and odor problems and stain pipes, bathroom and kitchen fixtures, and clothes. In addition, anaerobic organisms excrete metabolites that increase the concentration of organic matter. The organic matter may react with disinfectants used for drinking water purification to form hazardous byproducts such as trihalomethanes. The microbial metabolites may also dissolve cadmium, copper, lead, and zinc oxides, facilitating their passage into the drinking water distribution systems (Francis and Dodge, 1988).

The need for large chemical inputs to stimulate the organisms is a third limitation, applicable to both aerobic and anaerobic pathways. Both

Construction of an infiltration trench for delivering fluids in an in situ bioremediation system. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

aerobic and anaerobic processes require the input of electron donors to provide the primary energy sources for the bacteria. Often, the mass of electron donor to the mass of chlorinated solvent biotransformed is extremely large, ranging from 100:1 to 1,000:1. Delivering these large quantities of chemicals to the proper locations is difficult at geologically complex sites and sites where the locations of contaminants are unknown. In addition, injecting large quantities of electron donors results in the buildup of large amounts of end products such as carbon dioxide, methane, and biomass—much more than in bioremediation of hydrocarbons under aerobic conditions. How to control these byproducts is an important question yet to be resolved. Biomass growth is likely to fill up the pore space, markedly reducing the formation's permeability. Plugging will in turn interfere with proper delivery of the required chemicals.

An additional limitation is that if appropriate microorganisms for carrying out the desired contaminant transformation are not present, then introduction of a specific population may be required. While most subsurface environments are inhabited by diverse microbial communities that can eventually adapt to the contaminants, for recalcitrant contaminants such as chlorinated solvents adaptation may require a long time, and addition of nonindigenous microbes may be necessary to speed the process. However, introducing new microorganisms to the contaminated zone is difficult because the subsurface is an efficient filter medium that generally restricts microbial transport. In addition, the viability of introduced organisms—whether they will survive once injected in the subsurface—is poorly understood.

As for bioremediation of hydrocarbons, the extent to which this process can lower concentrations of chlorinated solvents is limited by the requirement for a minimum concentration threshold to stimulate microbial activity. In field trials, residual concentrations of chlorinated hydrocarbons have remained above typical health-based standards of 1 to 5 μg/liter (Major et al., 1991; Semprini et al., 1991). However, residual concentrations below 1 μg/liter have been observed in laboratory microcosms (Wilson et al., 1986). Consequently, it may be possible for optimized biotransformation systems to meet relevant regulatory end points.

A final potential limitation of anaerobic reductive dechlorination is the time required for the metabolic reactions to proceed. Aerobic cometabolism of chlorinated solvents by methanotrophs is rapid, with half-lives ranging from hours to days (Semprini et al., 1990). However, anaerobic reductive dechlorination rates appear to be slow, with half-lives on the order of weeks to months in acclimated laboratory systems (Bouwer and Wright, 1988). Extrapolation of optimal rates presently observed in the laboratory suggests cleanup times of years in the field. Such slow rates may be problematic with regulatory timetables.

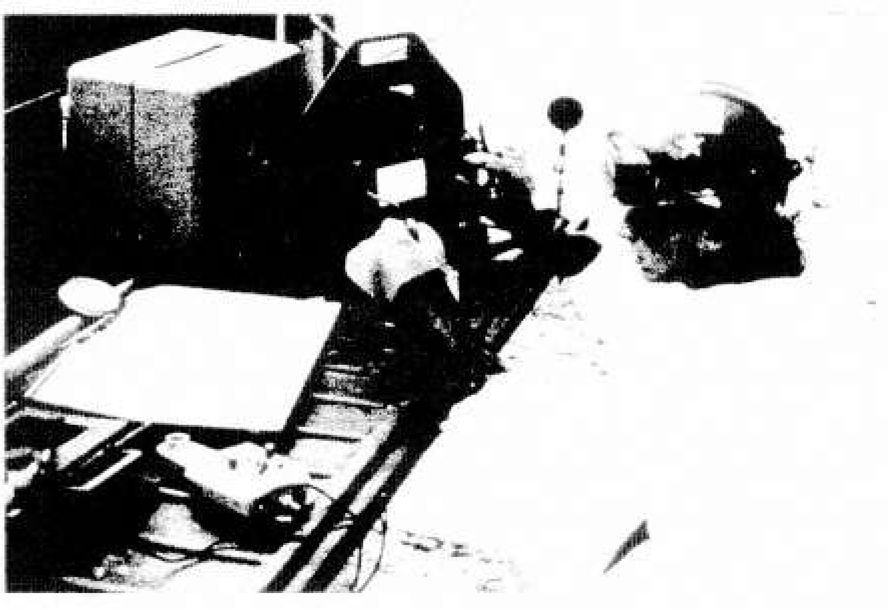
Advantages

Like in situ bioremediation of hydrocarbons, in situ bioremediation of chlorinated solvents is advantageous because it has the potential to completely convert the contaminants to innocuous products, instead of simply extracting them for disposal elsewhere. In addition, the pumping rates for delivering growth-stimulating materials to promote bioremediation are lower than pumping rates for contaminant extraction. Finally, while in situ bioremediation using reductive dechlorination may be slow, in situ bioremediation using methanotrophs is relatively rapid.

In Situ Bioremediation—Metals

Description

The physical systems used to promote in situ bioremediation of metals are like those for bioremediation of hydrocarbons and chlorinated solvents (see Figure 4-2). However, while bacteria can destroy hydrocarbons and chlorinated solvents, they can change the form of metals but cannot destroy them. Therefore, in situ bioremediation of metals relies on manipulating bacteria to either dissolve the metals, which mobi lizes the metals for extraction with a pump-and-treat system, or to precipitate the metals, which immobilizes them to prevent their further migration.



Measuring dissolved oxygen levels at a site being treated by in situ bioremediation. Courtesy of Ground Water Services, Houston, Texas.

Microbial activity against metals occurs primarily under anaerobic conditions. Anaerobic microorganisms can affect metal dissolution and precipitation by one or more of the following mechanisms: (1) direct enzymatic reduction of the metal, (2) biochemical alteration of conditions that influence the oxidation state of the metal, (3) excretion of microbial metabolites or decomposition products that can chelate or sequester the metal, and (4) bioaccumulation and release of metals elsewhere in the subsurface. At metal-contaminated sites, it may be possible to stimulate anaerobic microbial activity and control these mechanisms to influence the state of the metals.

Application

Of all the applications of in situ bioremediation, cleanup of metals is the least tested, with few published studies available. A nitrogen-fixing bacterial species isolated from coal-cleaning waste was capable of dissolving several metal oxides under anaerobic conditions (Francis and Dodge, 1988). This species dissolved iron (Fe_2O_3) and manganese (MnO_2) oxides by direct enzymatic reduction. The species dissolved ox ides of cadmium (CdO), copper (CuO), lead (PbO), and zinc (ZnO) by indirect action from the production of metabolites and the lowering of the pH in the growth medium. Recently, researchers discovered anaerobic bacteria that rapidly reduce uranium(VI), which is soluble, to uranium(IV), which precipitates (Lovley and Phillips, 1992). Thus, it may be possible to immobilize uranium and other radioactive metal contaminants, such as plutonium and technetium, by stimulating microbial reduction of the metal in the subsurface (Lovley et al., 1991).

Limitations

All of the difficulties associated with introducing chemicals for stimulating microbial activity that apply to in situ bioremediation of hydrocarbons and chlorinated solvents also apply to in situ bioremediation of metals. In addition, the movement of metal contaminants mobilized by microbial activity must be carefully controlled to prevent detrimental migration. Finally, the long-term integrity of using microorganisms to immobilize metal contaminants is not well known.

Advantages

In situ bioremediation is particularly superior to ex situ methods because it eliminates the requirement for extracting the metal and treating it at the surface. It is advantageous over chemical treatment methods because microbial reactions with metals are often specific to the metal, whereas chemicals added to treat the metal may react with a variety of subsurface compounds. In addition, for some metals the microbial reactions are more efficient than equivalent chemical reactions at low contaminant concentrations.

Air Sparging

Description

Air sparging, also known as in situ aeration, uses circulated air to remove volatile contaminants. The principles upon which air sparging is based are similar to those for soil vapor extraction, except air sparging applies to the saturated zone while soil vapor extraction is primarily for the unsaturated zone. Air sparging systems inject air either directly into the aquifer formation or into specially designed extraction wells. Air is injected into the formation under pressure, where it displaces pore water and rises through the saturated zone into the vadose zone. The air stream must then be captured by a properly designed soil vapor extraction system and treated prior to release. Figure 4-4 shows a schematic diagram of one configuration for air sparging.

Conceptually, air sparging promotes contaminant removal by both physical and biological mechanisms. Dissolved volatile compounds partition into the air following Henry's Law. Volatile compounds present as NAPLs will also volatilize into the air stream. Adsorbed compounds desorb directly into the passing air stream (a more rapid process than desorption into water). Air sparging also can enhance aerobic biodegradation of certain contaminants by increasing the oxygen content of the saturated zone.

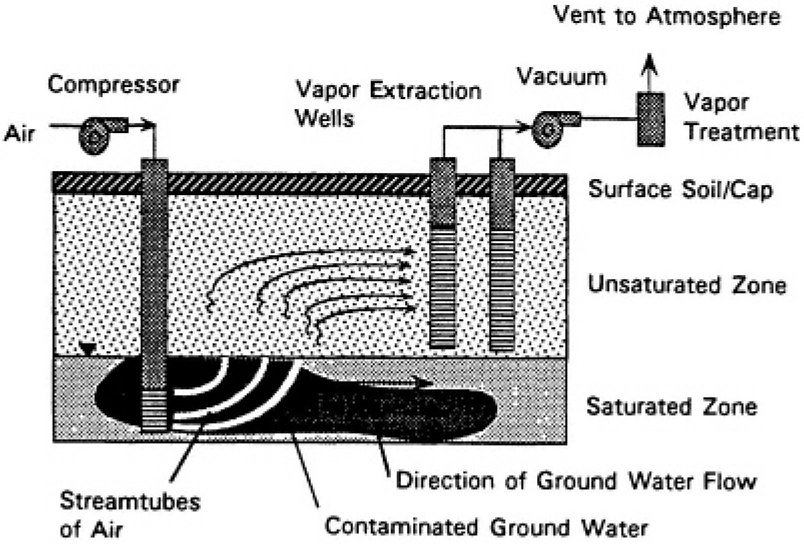


FIGURE 4-4 Process diagram for air sparging.

Application

Air sparging has been tested in laboratories and at numerous field sites. A recent evaluation of air sparging that reviewed 21 published case studies concluded that air sparging is effective for removing substantial quantities of volatile aromatic and chlorinated hydrocarbons in a variety of geologic settings (Loden and Fan, 1992). In the case studies, air sparging reportedly reduced contaminant concentrations below 1 mg/liter within a matter of months. Another recent report of several case studies showed that air sparging can reduce benzene concentrations below regulatory levels (0.5 µg/liter) (Marley, 1992). Laboratory-scale tests using high volumes of air sparged vertically through small columns have demonstrated nearly complete removal of gasoline present as a NAPL and as a residual product in sand with an average diameter of 0.9 mm (Baehr et al., 1989).

As for soil vapor extraction, the effectiveness of air sparging depends on the geologic characteristics of the site. The saturated zone must be sufficiently permeable to permit air flow. Empirical observations suggest that aquifers having hydraulic conductivities in either the horizontal or vertical directions of less than 10^{-5} cm/s will not be amenable to this technology (Brown, 1992). Others suggest a more stringent limit of greater than 10^{-3} cm/s as a prerequisite for sufficient subsurface air flow (Middleton and Hiller, 1990).

The soil grain size is also important. Typically, if the size of the porous medium exceeds 1 mm, air bubbles will migrate to the surface. For very large grain sizes, such as in gravel, the air bubbles will migrate to the surface so readily that the radius of influence of the air sparging wells will be very small, but this is an uncommon situation. On the other hand, for grain sizes less than 1 mm, air channels will form (Johnson et al., 1992). These air channels will bypass the less permeable zones in the aquifer, leaving substantial zones of residual contamination. It is probable that air channels will form in most applications of this technology because of the frequent presence of fine-grained (diameter less than 0.5 ram) soil in most aquifers.

The effectiveness of air sparging, like that of soil vapor extraction, also depends on contaminant chemistry. For dissolved contaminants, sparging appears to be effective when the Henry's Law constant is greater than 10^{-5} atm-m^3/mole and the aqueous solubility is less than 20,000 rag/liter (Brown, 1992). For successful volatilization of contaminants present as NAPLs, experience suggests that the vapor pressure should be greater than 1 mm Hg (Angell, 1992).

Finally, performance depends on system design. Key design parameters include the injection air pressure, the number and spacing of injection wells, the volume of air to be injected, the depth of air injection, and the size of the screened section of the well. Most published data on installed systems reflect experience in relatively shallow contaminated aquifers (generally at depths less than 15 meters), with the exception of field tests conducted at the Department of Energy's (DOE's) Savannah River site (at which wells extend to depths of 45 meters) (Schroeder et al., 1992). Principal constraints on the use of air sparging at great depths are the uncertain flow path of the air stream and poor penetration of low-permeability layers within more permeable soils.

Other Configurations

An alternative to injecting air through vertical wells is to inject it through perforated pipes installed horizontally in the subsurface. Figure 4-5 shows a schematic of a horizontal well. Injected air flows upward through the saturated zone, volatilizing contaminants and carrying them into the vadose zone, where they are captured by a vapor extraction system (Angell, 1992). Horizontal wells appear to improve vertical transport of air bubbles through the aquifer, enhancing contact with the contaminants. The design parameters for horizontal wells are similar to those for standard vertical well air sparging systems.

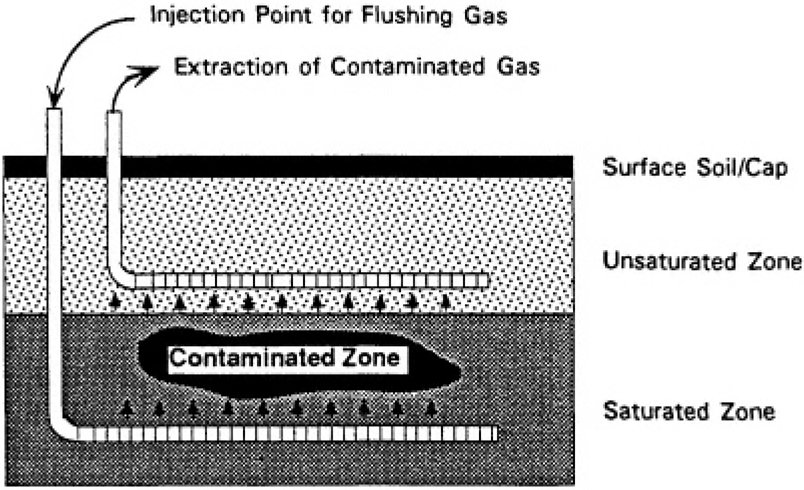


FIGURE 4-5 Process diagram for horizontal wells.

A field trial conducted at the Savannah River site indicated that two horizontal wells were effective at removing a mixture of volatile chlorinated solvents (Looney et al., 1991). One well (90 meters long and 45 meters deep) was placed below the water table in a contaminant plume and was used to inject air and strip the contaminants from the ground water. The second horizontal well (50 meters long and 20 meters deep) was placed in the vadose zone to capture contaminants stripped from the ground water and to extract residual contaminants from the vadose zone. The system removed about 7,250 kg of contaminants during the 139-day test. The extraction efficiency with the two horizontal wells was five times higher than the performance of a vertical vacuum extraction well operated at the same test site. Significantly, the horizontal well system lowered costs by about 48 percent compared to a conventional pump-and-treat system with soil vapor extraction (Schroeder et al., 1992).

An alternative to injecting air into the aquifer is using in-well aeration. With this technology, air is injected into the well casing, where it strips volatile contaminants from the water as the water is extracted through the well. The air is then captured at the ground surface and treated as required. Several technologies of this nature have been or are under development. In Germany, ground water remediation has been achieved using the so-called vacuum vaporizer wells (or UVB, the German acronym for this technology). The system consists of a unique well design coupled with an air injection system. The well contains two well screen sections, one near the bottom of the well and another just above the water table. Air is injected into the well casing beneath the water table, causing the water to rise and establishing a vertical circulation system with a radius of influence dependent on aquifer parameters, ground water flow, and rate of air injection (see Herrling et al., 1990, 1991a,b). Contaminants are stripped from the water in the casing, and the air stream is captured at the surface and treated. This technology is reportedly widely used in Germany, and several installations now exist in the United States. However, no thorough evaluation of the performance of the technology has been reported.

A second technology under development uses an air injection system in the well casing (Gvirtzman and Gorelick, 1992). Air is pumped into the well casing below the water table, which causes the water to flow upward. At the same time, rising air bubbles collect volatile contaminants from the water. The stripped water rises up the casing and is then deflected into a distribution channel, where it infiltrates back into the vadose zone. Theoretical calculations indicate that this technology will work, and a field test is imminent.

The major advantage of in-well technologies compared to other air sparging systems is that stripping occurs in the well, thus avoiding channeling problems. However, these technologies also must overcome the geologic and mass transfer barriers that interfere with the other types of treatment systems. Further development is expected.

Limitations

Although air sparging shows promise, particularly when the contaminants are volatile and biodegradable, significant questions remain about the ability of this technology to achieve health-based cleanup levels throughout the saturated zone. While laboratory studies of these technologies have been published, no peer-reviewed articles exist that demonstrate their efficacy in the field. Most of the claims of success have come from equipment vendors or engineering companies with a commercial interest in demonstrating success.

In addition to uncertainties stemming from a lack of peer-reviewed research, the technology has significant technical limitations. As with conventional pump-and-treat systems, diffusion-limited processes can slow cleanup. Contaminants trapped in low-permeability zones and dead-end pores will generally control the cleanup time.

Air sparging also has other limitations unique to the technology. Extracting multicomponent mixtures can be problematic. For example, a gasoline mixture will at first respond favorably to air injection, but the extraction efficiency will decline over time as the mixture's boiling point increases with the loss of the more volatile fractions. Use of air sparging at depths greater than approximately 10 meters below ground surface may also be problematic because the air flow path may be difficult to predict. If not properly controlled, air sparging can cause unanticipated contaminant spreading due to unexpected air flow paths. Finally, air sparging can cause dissolved ferrous iron to precipitate, resulting in clogged well screens and system failure.

Advantages

Air sparging can be advantageous over conventional pump-and-treat systems for removing volatile components of NAPLs because transfer of these contaminants to air is faster than transfer to water. In addition, pumping air is more efficient and less costly than pumping water because of the lower viscosity of air and the lower head loss incurred when pumping air. Air sparging also increases the likelihood of extracting contaminants by promoting mixing in the subsurface. An additional advantage of air sparging is the stimulation of aerobic bioremediation.

Soil Flushing

Description

Soil flushing enhances contaminant recovery in conventional pump-and-treat systems by increasing the quantity of contaminants transported with the pumped water. Soil flushing systems use injection wells, drains, or infiltration basins to flood the contaminated zone with chemical agents. The injected agents mobilize contaminants by increasing hydraulic gradients, reducing interfacial tension between NAPLs and water, increasing contaminant solubility, and/or reducing NAPL viscosity. Once the contaminants are mobilized, the system sweeps them to recovery wells or drains. At the conclusion of the flood, the flushing solution can be displaced to the recovery system by injecting water via the delivery system. Figure 4-6 shows a schematic of such a system.

Application

Soil flushing can be used to enhance recovery of contaminants with low water solubility, pools and discontinuous ganglia or globules of NAPLs, and sorbed contaminants. Two types of chemical agents can enhance contaminant recovery: cosolvents and surfactants.

Cosolvents are substances that, when mixed with water, enhance the solubility of some organic compounds. Examples are alcohols, such as methanol, and ketones, such as acetone. For example, in one set of tests the solubility of naphthalene in methanol-water mixtures increased by three orders of magnitude as the fraction of methanol increased from 0 to 1 (Fu and Luthy, 1986a). The injection of water-miscible cosolvents may therefore substantially increase the solubility and decrease the retardation factors of NAPLs, facilitating their extraction (Fu and Luthy, 1986b). Cosolvents that microbes can use as substrates may have the added advantage of promoting contaminant degradation by cometabolism if the cosolvents are used at nontoxic levels.

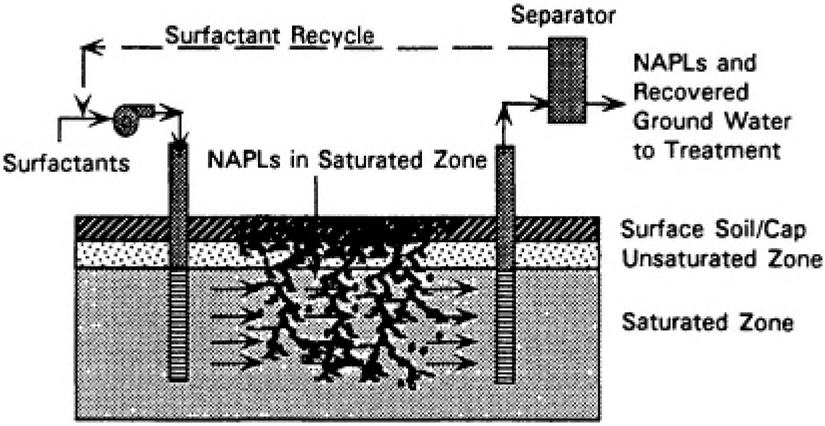


FIGURE 4-6 Process diagram for soil flushing.

Surfactants are molecules with two structural units: one with an affinity for water (the hydrophilic portion) and one with an aversion for water (the hydrophobic portion). Hydrophobic contaminants may partition into the hydrophobic core of a surfactant, increasing their mobility in the water (Edwards et al., 1991). Surfactants are especially useful for dissolving NAPLs and enhancing NAPL mobility by lowering the interfacial tension between the NAPL and water. Surfactant solutions may also enhance recovery of sorbed contaminants.

The amount of organic contaminant mobilized during soil flushing depends on the chemical structure of the cosolvent or surfactant, the cosolvent or surfactant concentration, geochemical conditions, the chemical structure of the contaminant, and temperature. Cosolvent concentrations must typically be greater than 20 percent to cause effective mobilization. Surfactants require much lower concentrations—an advantage over cosolvents. At low concentrations, the surfactant exists predominantly in monomeric form. As more surfactant is added, a concentration range is reached, termed the critical micelle concentration (CMC), at which mono mers begin to assemble in ordered, colloidal aggregates known as micelles. At surfactant concentrations greater than the CMC, additional micelles form to incorporate the excess amount of surfactant added. Hydrophobic contaminants dissolve in the micelles (Rosen, 1989). If the micelles move with the water, they increase the ability to extract contaminants with the water. Surfactant flushing has been the subject of several laboratory investigations for removal of anthracene and biphenyls (Vignon and Rubin, 1989), petroleum hydrocarbons (Ellis et al., 1985), automatic transmission fluid (Abdul et al., 1990), and polychlorinated biphenyls (Abdul and Gibson, 1991).

Some researchers have suggested that surfactants may improve bioremediation by increasing the accessibility of the contaminant to microorganisms. However, surfactant-contaminant interactions must be considered to determine whether the surfactant solutions are toxic to the microorganisms. In one laboratory study, surfactants inhibited phenanthrene mineralization at surfactant concentrations in excess of the CMC (Laha and Luthy, 1991). The mechanism for this inhibition remains unclear. The inhibition may have resulted from surfactant molecules interfering with the microorganism's biochemistry or from limited bioavailability due to low contaminant exit rates from the micelies.

Limitations

As with conventional pump-and-treat systems, geologic conditions can limit the performance of soil flushing systems. Soil flushing systems, like conventional pump-and-treat systems, are most effective in permeable, uniform media. Heterogeneous and low-permeability soils with mixtures of contaminants will generally result in reduced sweep efficiency, longer project duration, and less successful recovery. As a result, complete mobilization and removal of NAPLs has not been observed in the field with normal working concentrations of the chemical amendments, even though ongoing laboratory studies with pure solvents and controlled surfactant additions have demonstrated that near complete mobilization is possible.

Soil flushing systems also have other limitations. Fluids containing the large amount of cosolvent required for NAPL mobilization have densities and viscosities that differ substantially from those of water, complicating prediction of transport behavior. Further, the movement of contaminants mobilized by the cosolvent or surfactant must be carefully controlled. Controlling contaminant movement generally requires pumping a larger volume of ground water than the soil flushing system injects; this excess volume of extracted water must be treated and discharged elsewhere. Finally, other potential adverse reactions caused by the solution, such as permeability reduction, coating of aquifer solids, and water quality changes due to residual cosolvent or surfactant in the ground water, are also important to consider.

Advantages

Soil flushing systems may significantly increase the mobility of NAPLs, improving their removal rate. Because they increase the quantity of contaminants extracted with the water, these systems may reduce the cleanup time and total volume of water that must be extracted to achieve cleanup goals.

In Situ Chemical Treatment

Description

In situ chemical treatment uses chemicals to transform contaminants in place in the subsurface, as shown in Figure 4-7. Added chemicals can oxidize or reduce contaminants, converting them to nontoxic forms or immobilizing them to minimize contaminant migration. Possible oxidizing agents include hydrogen peroxide, Fenton's reagent, ozone, and potassium permanganate (Cho and Bowers, 1991). (Chlorine, while a strong oxidant, is not recommended because of the likely formation of chlorinated byproducts that pose a risk to human health.) Possible reducing agents include sulfur dioxide; sulfite salts (sodium bisulfite, sodium metabisulfate, or sodium hydrosulfite), ferrous sulfate, metallic iron and zinc, and sodium borohydride.

Application

Evidence on the application of in situ chemical treatment is very limited. Based on the existing evidence, it appears that this technology may be promising for treating the unsaturated carbon-carbon bonds in perchloroethylene (PCE) and trichloroethylene (TCE). For example, Farquhar et al. (1992) demonstrated that addition of potassium permanganate to PCE residual in soil completely destroyed the contaminant.

Chemical treatment also could enhance in situ bioremediation. Preoxidation of refractory organics with ozone or hydrogen peroxide can increase their biodegradability. One way to implement this approach is to use a vacuum extraction system with air or oxygen containing ozone. Ozonation of an organic compound usually creates compounds that are more polar than the parent compound (Hoigné, 1988) and thus often increases the compound's aqueous solubility and improves its bioavailability. Additional effects of ozonation include formation of hydroxyl, carbonyl, and carboxyl groups, loss of double bonds and aromaticity, and a shift to compounds with lower molecular weight. An advantage of coupling chemical and biological reactions is a reduction in the amount of oxidant required to destroy the compound.

Limitations

In situ chemical treatment has several potential limitations.

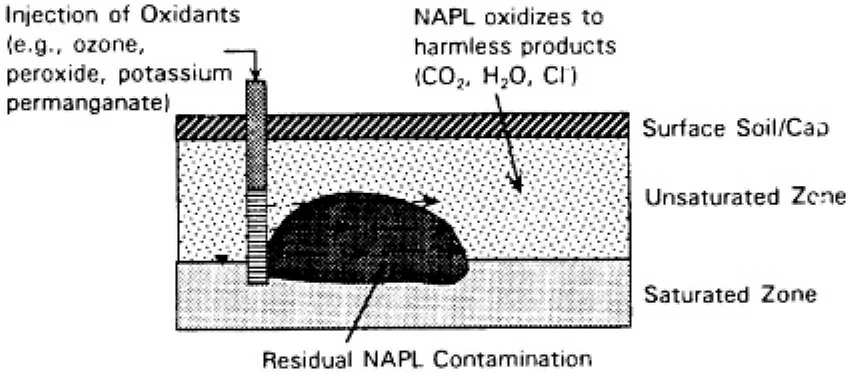


FIGURE 4-7 Process diagram for in situ chemical treatment.

First, like in situ bioremediation, this method is limited by geologic complexities that complicate delivery of chemicals to the contaminants. Second, the chemical reactions are often nonspecific, and the oxidant is capable of reacting with Fe(II), Mn(II), H_2S, and other inorganic and organic reductants in the soil, in addition to reacting with the contaminant. As a consequence, chemicals must be added in amounts that far exceed the amount necessary to eliminate the contaminant. Third, chemical additions are likely to alter redox conditions and pH locally within the aquifer and cause undesirable side reactions. For example, chemical addition may cause precipitation of metals that may clog the aquifer and injection and extraction wells. Alternatively, chemical additions designed to immobilize a target metal may mobilize other metals, which then must be handled with another treatment process. Fourth, the reaction rates are often strongly dependent on the pH, and possible shifts in pH due to chemical treatment may cause a drastic reduction in contaminant removal rates. Finally, although theoretical reaction rates are fast, destruction efficiencies are in most cases insufficient to achieve health-based cleanup levels. A great deal more development work is needed to identify possible chemical reactions and their application in subsurface systems.

Advantages

Like in situ bioremediation, in situ chemical treatment reduces pumping requirements and worker exposure to contaminants by treating contaminants in place. In addition, chemical treatment can transform contaminants that resist biodegradation. Finally, because chemical oxidants and reducing agents are nonspecific, they may be suitable for treating mixtures of contaminants.

In Situ Thermal Technologies

Description

All of the physical, chemical, and biological phenomena that can be used to remove contaminants from the subsurface depend on temperature. In contrast to most remediation technologies, which operate at site-specific temperatures, in situ thermal technologies are designed to increase the temperature of either the unsaturated or saturated subsurface soil, thereby accelerating the various removal mechanisms. The added heat can either mobilize or transform contaminants to accelerate removal or, at very high temperatures (greater than 1000°C), permanently immobilize contaminants (a process known as in situ vitrification). Since rates of many physical and chemical properties increase with increasing temperatures, heat addition promises enhancements in both the rate and effectiveness of contaminant removal. Organic contaminants will mobilize more rapidly due to enhanced volatilization (if present as residual organic liquids), enhanced desorption from the soil, increased water solubility, and increased fluid flow rates (due to the reduced viscosity at higher temperatures). Higher temperatures can also accelerate biodegradation (within certain physiological temperature limits of the microorganisms) and certain abiotic transformation or decomposition reactions.

Application

Several technical alternatives exist for adding heat to the subsurface. Heat can be introduced by injection of heated fluids such as air, water, or steam. Alternatively, heated fluids can be pumped through buried pipes, with conductive heat transfer being the primary mechanism of heat addition. Other means of heat addition include installation of vertical electrodes that provide resistance heating by passing electrical current through the soil between the electrodes, with the amount of heat controlled by the amount of electrical current. Finally, heat can be added by installation of modified radio transmitters either vertically or horizontally into the formation, a process known as radio frequency heating. Such heating, analogous to microwave cooking, can raise the soil temperature well above the boiling point of water.

Of the numerous technical options, steam injection, radio frequency heating, and in situ vitrification have shown the greatest promise for subsurface remediation and have been tested at the field scale. Only steam injection and radio frequency heating are applicable to the saturated zone, however, and radio frequency heating would require dewatering of the contaminated zone. The capabilities, advantages, and disadvantages of these two technologies are described below. A useful review of these technologies can be found in Smith and Hinchee (1993).

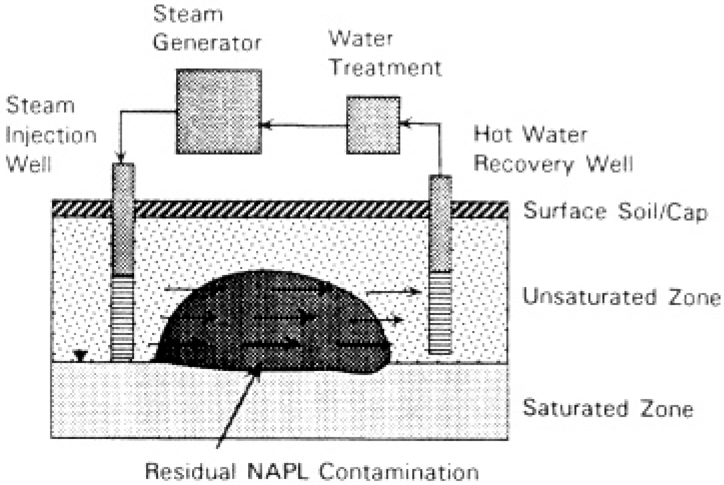


FIGURE 4-8 Process diagram for steam-enhanced extraction.

Steam-Enhanced Extraction

Description

Steam injection has been proposed as a technique to enhance the extraction of a variety of contaminants that are difficult or impossible to remove by water flushing. Steam injection is widely used in the petroleum industry to enhance petroleum extraction from deep formations. Extension of this technology to contaminant removal from the subsurface is a recent development, with active research at the laboratory and field scales under way at several universities and other institutions in the United States. In addition, several companies currently offer patented or patent pending techniques for steam injection and recovery for subsurface remediation (see, for example, EPA, 1991).

Conceptually, this technology uses the heat of steam to enhance contaminant mobilization. Steam is injected through vertical wells at appropriate depths, rates, and pressures (see Figure 4-8). As the steam passes through the subsurface, a steam front with three distinct zones forms. In the first zone, temperatures are near 100°C, and all compounds with vapor pressures greater than 1 atm at 100°C volatilize completely. Compounds with lower vapor pressures at this temperature will also volatilize at rates far higher than would be observed at normal subsurface temperatures but in proportion to their vapor pressures (Stewart and Udell, 1988; Udell and Stewart, 1990). In the second zone, steam and organic vapors condense due to heat transfer to the soil and fluids present in the pore space. In this zone, a complex mixture of condensed steam, organic liquids, and the original water in the pores moves in the direction of the steam front. In the third zone, contaminants are present in their original distribution, awaiting the arrival of the moving steam front.

A significant practical issue associated with steam injection is recovery of the mixture of injected fluids and mobilized contaminants. Recovery can be accomplished with extraction trenches or extraction wells or through the use of vacuum extraction technology. Vacuum techniques are preferable because they prevent unintended contaminant spreading.

Application

This technology has been tested in laboratory columns and at a few field sites. Hunt et al. (1988a,b) report on nearly complete removal of several DNAPLs and LNAPLs by injection of steam into laboratory-scale columns. Lord et al. (1987) completely removed kerosene from sand columns using 126 pore volumes of steam injected at a temperature near 100°C. Hunt et al. (1988a,b) presented results of successful mobilization of NAPLs from laboratory-scale models of porous media.

While laboratory tests have shown nearly complete removal of volatile and semivolatile organic contaminants with steam injection, field tests have shown promise but have not resulted in complete contaminant removal, probably due to the presence of low-permeability zones through which the steam will not flow. Udell carried out a detailed assessment of steam technology to remove LNAPLs at a gasoline spill site (K. S. Udell, University of California, Berkeley, personal communication, 1993). Of the estimated 4,500 kg of gasoline in the subsurface, up to 40 percent could be recovered with steam injection. Udell and Stewart (1989) tested steam injection for removing volatile organic compounds (VOCs) from the saturated zone at a former solvent recycling facility; they reported recovery of substantial quantities (in the range of 100 kg) of VOCs, which were present in the dissolved, adsorbed, and organic liquid phases. Ghassemi (1988) reported reducing total petroleum hydrocarbon (TPH) levels in the unsaturated zone from over 1,000 mg TPH/kg of soil to the required level of less than 100 mg/kg. However, this report did not include a mass balance to determine the overall efficiency of the process.

Because steam injection is still in a developmental stage, only limited information is available on system design parameters. According to Udell and Stewart (1990), up to 350 pore volumes of steam may be needed to displace 1 pore volume of contaminated water. Reported steam injection pressures range from gauge pressures of 0.7 to 4 kg/cm^2 (10 to 60 psi). Udell (personal communication, 1993) recommends that maximum steam injection pressure not exceed a gauge value of 0.1 kg/cm^2 per meter of depth (0.5 psi per foot of depth) to the top of the injection interval in the well to avoid possible fracturing of the subsurface and the formation of channels that would cause the steam front to short circuit the contaminated zone. Wilson and Clarke (1992) present a simplified model of the steam injection process that can be used to determine the optimum number and placement of injection wells. Information on the efficiency and design of this process is also available through the EPA's Superfund Innovative Technology Evaluation (SITE) program. Through this program, the EPA evaluated a patented steam injection system known as Toxic Treatment, which applies steam through an in situ soil drilling and mixing system. The evaluation indicated that treatment costs for this system may be less than for ex situ soil treatment.

Limitations

Although this technology should significantly enhance recovery of contaminants from the subsurface, provided that the mobilized contaminants can be effectively captured, limitations on achievable removal efficiencies can be anticipated. In the case of NAPL removal in a source area, some residual saturation is expected even in the permeable zones where significant steam flow can be achieved due to entrapment of the NAPL in small volumes of low-permeability soils. Steam extraction will also be limited by subsurface heterogeneities and the presence of contaminants in low-permeability zones. If such zones contain a significant fraction of the contaminant mass in the vadose or saturated zones, extensive remediation will be severely restricted because only a small fraction of the steam flow may pass through some of these areas, depending on the relative permeabilities of the zones. Other concerns regarding the efficiency of this technology include possible mobilization and loss of NAPLs into unanticipated channels and vapor loss through the surface. It is likely that this technology will also face a depth limitation controlled primarily by the difficulties in recovering the mobilized material at significant depths (greater than 30 meters).

Advantages

The increase in temperature provided by steam injection enhances contaminant recovery in several ways. Organic compounds with low boiling points (such as TCE and other common solvents) will vaporize, and semivolatile compounds (such as naphthalene and other polycyclic aromatic hydrocarbons) will partially evaporate. (For example, the vapor pressure of naphthalene increases from 1.4 mm Hg at room temperature to 389 mm Hg at 100°C.) The steam front will displace and mobilize low-viscosity fluids. The desorption rate for compounds attached to the soil particles will significantly increase, as will the rate of abiotic transformation processes. Steam can also enhance extraction of contaminants from low-permeability zones through conduction heating. All of these processes have the potential to significantly decrease cleanup time.

Radio Frequency Heating

Description

Radio frequency heating involves injecting heat into the subsurface through electromagnetic radiation generated at frequencies ranging from 45 Hz to 10 GHz, a frequency band allocated to the industrial, scientific, and medical sectors. Modified radio transmitters serve as the power source, with transmission through vertical tubular electrodes installed in the subsurface or horizontal electrodes positioned on the soil surface. Soil temperatures well above 80°C can be easily achieved. Water in the soil vaporizes, producing steam. Organic contaminants then vaporize, desorb, or decompose, with released contaminant gases captured through soil vapor extraction systems or with the use of a surface vapor barrier and appropriate appurtenances for gas management and treatment. A typical system consists of the radio frequency energy deposition array (electrodes), a radio frequency power generation source, vapor control, and a gas and liquid condensate handling and treatment system.

Application

Radio frequency heating is primarily applicable for removing contaminants with boiling points above 80°C from the unsaturated zone or from dewatered portions of the saturated zone. Examples include the longer-chain aliphatic and aromatic hydrocarbons, found in gasoline and jet fuel, and chlorinated solvents, such as tetrachloroethane, hexachlorobenzene, and tetrachloromethane. The technology has been under development since the early 1980s, principally at the Illinois Institute of Technology (see, for example, Dev et al., 1984). Currently, at least one patent on this process has been granted, and the technology is licensed by at least one remediation company. Bench, pilot, and field tests of the technology have been completed (Dev et al., 1987, 1988), with results published through the EPA's SITE program (Dev et al., 1989). Results have been reported for laboratory and field tests for removal of numerous organic contaminants, including hexachlorobenzene, tetrachloroethene, and JP-4 and JP-8 jet fuels.

Test results are too limited to provide detailed guidance on design, expected removal efficiencies, and estimated unit treatment costs. The key design parameter is the operating frequency of the radio frequency generator, determined on the basis of soil properties, contaminant properties, soil moisture, and speed of cleanup desired. Bench and pilot tests have reportedly achieved removal efficiencies above 90 percent. High removal efficiencies have also been reported in the field (Dev et al., 1989), but overall mass balances are difficult to make under these circumstances, and thus actual efficiency under real field conditions is still uncertain.

Limitations

Using radio frequency heating to treat dewatered zones may be problematic because of the residual water saturation. Field tests are limited, and application to heterogeneous subsurface environments may be difficult. As for other technologies, contaminants must still diffuse out of low-permeability zones to reach the gas capture system, and supplemental gas flow through soil vapor extraction may be required. Other limitations include the potentially negative impact of high soil temperature on the soil microbial population, effectively minimizing or eliminating biodegradation. Costs are uncertain, as is the durability of equipment under diverse field conditions. Further testing of the technology under controlled field conditions is necessary.

Advantages

Like steam-enhanced extraction, radio frequency heating may increase the contaminant removal rate by speeding contaminant volatilization and desorption.

ALTERNATIVE TECHNOLOGIES

Pump-and-treat systems require a continuous energy input for pumping fluids. These systems thus require continuous site management and maintenance, which are generally expensive processes. Non-pumping approaches that do not require a continuous energy input are being developed. The approaches under investigation rely on the aquifer's intrinsically favorable conditions for biodegradation, contain the contamination, or use hydraulic barriers to direct ground water flow through a reactive medium. While these methods show promise, they are in the development stage and have not yet been demonstrated.

Intrinsic Bioremediation

Description

Intrinsic bioremediation is essentially in situ bioremediation without human intervention. In this approach, the native microbes transform contaminants without stimulation from added electron acceptors, nutrients, or other materials (although these materials must be present naturally for biodegradation to occur). The biodegradation processes in intrinsic bioremediation are the same as those occurring in the engineered bioremediation systems discussed earlier in this chapter, but nothing is used to accelerate these natural processes. In most cases, such intrinsic bioremediation supplements conventional remediation techniques. For example, prior to use of intrinsic bioremediation, removal of the contaminant source may be necessary to prevent toxic inhibition of microbial activity. Similarly, conventional pump-and-treat systems may be used to lower the contaminant concentration, with intrinsic biotransformation allowed to complete the remediation after the pumps are turned off.

Although intrinsic bioremediation does not involve active site manipulation, it requires construction and maintenance of a monitoring system. The monitoring system should include interior wells to monitor the plume distribution and indicator parameters of biodegradation, such as dissolved oxygen concentration, changes in redox potential, pH, and availability of nutrients. It should also include wells outside the contaminated area to monitor potential off-site migration and determine if additional remedial measures are required.

Application

Many recent studies have demonstrated that diverse microbial populations indigenous to subsurface environments can degrade important classes of organic contaminants. However, whether intrinsic bioremediation is sufficient to eliminate the contamination is highly site specific. The extent of intrinsic bioremediation depends on the biodegradability of the contaminant and on the site's hydrogeologic and chemical characteristics.

A number of studies have demonstrated that plumes of dissolved hydrocarbon contaminants may attenuate without human intervention. Creosote biodegradation was observed in contaminated ground water at a former wood preserving facility in Conroe, Texas. Contaminant removals correlated with the availability of dissolved oxygen (Wilson et al., 1985). Field studies at a contaminated aquifer in St. Louis Park, Minnesota, showed that methane production was occurring in zones within the aquifer that had been contaminated with creosote, indicating biodegradation by methane-producing organisms (Godsy et al., 1983). Similar work at an abandoned creosote plant in Pensacola, Florida, demonstrated that a wide variety of organic compounds present in the aquifer was undergoing biodegradation by methane-producing organisms. Transport distances in the aquifer correlated with biodegradation rates derived from laboratory batch experiments (Goerlitz et al., 1985). At a gasoline plant in northern Michigan, investigators have observed intrinsic biodegradation of benzene, toluene, and xylene (Chiang et al., 1989). The biodegradation rate at this site closely matches the rate that researchers predicted in modeling studies.

In general, four types of hydrogeologic and geochemical characteristics determine whether relying on intrinsic biodegradation instead of an engineered cleanup system may be possible (National Research Council, 1993). First, the ground water flow direction should be predictable and consistent throughout the seasons. Predictability of flow is necessary to analyze whether the native microbes will degrade the contaminant more quickly than it spreads. Second, the site must have a concentration of electron acceptors—such as oxygen, nitrate, sulfate, or ferric iron—sufficient to support increased microbial growth. Third, the site should have adequate capacity to buffer against pH changes that may occur with the increased microbial activity. Carbonate minerals such as limestone, dolomite, and shell material can provide buffering capacity. Finally, the site must have a natural supply of the elemental nutrients (especially nitrogen and phosphorus) necessary for microbial metabolism.

Limitations

At present, very little operating history exists to judge the effectiveness of intrinsic bioremediation. While at many low-priority sites regulators may have assumed that intrinsic biodegradation would adequately control contaminant migration, very few of these sites have been monitored sufficiently to determine if this approach is actually effective or to identify factors that influence the efficiency of intrinsic bioremediation. Use of intrinsic bioremediation involves somewhat greater risk of failure than engineered bioremediation because active measures are not used to control plume migration. Reliable methods need to be developed for predicting the effectiveness of intrinsic biodegradation (National Research Council, 1993).

Use of intrinsic bioremediation is also subject to institutional limitations. Regulators, environmental groups, and the public may be unwilling to accept this approach, which they may perceive as equivalent to doing nothing. In addition, a contaminant plume left in place to biodegrade intrinsically may migrate under an adjoining property. Adjoining property owners are likely to have strong concerns about the potential risks and effects on property values posed by plume migration.

Advantages

Intrinsic bioremediation minimizes treatment costs by requiring little or no energy input. In addition, at sites where contaminants have low mobility, it eliminates the chance of remobilizing contaminants or causing additional contamination by pumping.

Containment Technologies

Description

Because of the limitations of conventional pump-and-treat systems, interest in physical containment technologies has increased, both for isolating contaminant source zones and containing contaminant plumes. Contaminated soil and ground water can be physically isolated with low-permeability barriers such as caps, liners, and cutoff walls. Contaminated soil can also be contained by solidifying it in place with either chemical fixatives or extreme heating (a process known as vitrification). Containment systems for ground water frequently include low-flow pump-and-treat systems to help control ground water flow and prevent contaminated water from escaping the confined area.

Application

Soil and ground water can be contained with barriers made of a variety of materials. The key requirement is that the material have a lower permeability than the aquifer. Typical materials include compacted clay, synthetic plastics (known as geomembranes and used as liners), soil and bentonite mixtures, cement and bentonite mixtures, and sheet piling. A barrier that completely encircles a contaminated region will provide better containment than nonencircling walls. Straight walls have limited effectiveness because ground water can flow around the ends of the walls.

New developments in the technology for constructing sheet pile cutoff walls have significantly reduced the potential for leakage through these walls (Starr and Cherry, 1992). Sheet piles can be made of interlocking steel, precast concrete, or wood sections. Sheet pile cutoff walls are constructed by driving individual sections into the ground using pile drivers. The interlocks can be grouted to seal the joints between sheets. This configuration can completely prevent advection of contaminated ground water through the cutoff wall.

As a possible alternative to installing physical barriers, soil can be solidified in place by mixing it with cementing agents. Possible cementing agents include pozzolan-portland cement, lime-flyash pozzolan, and asphalt. Complete mixing of the cementing agents with the contaminated soil is necessary for successful containment. Soil can also be solidified by heating it into a molten mass that solidifies upon cooling, a process known as in situ vitrification. During in situ vitrification, an electrical input heats the subsurface to between 1600 and 2000°C. The high temperatures pyrolyze organic contaminants, and vapors can be captured at the land surface for treatment. Inorganic contaminants and ash remain in the solid material formed from the molten mass. Solidification and in situ vitrification are most effective for contamination at shallow depths.

Limitations

The long-term performance of physical barriers is uncertain. Construction difficulties are common. For example, sheet piling is difficult to install in rocky soils, and questions remain about the ability to key into the confining layers below the aquifer without creating leaks in the formation. The layer underlying the aquifer must be reasonably free of flow channels to maintain the integrity of the barrier.

The long-term stability and leaching characteristics of contaminated materials that have been solidified or vitrified are unknown. In addition, vitrification may cause volatilization, mobilization, and migration of contaminants.

Advantages

Cutoff wall enclosures may be useful for sites where present technologies cannot clean up contaminant source areas. They can be used for pilot-scale evaluations of in situ remedial techniques and can improve the effectiveness of enhanced pump-and-treat methods. By isolating a portion of the subsurface, the enclosure can prevent off-site migration of treatment fluids and contaminants mobilized by the remedial process. The enclosure also can improve the effectiveness of the remedial process by minimizing dilution of the treatment fluids and by facilitating control of flow directions.

In Situ Reactive Barriers

Description

In situ reactive barriers treat the contaminant plume as it passes through permeable reactive zones or walls within the aquifer. As natural or induced hydraulic gradients move the water through the reactive zone, materials in the reactive zone remove or degrade the contaminants, leaving uncontaminated water to emerge from the downstream side. Figure 4-9shows a schematic of one possible configuration for an in situ reactive barrier, the "funnel and gate."

Application

Several approaches for installing the reactive wall or treatment zone are possible (Gilham and Burris, 1992). One approach, limited to shallow depths, is to excavate and backfill a trench with the reactive material. A second approach is to use slurry wall construction technology to create a deeper and larger permeable curtain. In this approach, a polymer mixed with reactive materials replaces subsurface materials as

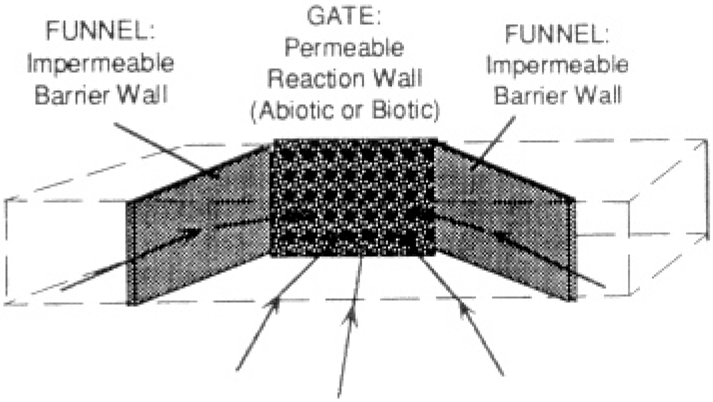


FIGURE 4-9 Process diagram for in situ reactive barriers.

excavation proceeds. When excavation is complete, the polymer is removed by pumping and biodegradation, leaving a permeable wall containing the reactive material. A third approach is to temporarily install sealable sheet piling to allow dewatering and construction of a reactive zone. For these three approaches, costs are likely to be high if a continuous wall is installed across zones of contaminated water. A promising alternative is to use sealable sheet piling to funnel the natural ground water flow to narrow openings in the wall in which the reactive material has been installed, as shown in Figure 4-9. This method provides greater control of the treatment zone and facilitates replacement or removal of the reactive material. Principles of reactor engineering can be applied to design the appropriate reaction zone length.

The reactive zone can use a combination of physical, chemical, and biological processes. One possible physical method uses granular activated carbon to adsorb organic contaminants. Other possible physical/chemical methods use redox controls to precipitate metals and metal catalysts to degrade halogenated organic compounds (Gilham and O'Hannesin, 1991). For example, in one set of laboratory studies a calcium apatite barrier system precipitated lead (Pb^{2+}) as lead phosphate via phosphate dissolution from the apatite (Xu and Schwartz, 1992). In another study, iron-bearing solids in a laboratory soil column removed chromate (CrO_4^{2-}) by reducing chromium(VI) to chromium(III).

Another possibility is to add nutrients and/or bacteria to the reaction zone to enhance contaminant biodegradation. Researchers are currently investigating several possible methods for creating biological reaction zones. For example, some researchers have tested biological removal of nitrate from ground water by periodically injecting a readily biodegradable organic compound to stimulate denitrifying bacteria, which convert nitrate to nitrogen gas (Gilham and Burris, 1992). Other researchers have used denitrifying bacteria to oxidize aromatic compounds while using nitrate as an electron acceptor (Hutchins et al., 1991). In tests at a commercial site in North Carolina, researchers have used a series of wells packed with briquettes that slowly release oxygen to stimulate aerobic bacteria that degrade gasoline components (Borden et al., in press). Researchers at Lawrence Livermore National Laboratory are testing ways to inject methanotrophs and methane to create an in situ microbial filter for passive decontamination (Taylor et al., 1992).

When barriers use exhaustible material such as granular activated carbon or chemical reactants, they must be installed as modules to enable periodic replacement.

Limitations

The technology of reactive barriers is in the conceptual and development stages, with the principles being studied on a small scale.

Two engineering challenges for the use of permeable reaction walls are installation of the reactive materials and provision of suitable amounts of these reactive materials. Using reactive barriers without source cleanup also raises institutional concerns because the barriers do not completely remediate the site.

Advantages

Like intrinsic bioremediation, reactive barriers lower costs by requiring little or no energy input once installed. Yet, because they capture the contaminant plume instead of allowing it to follow its natural course, they have the potential to be safer and more reliable than intrinsic bioremediation. In addition, because the reaction zone is limited in area, reactive barriers may be easier to design, monitor, maintain, and control than other systems.

IMPORTANCE OF COMBINING PROCESSES

Waste sites are rarely characterized by a single contaminant. Mixtures of contaminants with varying physical and chemical properties, such as chlorinated solvents and polycyclic aromatic hydrocarbons, chlorinated solvents and phenols, gasolines and acetone, and any organic contaminant with one or more heavy metals, are much more likely to be present. Because a single remedial process may be effective at removing only a subset of the compounds in a waste mixture, a combination or sequence of processes is likely to be necessary. From this perspective, each remedial technology should be treated as part of a treatment train— analogous to the sequence of processes used to treat drinking water or wastewater. More work is needed to develop combinations of treatment processes for addressing contaminant mixtures.

One simple example of combining processes is the use of bioventing. Bioventing uses vacuum extraction together with in situ biodegradation to remove contaminants, as shown in Figure 4-3. Vacuum extraction removes separate-phase globules of the contaminants and the bulk of the volatile contaminants, while biodegradation handles residual concentrations. Box 4-1 describes another example of combining processes. At the site described in the box, the remedial goal was achieved by a combination of free product recovery, in situ biodegradation, and venting/air stripping.

RELATIVE EFFECTIVENESS OF ENHANCEMENTS AND ALTERNATIVES

As for conventional pump-and-treat systems, the effectiveness of a specific alternative treatment technology is strongly related to site condi

BOX 4-1 TREATMENT TRAIN FOR GASOLINE CLEANUP—LONG ISLAND, NEW YORK

This example illustrates how the most effective strategy for cleaning up subsurface contamination often employs multiple technologies. At this site, free-product recovery, soil vapor extraction, in situ bioremediation, and pumping and treating were all combined to remove spilled gasoline from a Long Island, New York, aquifer. (For details, see Lee and Raymond, 1991.)

The gasoline at this site originated from a slow leak in an underground storage tank at a filling station. An estimated 106,000 kg leaked, creating a plume that reached a residential subdivision and released fumes into the basements of local homes. When the spill was discovered, the owners of the station initiated a response program and extracted more than 82,000 kg of the gasoline—more than 77 percent of what had spilled—using free-product recovery methods that skimmed the gasoline from the water table.

Samples after the free product was recovered showed that approximately 24,600 kg of gasoline remained in the subsurface in a 2.3-meter vertical section above and below the water table. In the next stage of cleanup, a soil vapor extraction system was installed to remove volatile contaminants from the soil and in situ bioremediation and pump-and-treat systems were installed to remove ground water contaminants. The in situ bioremediation system supplied oxygen via hydrogen peroxide and nutrients via a proprietary solution to stimulate indigenous organisms to degrade the gasoline. Monitoring showed a dramatic increase in the number of gasoline-degrading organisms corresponding with the oxygen additions and the decrease in gasoline concentrations. The ground water extraction system removed remaining volatile contaminants by air stripping.

Over an eight-year treatment period, the combined system removed nearly 99 percent of the 24,600 kg of residual gasoline. The remaining 270 kg of gasoline were confined to a 0.61-meter vertical zone occupying a small area. Levels of gasoline in soil and ground water outside this zone were undetectable.

Investigators at the site estimated that the air stripper used to treat the extracted water removed 6,240 kg, or 25 percent, of the gasoline. The soil vapor extraction system removed an estimated 450 kg, or 1.8 percent, of the gasoline. The majority—17,640 kg, or 72 percent—of residual gasoline was removed by in situ bioremediation.

REFERENCE: Lee and Raymond, 1991.

tions and contaminant chemistry. Table 4-1 gives the relative effectiveness of the enhancements and alternatives described in this chapter as a function of contaminant chemistry. The conditions ranked 1 represent those for which the technology is most effective, while those ranked 4 represent conditions for which the technology is least effective. The rankings are based largely on theoretical potential effectiveness, with some input from field experience where applicable. With contaminants that are volatile or biodegradable (columns 1 and 3), a relatively high degree

TABLE 4-1 Relative Effectiveness of Alternative Treatment Technologies as a Function of Contaminant Chemistry for Average Geology

	Contaminant Chemistry					
Alternative Technology	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved (nonreactive/ nonvolatile)	Sorbed, Dissolved (degrades/ volatilizes)	Sorbed, Dissolved (nonreactive/ nonvolatile)	Separate Phase LNAPL	Separate Phase DNAPL
Conventional pump and treat	1[a]	1	2	2	2-3	4
Vacuum extraction and bioventing	NA[b]	NA	2	NA	2	3
Air sparging (vertical or horizontal wells)	2	NA	2	NA	2	3
In situ bioremediation —hydrocarbons	1	NA	2	NA	2-3	3-4

	Contaminant Chemistry					
Alternative Technology	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved (nonreactive/ nonvolatile)	Sorbed, Dissolved (degrades/ volatilizes)	Sorbed, Dissolved (nonreactive/ nonvolatile)	Separate Phase LNAPL	Separate Phase DNAPL
In situ bioremediation —chlorinated solvents	1-2	NA	3	NA	NA	3-4
Cosolvent and surfactant flushing	NA	NA	NA	NA	2-3	2-3
Steam stripping	NA	NA	2	NA	2	3
In situ thermal desorption	NA	NA	2	NA	2	3
In situ chemical oxidation	3	NA	3	NA	3	3
In situ bioremediation —metals	1-2	NA	3	NA	NA	NA
In situ reactive barriers	2	NA	NA	NA	NA	NA
Intrinsic bioremediation	2	NA	2	NA	2-3	NA

[a] Relative effectiveness, where 1 is highly effective and 4 is least effective.

[b] "NA" denotes that the technology is not applicable for this type of situation.

of effectiveness (ranking 1 to 2) is expected using vacuum extraction, air sparging, in situ bioremediation, and steam stripping. Treatment is typically less effective (ranking 3 to 4) for sorbed contaminants or contaminants present as separate phases because of the slow rates of desorption and dissolution for such contaminants.

In Table 4-1, the hydrogeology corresponds to homogeneous multiple-layer formations or heterogeneous single-layer formations analogous to the middle rows in Table 3-2. The table includes technologies for cleaning up the unsaturated zone and technologies for cleaning up the saturated zone (some technologies apply to both). Technologies not applicable for certain contaminants are marked "NA." For example, bioremediation would not be employed for contaminants that do not degrade, and processes relying on volatilization, such as vacuum extraction, air sparging, and steam stripping, would not be employed for nonvolatile contaminants.

Table 4-2 summarizes the relative performance of the various treatment alternatives for cleaning up contaminant plumes, and Table 4-3 shows relative performance for cleaning up contaminant source areas. In these tables, plume remediation refers to treatment of dissolved contaminants emanating from contaminant source areas. Source remediation refers to treatment in the immediate vicinity of where the contaminant entered the subsurface, which typically contains separate-phase organic liquids and/or high concentrations of metals; it also refers to treatment of pools of NAPLs and other large accumulations of undissolved contaminants along the contaminant flow path. The tables give expected performance in terms of the residual contaminant concentration in the ground water, the residual contaminant concentration sorbed to solids in the aquifer or source area, and cleanup time. The relative number of peer-reviewed publications is an indicator of the maturity of the technology.

In Tables 4-2 and 4-3, the technologies listed as leaving "low" residual contaminant concentrations and as having "short" cleanup times perform much more effectively than those leaving "high" residual concentrations and requiring "long" cleanup times. However, depending on the site characteristics and contaminants, the performance of a specific technology can vary widely. Consequently, the tables show considerable overlap and similarity in the performance designations for the different technologies.

BARRIERS TO IMPLEMENTATION OF INNOVATIVE TECHNOLOGIES

Although the innovative technologies described in this chapter show promise for improving the effectiveness and reducing the costs of haz

TABLE 4-2 Relative Performance of Alternative Technologies for Plume Remediation

Alternative Technology	Residual Ground Water Concentration	Residual Sorbed Concentration in Aquifer	Cleanup Time[a]	Number of Peer-Reviewed Publications[b]
Conventional pump and treat	Low	Medium to high	Long	Many
Air sparging (vertical or horizontal wells)	Low to medium	Low to medium	Medium to long	Limited
In situ bioremediation—hydrocarbons	Low to medium	Low to high	Medium to long	Some
In situ bioremediation—chlorinated solvents	Low to medium	Low to high	Medium to long	Some
In situ bioremediation—metals	Low to medium	Low to high	Medium to high	Limited
In situ reactive barriers	Low	NA	Long	Limited
Intrinsic bioremediation	Low to medium	Low to medium	Long	Limited

NOTE: A "low" residual concentration and "medium" cleanup time reflect relatively good performance, while a "high" residual concentration and "long" cleanup time reflect much less effective performance. "NA" denotes that the technology is not applicable to this situation.

[a] Because few cases of achieving cleanup goals have been reported, these qualitative assessments reflect the judgment of the committee.

[b] "Limited" indicates that very little information about this technology is available in peer-reviewed publications, while "some" indicates a greater availability of information.

TABLE 4-3 Relative Performance of Alternative Technologies for Source Remediation

Alternative Technology	Residual Ground Water Concentration	Residual Sorbed Concentration in Source Area	Cleanup Time[a]	Number of Peer-Reviewed Publications[b]
Conventional pump and treat	Low to medium	Medium to high	Long	Some
Vacuum extraction and bioventing	NA	Low to medium	Short	Some
Air sparging (vertical or horizontal wells)	Low to medium	Low to medium	Short to medium	Limited
In situ bioremediation—hydrocarbons	Low to medium	Low to high	Short to medium	Some
In situ bioremediation—chlorinated solvents	Low to medium	Low to high	Medium to long	Some

Alternative Technology	Residual Ground Water Concentration	Residual Sorbed Concentration in Source Area	Cleanup Time[a]	Number of Peer-Reviewed Publications[b]
Cosolvent and surfactant flushing	Low to medium	Low to medium	Short to medium	Some
Steam stripping	Low to medium	Low to medium	Short	Some
In situ thermal desorption	Low to medium	Low to medium	Short	Some
In situ chemical oxidation	Medium (?)	Medium to high (?)	Medium (?)	Limited
In situ bioremediation—metals	Low to medium	Low to high	Medium to high	Limited
Intrinsic bioremediation	Low to medium	Low to high	Long	Limited

NOTE: A "low" residual concentration and a "short" cleanup time reflect relatively good performance, while a "high" residual concentration and a "long" cleanup time reflect much less effective performance. "NA" denotes that the technology is not applicable to this situation. (?) denotes a high degree of uncertainty regarding the performance of this technology.

[a] Because few cases of achieving cleanup goals have been reported, these qualitative assessments reflect the judgment of the committee.

[b] "Limited" indicates that very little information about this technology is available in peer-reviewed publications, while "some" indicates a greater availability of information.

ardous waste site cleanups, it has been widely recognized that numerous barriers have obstructed the implementation of these innovations, and significant efforts are under way by federal agencies and others to accelerate their use. Nevertheless, barriers remain in all three key phases in the life cycle of an innovative technology: the technology development phase, the selection phase, and the procurement or implementation phase.

Technology Development Phase

The first key phase in the life cycle of an innovative technology is the development of ideas conceived in the laboratory to the point where they can be commercialized. Technology development has been undertaken by numerous stakeholders, including entrepreneurs, university research laboratories, national federal laboratories, and private companies in the environmental technology business with sufficient financial resources. All of these potential developers make investment decisions based on their understanding of the potential market for such technologies. This market, in turn, depends on the potential purchasers or buyers of these future technologies. Potential purchasers of innovative technologies include federal agencies such as the EPA, the Department of Defense (DOD), and the DOE; private industries designated as potentially responsible parties; and other government entities such as state or local governments and publicly owned utilities. Each of these prospective buyers influences the potential size of and the timing of the demand for innovative technologies.

During this first phase in the life cycle of an innovative technology, numerous barriers may inhibit the translation of creative ideas into a potentially viable technology. These barriers can be classified as technical, institutional, and economic.

Technical Barriers

As discussed frequently in this report, ground water cleanup is subject to significant uncertainties arising from the heterogeneous nature of the subsurface and the usual lack of information on the size and timing of contaminant releases. These uncertainties increase the risk of failure for both conventional and innovative technologies. Site characterization activities attempt to minimize these uncertainties, but because of the heterogeneous nature of the distribution of contaminants and the physical and chemical characteristics of sites, significant unknowns are likely to persist. Consequently, it is difficult for potential technology developers to define a "standard market" for their products. Furthermore, this lack of a standard market makes it difficult to raise investment capital to commercialize a new technology.

Another significant barrier to the development of innovative technologies is the issue of scale-up. In most areas of process technology development, bench- or pilot-scale testing is a necessary precursor to implementation of the technology on a larger scale. However, innovative technologies for subsurface cleanup tested on the bench or small pilot scale often cannot be scaled up for field application due to the heterogeneous nature of the problem. Thus, at the early stages of technology development, full-scale demonstration of the technology is needed at each new site. As a technology becomes more widely used under a variety of conditions, such demonstrations may no longer be needed.

Institutional Barriers

Innovative technology development is further limited by institutional barriers that have a direct impact on the willingness of entrepreneurs and private investors to invest in new technologies. One significant institutional barrier is the lack of facilities for testing new technologies under controlled conditions. For example, the Safe Drinking Water Act bans the injection of hazardous wastes into most aquifers, unless the injection is part of a Resource Conservation and Recovery Act (RCRA) or Super-fund remedial action. In part because of this regulatory barrier, at the time this report was prepared injection of contaminants into the subsurface for the purpose of testing new technologies was permitted at only one site, the Moffett Air Force Base in California. As a result, many U.S. researchers rely on results from Canada, where researchers at the Waterloo Centre for Ground Water Research have been permitted to inject NAPLs and other contaminants under controlled conditions to test alternative technologies.

A second institutional barrier is the slow development of new technologies being researched in government laboratories, due either to changing budget priorities or to a lack of efficient technology transfer from the national laboratories to commercialization. A third institutional barrier is the uncertainty about whether the public will accept innovative technologies at sites where public comment is either encouraged or statutorily required. Although public groups may be strongly in favor of some innovative technologies that have the potential to reduce the toxicity and mobility of contaminants or to provide permanent solutions, acceptance by public groups is another uncertainty that can inhibit investor interest in innovative technologies.

Economic Barriers

The primary economic barrier faced by developers of new technologies is difficulties in raising sufficient capital for successful commercialization. Although the demand for new technologies appears large based on the magnitude of the contamination problem (EPA, 1993), predicting the timing of that demand has proven elusive. For example, projections by both the federal government and private organizations on the rate of expenditure for waste site remediation have been significantly inaccurate. Many companies formed in response to such projections only to find that the actual timing of the demand was delayed substantially, from two to five years. Some of these companies have had an early demise in the marketplace. There has been a general consolidation of the remediation industry, with the number of firms and investor interest declining. (Environmental stocks were one of the worst-performing sectors in 1993.) These economic uncertainties limit the ability of private parties to obtain sufficient venture capital to undertake development of remediation technologies, particularly in situ technologies. (For ex situ technologies, the degree of uncertainty in success is considerably lower, and therefore obtaining venture capital is easier.) Generally speaking, the amount of federal or state funds available for investment in new technologies is also limited, due to the inherent suspicion on the part of many government agencies as to the future outcome of such investments and debates over who benefits and who should benefit.

An additional economic barrier is the inability to define accurately the potential rates of return on investment in new technologies. Under this high degree of uncertainty, the enthusiasm of entrepreneurs and other entities for investing in environmental technologies is limited.

Technology Selection Phase

The second key phase in the life cycle of an innovative technology is selection of the appropriate technological combinations required for site cleanup. The process of selecting technologies for hazardous waste site remediation is well defined under both RCRA and the Superfund act and has been presented in detail in various EPA guidance documents. Either a feasibility study or corrective measure study, under the Superfund act or RCRA, respectively, provides the background for screening and selecting innovative technologies. If an innovative technology is found to be suitable for use at a particular site, it can then be identified in the Superfund Record of Decision or in the RCRA Corrective Measure Implementation Plan. The final step in the selection of technologies is public review and acceptance or rejection.

The selection process involves numerous stakeholders, including environmental consultants, engineering and construction contractors, the regulated community (primarily the potentially responsible parties), and the public, which by statute and regulations is asked to comment on the selection of technologies at numerous milestones during the project. As was the case in the technology development phase, significant technical, institutional, and economic barriers to innovative technologies exist in the technology selection phase.

Technical Barriers

The major technical barriers to the selection of innovative technologies are uncertainties due to site complexity and the inadequacy of site characterization techniques for minimizing these uncertainties. Technological uncertainties due to site complexity pose difficult dilemmas for consultants and regulators, who may be either unfamiliar with the potential effectiveness of an innovative technology or unable to obtain information on the potential applicability of that technology. On the one hand, innovative technologies may promise cost and efficiency advantages for site cleanup compared to conventional technologies. On the other hand, the cost and efficiency data taken at one site, or under very controlled conditions, may not be easily extrapolated to another site. Generally, the lack of information on the efficiency, cost, and suitability of an innovative technology under various site conditions, combined with significant technical uncertainty regarding site characterization, often causes consultants, owners and regulators to reject an innovative technology. This unwillingness to take risks characterizes the technology selection process at hazardous waste sites in the United States.

Another significant technical barrier to innovative technology selection is the setting of cleanup levels that are unlikely to be achieved by any technology, including an innovative one. This barrier is especially important for very complex sites such as those in category 4 in Table 3-2. There is little incentive to select an innovative technology if cleanup levels cannot be achieved in technically practical time frames.

Institutional Barriers

Technical uncertainty, in turn, raises institutional barriers to innovative technology selection. One institutional barrier is lack of adequate technical expertise on the part of consultants and regulators, leading to conservative decisionmaking. A second barrier is the potential for liability if the technology fails. There is a pervasive unwillingness to share risks of selecting innovative technologies between the regulator, the con sultant, and the technology vendor or construction contractor. The lack or shortage of insurance coverage for the selection of innovative technologies amplifies the liability problems; the consultant, or the engineering contractor, must bear the brunt of the risk, limiting the number of firms willing to take such financial risks to major companies that are financially stable and able to self insure. Also contributing to the liability problem is the unwillingness of many federal agencies or potentially responsible parties to indemnify consultants and engineering contractors when innovative technologies are recommended or selected.

A key difference in the selection of technologies for Superfund sites compared to selection of technologies at non-Superfund sites is the need for public approval of the remedy. In some cases, public groups will strongly support innovative technologies. Because public groups tend to be risk averse, however, there is the potential for rejection of some innovative technologies, such as those involving use of thermal treatment methods or genetically engineered microorganisms. In balance, however, the posture of public groups may in fact be a positive support for the development and selection of innovative technologies. The impact of public involvement in remedy selection —whether positive or negative— has not been evaluated.

Economic Barriers

The major economic barrier to innovative technology selection is cost uncertainty. The lack of cost history available for new technologies exacerbates the level of uncertainty facing the engineer or the regulator and makes private parties responsible for cleanup hesitant to select new technologies. Contributing to cost uncertainty is the likely increase in costs due to project delays, a result of institutional barriers that must be overcome by testing the technology. Another component of the cost problem is unwillingness to fund the treatability studies and other developmental tests required to demonstrate that an innovative technology may be successful at a particular site. The selection of innovative technologies may also be inhibited by fears of patent infringement and unknown licensing fees for innovative technologies that are still in the development stage. All of these factors represent barriers to the selection of innovative technologies, particularly under conditions in which there is an urgency to arrive at a remedy selection. Many of these factors, however, are similar to barriers facing the implementation of any new technology or scientific advance in society. The two unique factors associated with ground water remediation are the continuing uncertainty in the success of any technology because of uncertainty in site characterization and the litigious nature of many site remediation projects.

Technology Implementation/Procurement Phase

The final phase of the life cycle of an innovative technology is the procurement, construction, and operation of the technology. The transition from the Record of Decision, remedial action plan, or corrective measure implementation plan to the final implementation of a remedial action is complex, with the details dictated by the ultimate owner of the technology. Various procurement options are used, including several different contractual mechanisms, depending on whether the remediation is being overseen by a government agency or a private party. The most common are the fixed-price or lump-sum contract, the unit pricing contract (often preferred by private parties), and the time and materials contract. The latter has been used less frequently than the fixed-price and unit-price contracts. At this stage in the life cycle of an innovative technology, as in the two prior stages, technical, institutional, and economic barriers exist.

Technical Barriers

During the procurement stage, site complexities and the heterogeneities decrease the willingness of contractors to guarantee the effectiveness of their technology. This is particularly true for innovative technologies for which only limited data are available. The general unwillingness of contractors to guarantee the effectiveness of an innovative technology may cause site owners to reject that technology. The issue at hand is who should take the risk of failure: the responsible party/owner or the owner/developer of the technology. Another technical barrier to procurement is the likely need for a combination of technologies to achieve desired cleanup levels. If more than one innovative technology is included, the project becomes even more complex and more difficult to implement.

Institutional Barriers

Many of the institutional barriers complicating the selection process for innovative technologies are also relevant to the procurement stage. As noted above, technical uncertainties result in a major institutional barrier: the unresolved debate over who should bear the brunt of the risk for the possible failure of the technology. For example, the EPA recently altered its position on indemnification of remedial action contractors operating at Superfund sites. The previous policy was to provide unlimited indemnification. The new policy, approved during the final days of the Bush administration, provides indemnification only in the event that there are insufficient bids during the procurement process and that the insufficiency is due to the lack of government indemnification. The indemnification limits have been set at $75 million for EPA contractors and $50 million for all other remedial action contractors (HMIR, 1993). This new policy may reduce the number of sureties willing to provide bonding coverage for remedial action contractors and cause further delays in the overall Superfund remedial action program. Presumably, similar problems will occur under the RCRA corrective action program.

Other institutional barriers involve the nature of the federal procurement process. For example, a contractor who undertakes treatability studies cannot compete for construction of the innovative technology at full scale because the Federal Acquisition Regulations specify that any contractor involved in the selection or testing of a technology is not eligible for construction. Consequently, the developer of that technology will be reluctant to support such essential studies. Another barrier is excessive bonding requirements, which may reduce the number of contractors willing to compete.

Economic Barriers

The principal economic barrier to procurement of innovative technologies, like selection of innovative technologies, is uncertainty over costs of both the innovative technology and total site remediation. For organizations like the Army Corps of Engineers that prefer lump-sum or fixed-price contracts, a major barrier arises. Such contracting mechanisms are not suitable for sites where a high degree of uncertainty exists, either with respect to the extent and nature of the contamination or with respect to the applicability of the technology to the particular site. An alternative to the lump-sum contract is the indefinite delivery contract, in which each task of a project is negotiated in sequence rather than bidding the entire project at once. However, some federal procurement agencies perceive that such contracts may lead to higher total costs (including construction costs) for the remediation project. Such potential cost increases would be justifiable if an innovative technology could provide substantial efficiency and life cycle cost savings. However, such cost savings are often difficult to predict with a level of accuracy that overcomes the reluctance of agencies to take the risk on larger short-term costs.

Adequacy of Action to Address Barriers

Despite these barriers, use of innovative technologies to clean up waste sites has increased substantially. For example, in 1984, only one innovative technology was selected for use at Superfund sites. In 1992, 59 were specified (Kelly, 1994). However, nearly half of these involve soil vapor extraction, which is suitable primarily for soils, not ground water. Significant efforts to expand the use of innovative technologies are under way through government programs and laboratories, cooperative research agreements between government agencies and private organizations, and various educational initiatives.

Overcoming Technical Barriers

The federal government is making significant investments in development of new waste site characterization and cleanup technologies through the EPA, DOE, and DOD. The major EPA program for promoting development and demonstration of new technologies is the SITE program, which evaluates and compiles data on new technologies. The EPA also sponsors five hazardous substance research centers, authorized under 1986 amendments to the Superfund law, and four university research centers whose research missions address issues related to hazardous waste site remediation. In addition to these EPA programs, the DOE and DOD are investing significant amounts in development of new technologies that could be used to clean up defense and weapons manufacturing facilities. For example, in its 1995 budget request the DOE allocated $426 million—about 7 percent of its $6 billion environmental management budget—for technology development, some of which will be used to develop new ground water and soil cleanup technologies (Department of Energy, 1994). The DOD's 1995 budget request calls for $30 million for technology demonstrations for the DOD environmental cleanup program and $15 million for an environmental security technology certification program, which will assist in transferring promising technologies tested in the laboratory to the field (Department of Defense, 1994).

Other initiatives are under way to identify federal facilities that government agencies and private industries can use as test sites for innovative technology evaluation. The mechanism for implementing such agreements is the Cooperative Research and Development Agreement (CRADA), which specifies the terms and conditions to be established between federal agencies and other entities to undertake research at federal facilities. A recent CRADA signed by the EPA, the Air Force, Clean Sites, Inc., and several private companies involves the use of McClellan Air Force Base in California as an innovative technology test site (Clean Sites, Inc., 1992). Another major initiative currently in progress involves a CRADA between the Western Governors Association and numerous federal agencies, including the EPA and the Departments of Defense, the Interior, and Energy. Under the memorandum of understanding between these agencies, the Western Governors Association has created task forces to guide development, testing, and implementation of innovative technologies for cleaning up federal facilities located in the western United States.

A few states have also undertaken programs to assist in the development and implementation of innovative technologies. The state of California, for example, has an Office of Appropriate Technologies, which has used cost-sharing approaches to encourage innovative technology development.

Overcoming Institutional Barriers

Several initiatives are under way to reduce institutional barriers to innovative technologies. The EPA, through the Technology Innovation Office (TIO), has made major strides in developing data bases to provide information on the efficacy and cost of both conventional and innovative cleanup methods (EPA, 1992a,b,c,d). The TIO has developed a vendor data base (the Vendor Information System for Innovative Treatment Technologies, or VISITT) that provides relevant information on vendors of remediation technologies and is updated annually. Several of the DOE's national laboratories have instituted an extensive program of technology transfer to accelerate the translation of research concepts into new technologies. This effort is planned as a major focus of the national laboratory network as it makes a transition from weapons production to civilian missions. Significant support is now anticipated from the regulatory community for the testing of innovative technologies, particularly in the context of the CRADAs being initiated across the country.

Deficiencies in the training of personnel who have the responsibility to select and implement technologies for site cleanups have led to the proliferation of training programs addressing a wide range of topics. These workshops, short courses, conferences, and satellite video conferences are sponsored by the private sector, federal and state agencies, universities, and professional societies. Additionally, the TIO, in conjunction with a number of professional organizations, has launched the Waste Tech Initiative, which will culminate in the publication of eight monographs on innovative technologies appropriate for cleanup of contaminated soil and ground water.

Overcoming Economic Barriers

A variety of federal efforts are under way to reduce economic barriers to use of innovative technologies. For example, the EPA and other federal agencies have undertaken major efforts to develop a contracting approach that is more suitable for engineering under the level of uncer tainty characteristic of waste site remediation (EPA, 1992b,c,d). (One example is the EPA's use of level-of-effort contracts, which specify the approximate number of hours or people that may be required for the duration of the contract, with hours negotiated on a task-by-task basis.) The DOE and DOD, through the Small Business Administration's Small Business Technology Transfer Program, are funding small businesses to carry out research and pilot studies of innovative cleanup technologies (SBA, 1994). In addition, the EPA's Superfund Accelerated Cleanup Model, currently in a trial mode at one site in each EPA region, urges early evaluation of innovative technologies. Finally, the EPA has issued guidance documents on the use of innovative technologies and, through the efforts of the TIO, continues to attack the problem of the lack of cost and efficacy data for innovative technologies. The list of vendors prepared by the TIO suggests that competitive pressure does exist for some innovative technologies and that costs of innovative technologies will likely decrease in the future.

In summary, although considerable efforts have been and are being invested in the development and implementation of innovative technologies, there is insufficient information available to objectively assess the success of these efforts. Such a task would not be straightforward. It would be analogous to a private company trying to show that its investments in new technologies have provided significant return to the owners. In the private sector, the marketplace provides an answer to this question. In the public sector, the "investments" are being made by a number of federal and state agencies, and the "benefits" are difficult—if not impossible—to quantify. The committee recommends that the EPA, DOE, DOD, and other federal agencies supporting the development of innovative technologies either collectively or individually assess, on a regular basis, the effectiveness of the programs to promote new environmental technologies for hazardous waste site remediation. The efforts of government agencies should also be compared to investments in the private sector to determine what, if any, lessons can be learned regarding the success or failure of different policy initiatives.

RESEARCH NEEDS FOR ADVANCING THE DEVELOPMENT OF INNOVATIVE CLEANUP TECHNOLOGIES

This chapter has described a range of potential enhancements and alternatives to pump-and-treat systems. However, the majority of these technologies are in the development stage, with few quantitative data sets for predicting how well they might perform at a given site. For the majority of technologies discussed in this chapter, field testing is needed to establish the reliability of the technology, to provide data for preparing design manuals, and to identify the inherent limitations for users. These field tests should evaluate performance for a range of chemical contaminants and contaminant mixtures (such as petroleum hydrocarbons, chlorinated solvents, polychlorinated biphenyls, and metals) and site conditions (such as shallow and deep aquifers and homogeneous and heterogeneous geology). They should be designed to allow a mass balance analysis comparing the amount of contamination present in the subsurface with the amount removed. Data from the field tests should undergo scientific peer review.

In addition to field tests, focused research is needed to answer more fundamental questions about the technologies. The committee believes that focused research could lead to especially promising advances for engineered in situ bioremediation, intrinsic bioremediation, soil vapor extraction, air sparging, containment methods, and inorganic contaminant treatment methods.

Engineered And Intrinsic In Situ Bioremediation

Engineered and intrinsic in situ bioremediation are promising cleanup methods because they treat contaminants in place instead of requiring extraction, can convert contaminants to innocuous products, and minimize or eliminate pumping requirements. However, the microbial processes underlying bioremediation and how to optimize these processes are still not fully understood. Especially important is research to address the following questions:

- Under what chemical conditions are contaminants susceptible to biodegradation?
- What genetic characteristics and biochemical mechanisms control microbial degradation of particular types of contaminants?
- What are the ecological relationships between the various microbial communities involved in biodegrading contaminants?
- How can subsurface microbial populations be selected and manipulated to carry out specific biotransformations?

In addition to advanced understanding of microbial processes, improvements are needed in the engineering systems used to promote bioremediation. The key engineering challenges are delivering adequate growth-stimulating materials to the microorganisms and ensuring adequate contact between the organisms and the contaminants. Research addressing the following questions would advance the design of bioremediation systems:

- How can systems for delivering oxygen and other growth-stimulating materials be optimized to provide sufficient quantities of the necessary materials, especially in low-permeability and heterogeneous soils? How can these delivery systems be improved to ensure mixing throughout the contaminated zone and prevent excessive microbial growth near the injection point?
- What is the efficiency of methods such as surfactant and solvent flushing in enhancing contact between the microorganisms and the contaminants?
- What is the ultimate fate in the subsurface of surfactants and solvents designed to promote microbial contact with contaminants?
- How can protocols for monitoring and evaluating the progress of bioremediation be improved?

Soil Vapor Extraction and Air Sparging

Soil vapor extraction and air sparging have the potential to rapidly remove large quantities of volatile organic contaminants from shallow zones, as documented in this chapter. However, accurately predicting mass removal rates and operating times for these systems is difficult because of limited process-level understanding. Research addressing the following questions would advance the state of the art for soil vapor extraction and air sparging:

- What is the relationship between air velocity and attainment of local equilibrium?
- What is the importance of diffusion-limited processes, such as movement of contaminants from low-permeability zones and dead-end pores, in the performance of vapor extraction and air sparging systems?
- What are the implications of assuming laminar flow versus assuming turbulent flow in design calculations?
- What is the response of multicomponent contaminant mixtures, such as gasoline, to removal by volatilization? How does the extraction efficiency decrease over time with loss of the more volatile fractions?
- How can the optimal well spacing be determined?
- What are the appropriate models for describing two-phase hydrodynamic conditions generated by air flow in the saturated zone?
- How does the elevated air supply influence chemical and biological reactions?
- What is the most cost-effective balance between designing air delivery systems to promote contaminant volatilization and designing them to promote contaminant biodegradation?

Containment Technologies

Construction difficulties and questions about long-term reliability have limited the application of containment technologies in the past. Research addressing the following questions would improve the ability to design effective containment systems:

- How can methods for detecting defects in containment systems be improved?
- How can the bottoms of vertical walls be effectively sealed?
- What is the long-term reliability of different materials used for containment?
- How significant is diffusive transport of contaminants across barriers over long time scales?

Treatment Methods For Inorganic Compounds

Most of the enhancements and alternative technologies reviewed in this chapter are for treating organic contaminants. However, as described in Chapter 1, metal contaminants such as lead and chromium are present at hundreds of Superfund sites as well as at the many other types of waste sites. One example of a metal removal technique currently being researched is electro-osmotic purging (Acar, 1992), in which electrodes are inserted in the soil to enhance the diffusion of metals and facilitate their extraction from low-permeability soils. Other suggested methods for treating metals involve using chemicals or microbes to either dissolve the metals and improve their recovery or immobilize the metals for long-term containment. In general, however, the techniques for removing metals are much less developed than those for removing organic compounds. Therefore, research is needed to develop existing metal recovery methods and to explore possible new techniques.

EDUCATIONAL NEEDS

As discussed in this chapter, an important barrier to the use of innovative technologies is lack of technical expertise on the many possible innovative cleanup methods. Advancing use of these technologies will require improved education, especially of the people in direct decisionmaking positions. The committee recommends three types of educational programs:

- *Formal interdisciplinary programs*: The nation's formal academic educational programs need to be updated and the interdisciplinary op portunities within these programs expanded to train future generations of technical personnel.

- *Technical training courses*: Training courses are needed to improve the knowledge of existing technical personnel.
- *Opportunities for representatives of industry, researchers, regulators, consultants, and contractors to exchange ideas and experiences*: Opportunities are needed to discuss successes and failures, barriers to using more efficient treatment methods, and steps that could be taken to increase the diversity of available technologies.

CONCLUSIONS

Based on technical reports about innovative subsurface cleanup technologies and an assessment of the application of these technologies at contaminated sites, the committee reached the following conclusions:

- **Enhancements to conventional pump-and-treat systems can significantly increase the mass of contaminants removed from the subsurface and the rate at which they are removed**. Pulsed pumping can improve cleanup cost efficiency by allowing contaminants to desorb and diffuse into mobile fluid zones, increasing the mass of contaminant extracted with each volume of pumped water. In situ bioremediation and in situ chemical treatment can improve cleanup efficiency by promoting contaminant destruction in place, eliminating or minimizing the need to extract the contaminants. Soil vapor extraction, air sparging, and horizontal wells can improve cleanup efficiency by removing volatile contaminants via air, a more effective transport medium than water. Soil flushing and in situ thermal technologies can improve cleanup efficiency by enhancing contaminant removal from soil above the water table, preventing contaminant migration into the ground water.
- **Although enhancements can substantially increase the efficiency of pump-and-treat systems, they are subject to similar limitations as conventional systems because they involve pumping fluids such as water, water solutions, and/or air**. Geologic complexities can interfere with delivery of the fluids to zones where contaminants may be lodged. Contaminant sorption to solid materials and the presence of NAPLs can limit the availability of contaminants for capture or treatment by the circulating fluids. Sorption and NAPLs can also limit contaminant contact with microorganisms, which is required for in situ bioremediation.
- **In situ nonpumping alternatives to pump-and-treat systems may reduce cleanup costs, but they have important limitations**. Nonpumping alternatives reduce costs by eliminating the need to circulate fluids through the subsurface, which can have a high energy cost. Nonpump

ing approaches can contain the contamination, route the dissolved contamination through a stationary reactive medium, or use the capability of indigenous microbes to degrade the contamination without human intervention. However, the long-term integrity of containment systems is unproven, stationary barriers for treating contamination have been tested only in small-scale laboratory experiments, and very little operating history exists to judge the effectiveness of intrinsic biodegradation. In addition, members of the public may be unwilling to accept these approaches, which they may perceive as equivalent to no action or as resulting in incomplete site remediation.

- **No known technology can overcome all of the limitations to ground water cleanup**. For innovative cleanup technologies as for conventional pump-and-treat systems, the geologic conditions at the site and the chemical nature of the contaminants can prevent restoration of ground water to health-based standards. Nevertheless, the use of innovative technologies should be encouraged even if the technologies cannot currently reach health-based cleanup goals, because new technologies may outperform conventional systems and because wider use of the technologies may lead to discoveries that improve their performance.
- **For enhanced pump-and-treat systems and nonpumping alternatives, thorough site characterization, pilot testing, and monitoring are critical to effective performance**. An observational approach to remediation, in which the treatment system is adjusted as new information becomes available, is even more important for innovative technologies than for conventional pump-and-treat systems because of the greater uncertainties associated with the innovations.
- **A combination or sequence of remedial technologies is likely to be more effective—and necessary—at most sites**. The majority of waste sites contain mixtures of contaminants with varying physical and chemical properties. A single remedial process is typically effective at removing only a subset of the compounds in a waste mixture. Treatment trains that couple remedial techniques may be necessary to treat the different types of contaminants that may be present at the site.
- **Despite the potential for innovations to increase the efficiency and reduce the costs of ground water cleanup, significant barriers have obstructed the development and application of these innovations** . A combination of technical, institutional, and economic barriers discourages those involved in cleanups from assuming the risks associated with using technologies that lack proven track records. Options need to be explored for developing mechanisms that allow risk sharing when innovative technologies are used, so that neither the site owner nor the technology developer must assume the full burden of risk if the technology fails.

- **Federal agencies supporting innovative technology development should assess the effectiveness of current technology development efforts.** Cooperative research and development agreements among government agencies, the DOE's research at its national laboratories, and the EPA's efforts under the SITE program, through the TIO, and through the hazardous substance research centers are important steps in expanding use and development of innovative technologies. However, whether these programs are sufficient to overcome the many barriers to technology development is unknown. Given the size and cost of the ground water cleanup problem, the importance of ensuring that adequate resources are directed toward technology development cannot be overstated.

NOTE

1. Technologies that circulate air specifically to promote biodegradation are known as bioventing systems and are described later in this chapter.

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5

Characterizing Sites For Ground Water Cleanup

The previous chapters have discussed how the complexities of the subsurface environment and the types of contaminants present in the subsurface limit the ability of existing technologies to clean up contaminated ground water. However, the poor performance of ground water cleanup systems at many sites to date is not just a function of site complexity and technical limitations; it is also a result of insufficient or inaccurate characterization of the problem prior to cleanup, which has resulted in a flawed design of the cleanup system. For example, at 18 of the 77 sites listed in Appendix A, the remedial actions have failed to contain the ground water contamination. It is likely that the failure of containment at many of these sites is due to inaccurate characterization of the horizontal and vertical extent of contamination. The lack of proper characterization has often occurred even after huge sums of money have been spent and considerable time has elapsed in characterizing the site.

Proper site characterization is an essential component of designing a ground water cleanup system, but at the same time perfection in site characterization is unattainable. Given the complexity of the subsurface, the enormous range of scales that must be taken into account, and the inability to view the subsurface directly, developing a precise image of the contaminated environment is impossible. In fact, attempting to achieve perfection in site characterization can be counterproductive because excessive drilling for the purpose of sampling would destroy the structure that it aims to portray. Thus, site characterization must achieve a balance between providing enough information to design an effective remediation system and recognizing that significant uncertainties about the site will remain. This chapter discusses the site characterization process and provides the Committee on Ground Water Cleanup Alternatives' assessment of what level of site characterization is adequate.

Site characterization is an extensive subject and is covered only briefly in this chapter. For detailed information about the mechanics of site characterization, readers should refer to the guidance documents referenced at the end of this chapter (EPA, 1988a, 1988b, 1989, 1990, 1993a; Mercer et al., 1990; NJDEPE, 1992; Cohen and Mercer, 1993).

GOAL OF CHARACTERIZATION

Characterization of sites with ground water contamination is conducted to determine the extent of contamination and to select and design a remedy. Site characterization studies should be planned with these purposes in mind. Site characterization studies need not be designed to develop as complete a picture as possible of the subsurface environment. Highly detailed characterization studies may be appropriate at research sites, but they are not needed at most sites. The committee has observed that the characterization process often drags out and produces substantial quantities of the wrong kinds of data because the main goals of the characterization process are forgotten.

Various Environmental Protection Agency (EPA) documents accurately convey the purpose of site characterization. For example, the regulation implementing the Superfund law, which is known as the National Contingency Plan, describes the purpose of site characterization in the following language:

> The purpose of the remedial investigation/feasibility study (RI/FS) is to assess site conditions and evaluate alternatives to the extent necessary to select a remedy.

The EPA's guidance document on conducting remedial investigations and feasibility studies (EPA, 1988a) states:

> The objective of the RI/FS process is *not* the unobtainable goal of removing *all* uncertainty, but rather to gather information sufficient to support an informed risk management decision regarding which remedy appears to be most appropriate for a given site. The appropriate level of analysis to meet this objective can only be reached through constant strategic thinking and careful planning concerning the *essential data* needed to reach a remedy selection decision [emphasis added].

The EPA's memorandum outlining policies for addressing sites with dense nonaqueous-phase liquid (DNAPL) contaminants (Clay, 1992) reflects a similar intention:

> The degree of effort expended in locating DNAPL accumulations should be based on the degree of characterization necessary for remedy selection. Locating DNAPL in small stratigraphic or structural discontinuities is generally not possible. However, efforts should be made to identify subsurface geologic environments where DNAPL accumulations may be present.

Given the purpose of site characterization as expressed in these documents and the limited number of currently available remedial alternatives for contaminated ground water, it follows that site characterization studies can focus on collecting the data required to choose among a limited number of alternatives.

PLUME VERSUS SOURCE

Conceptually, the contaminated ground water environment consists of two distinct parts, as explained in Chapter 2: (1) the plume of dissolved contaminants and (2) contaminant source areas. Contaminant source areas include not only typical near-surface sources such as leaking drums, process wastes, and sludges, but also deep subsurface sources such as residual nonaqueous-phase liquids (NAPLs), pools of NAPLs, and metals that have precipitated in mineral phases having low solubility. The prospects for ground water cleanup are much different for the plume of dissolved contaminants than they are for the source areas. Based on this observation, it is clear that site characterization studies should be designed to define early the parts of the site that can be considered source areas and the parts that can be considered as the dissolved plume, because the potential remedial options are significantly different for the two parts.

Figure 5-1 illustrates hypothetically how the source and dissolved plume areas might appear for a site contaminated with trichloroethylene (TCE). As shown in the upper part of the figure, the source zone covers a small area relative to the plume of dissolved contamination, which extends far beyond the source zone. As shown in the lower figure, the source zone consists of not only the sludges and drums that were the original source of the TCE, but also accumulations of TCE as a nonaqueous phase along the contaminant flow path.

An example of a site with a large subsurface NAPL source is the King of Prussia site discussed in Box 3-5. At that site, the chemical 1,2,3-trichloropropane has migrated both horizontally and vertically large distances from the source area in fractured rock. Trichloropropane at residual sat uration on fracture surfaces remains as a long-term source of dissolved contaminants.

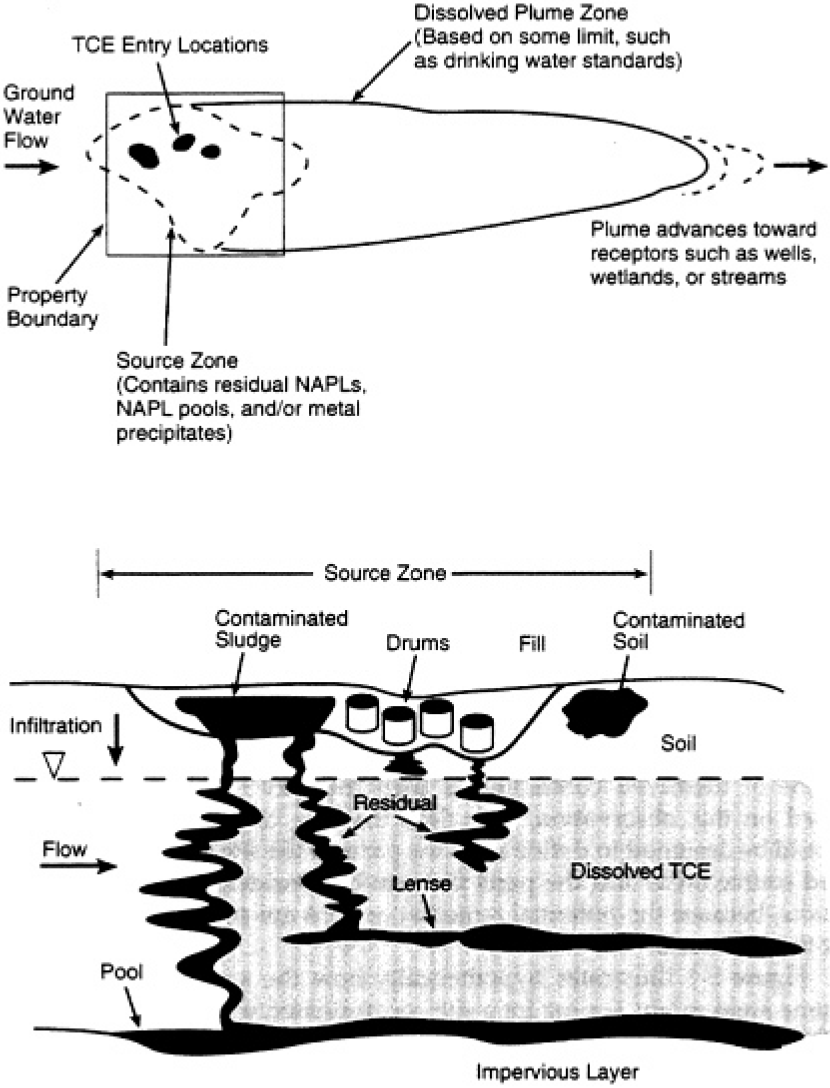


FIGURE 5-1 Source and dissolved plume areas for a hypothetical site contaminated with TCE. Source: After Cherry et al., 1992.

An example of a site with a mineral phase acting as a long-term source of ground water contamination is the United Chrome site in Oregon (listed in Appendix A), where chromium is the dominant contami nant (Palmer, 1992). At that site, most of the chromium in the subsurface is present in the mineral barium chromate, which is sparingly soluble. Ground water in contact with this mineral has an equilibrium chromium concentration of only, about 10 mg/liter, and as a result a very large number of pore volumes of water must be pumped through the contaminated zone to remove all of the barium chromate, which acts as a long-term source of dissolved chromium.

MANAGEMENT OPTIONS

The site characterization process is greatly simplified by the observation that there are not many remedial management options for contaminated ground water. The options, illustrated in Figure 5-2, are essentially (1) contain the contaminated ground water, (2) restore the contaminated ground water, or (3) do nothing if the contaminated ground water poses no risk and/or natural attenuation will be sufficient to resolve the problem. Characterization studies should determine early on which general remedial approach is appropriate for each subarea of the site. In many cases, the appropriate remedy for source areas will be containment, and the appropriate remedial goal for the plume of dissolved contaminants will be active restoration. Natural attenuation may be acceptable for some zones where it can be shown that natural biological, chemical, and physical processes will lower contaminant concentrations to cleanup goals before the contaminants reach receptors; it may also be acceptable for ground water that discharges into surface water bodies where it can be demonstrated that the ground water will not be used and the resulting concentrations in the surface water body will be below applicable standards. Once the goal of remediation is established, site characterization studies should be designed to collect the data required to design a technically effective and cost-effective remedial action to obtain the desired end result (whether containment, active restoration, or natural attenuation).

For some sites, determining the appropriate general remedial approach requires only a limited amount of data. For example, consider a site where residual polychlorinated biphenyls (PCBs) are found below the water table in fractured bedrock as the result of the past migration of a DNAPL containing PCBs. In most environments, migration of PCBs is very limited because of their strong tendency to sorb to solid materials in the aquifer, with the PCBs traveling at as little as one-hundredth the rate of the ground water. As a result, in most situations such a PCB plume consists of the area containing the DNAPL (generally present at residual saturation) and a very small fringe of dissolved PCBs. Because the plume of dissolved PCBs is very small, almost the entire plume can be considered as the source area. The appropriate remedial measure at such a site will likely be containment because of the inability to remove the PCBs with existing technologies as a result of their extremely low solubility.

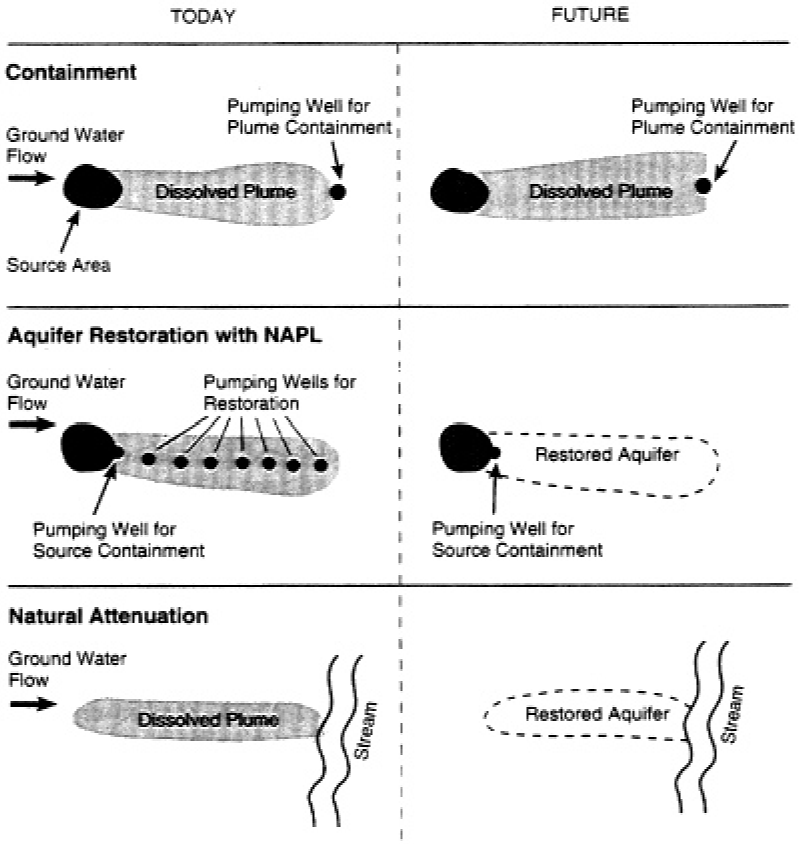


FIGURE 5-2 Options for managing sites with contaminated ground water. In the option shown at the top, a pumping well is installed to prevent enlargement of the plume of dissolved contaminants but not to clean up the plume. In the middle option, a system is installed to clean up the plume, while a containment system is installed around the contaminant source area. In the bottom option, site conditions are such that the plume, which has no significant remaining source areas, attenuates without human intervention. SOURCE: Adapted from Cherry et al., 1992.

DATA REQUIREMENTS

The level of characterization required to select a remedial action is that which is sufficient to determine the extent of contamination, the res toration potential of each subarea of the site, and potential receptors of the contaminated water. In simplest terms the required data include

- information to define or estimate the horizontal and vertical extent of ground water contamination,
- information to estimate the locations of contaminant source areas,
- information to describe the hydrogeologic setting, and
- information to estimate the site's restoration potential.

Hollow-stem auger used to obtain subsurface samples and install monitoring wells. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

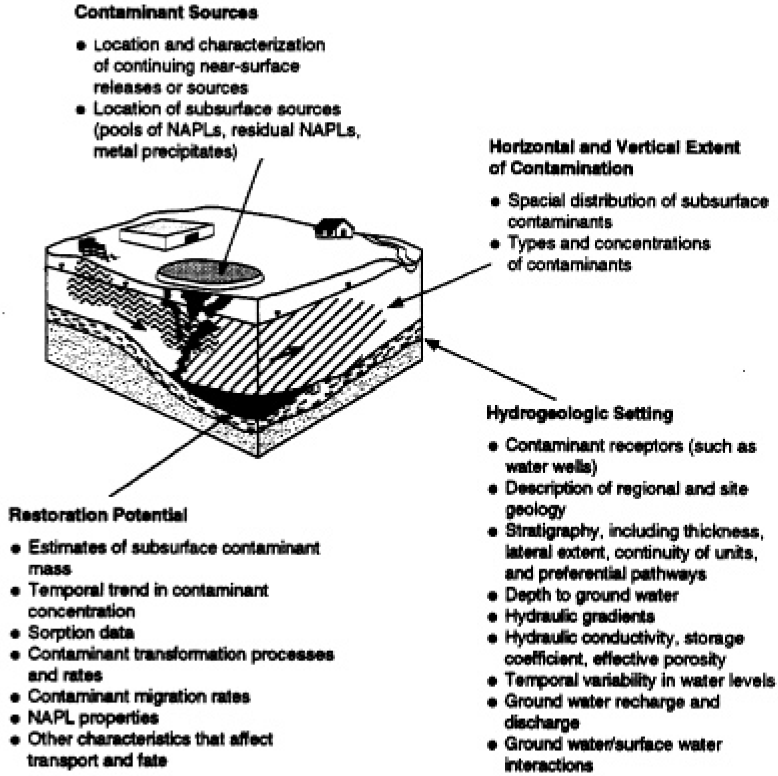


FIGURE 5-3 Categories of data required to select and design a ground water remedial action (adapted from EPA, 1993b).

These data are sufficient to formulate a conceptual model of the site that will be necessary for analyzing such fundamental questions about the contaminated ground water system as

1. Where is the contamination and what chemical compounds are present?
2. How can further migration of the contamination be stopped or reduced to acceptable levels?
3. What receptors are at risk, and can that risk be characterized?
4. Is restoration of the ground water possible with existing technologies, and if so, what are the technical options for remediation?

Figure 5-3 illustrates the basic elements of a site conceptual model.

Horizontal And Vertical Extent Of Contamination

Defining the areas of the subsurface that contain contaminants at concentrations in excess of health-based levels is the obvious first step in developing an appropriate management strategy for the contaminated ground water. Nevertheless, at many sites where remediation is ongoing, the horizontal and vertical extent of ground water contamination has not been defined. The main reasons for this are simple: (1) in complex hydrogeologic systems, defining the extent of contamination is expensive and time consuming, and (2) zones of ground water contamination seldom respect property boundaries, sometimes creating difficulties in obtaining permission to collect samples.

Defining the extent of contamination in complex hydrogeologic environments generally requires the drilling of a large number of boreholes from which samples of ground water are collected either directly or from monitoring wells installed in the boreholes. Many nonintrusive or minimally intrusive techniques are available for estimating ground water quality, as are many analysis techniques for estimating the extent of contamination from existing data on the hydrogeologic system, but none of these techniques is a reliable indicator of ground water contamination. Nondisruptive characterization methods—such as ground-penetrating radar, electroconductivity measurements, and microwave radiation—all require that the contaminant alter a physical property of the ground water to a degree detectable by the geophysical technique. Unfortunately, the relatively low contaminant concentrations typically found in ground water are difficult to measure with these nondisruptive methods. Similarly, minimally intrusive techniques, such as soil vapor analyzers, can be useful for indicating the location of plumes near the water table, but they are not useful for indicating deep areas of contamination. Even when used for indicating contamination in the water table zones, these methods are susceptible to a large number of both false positives and false negatives because they have detection limits of 1 to 10 μg/liter for many common organic chemicals, which is the range of health-based cleanup levels for many contaminants. The data collected from wells operated as part of a pump-and-treat system generally are not useful for defining the horizontal and vertical extent of contamination because these data only provide information on average conditions in the vicinity of the well, not precise concentrations for a given location. Therefore, in defining the extent of contamination, there are no true short cuts to collecting and analyzing ground water samples. In most situations, ground water samples are most efficiently collected from monitoring wells, and many—and often deep—monitoring wells are required to define the hor izontal and vertical extent of contamination. In some situations, the characterization process can be expedited by collecting samples directly from boreholes, but the usefulness of these techniques is limited because it is difficult to check sample reproducibility.

What constitutes adequate vertical definition of a ground water problem is a frequently asked question in site characterization studies. At many sites, especially those with DNAPLs in fractured rock, contamination can extend to depths of 300 meters and more. Adequate vertical definition for purposes of designing a remedy to protect human health and the environment does not necessarily require installation of monitoring wells below the zone of contamination. However, it does require an understanding of the flow direction in the deep zones and the flow paths emanating from the deep zones. If an existing monitoring system shows contamination in the deepest wells but also shows the existence of strong upward hydraulic gradients, then it is probably not necessary to install wells below the zone of contamination. On the other hand, if downward hydraulic gradients exist and there is no information on potential contaminant migration pathways, then most likely deeper monitoring points need to be installed.

Sampling requires entering property to collect soil samples, drill or sample wells, and perform other tests. As a result, the investigator must obtain permission from the landowner or have a legal right to enter for this purpose, and this can sometimes create problems. Federal and state environmental statutes typically grant government agencies and their delegates the right to enter private property to take samples at reasonable times for reasonable purposes related to the implementation of the statute. Typically, government agencies notify property owners and enter into voluntary access agreements that indemnify the property for any injury caused by sampling (Clay, 1991). However, in addition to compensation for damage caused by the sampling itself, in some cases the landowner may have a potential claim for property damage or personal injury relating to the ground water contamination if contamination is detected. The landowner may raise these claims when access is requested and may even attempt to condition access on resolution of such claims. In other cases, landowners may be reluctant to allow sampling on their property because they may fear being held liable for any contamination found.

Locations of Contaminant Source Areas

Successful site characterization requires identifying the locations of potential sources of contaminants so that they can be removed or contained. As illustrated by some of the case studies in Chapter 3, failure to remove or contain these sources will result in continuing dissolution of contaminants when the remediation stops, which will preclude aquifer restoration. Identification of shallow sources of dissolved contaminants and NAPL sources where the NAPL is less dense than water (i.e., LNAPLs), is relatively straightforward and is discussed in the guidance documents referenced at the beginning of this chapter. Identification of DNAPL sources and precipitated metals is not straightforward, although current EPA policy reflects the need to identify DNAPL sources (Clay, 1992; EPA, 1993b).

Monitoring the water level in a well during an aquifer pump test. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

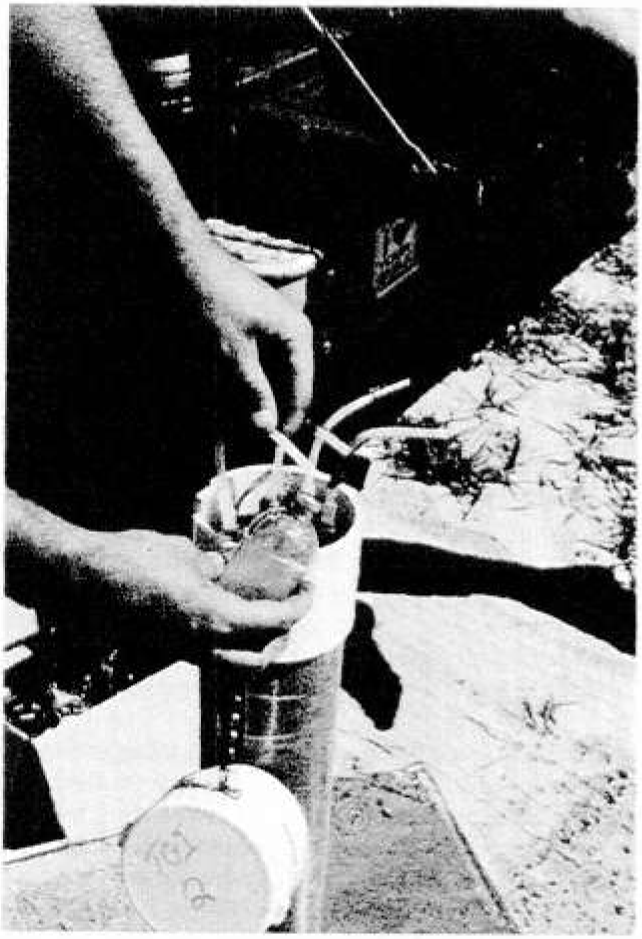
DNAPL sources are difficult to identify because they are denser than water, can migrate below the water table (often to great depths), and generally move along relatively discrete pathways. (In contrast, LNAPLs generally spread out on the water table in a relatively continuous plume that is easy to locate.) Ideally, DNAPL presence can be identified by visual examination of subsurface samples, but this is often not the case. The conventional model of subsurface DNAPLs (as illustrated in Figure 5-1) shows the DNAPLs pooling on low-permeability layers. At sites where most of the DNAPL is present in pools, the DNAPL can be observed in fluid samples taken from wells penetrating the DNAPL zone.

However, direct observation of DNAPLs is extremely rare. Field experience indicates that in many cases, the majority of the DNAPL is present not in pools, but as residual saturation (small globules trapped in the porous materials of the aquifer). In these situations, the free-phase DNAPL originally present in the aquifer migrated until it reached residual saturation. In general, DNAPL at residual saturation is not observable in subsurface samples. When the DNAPL at residual saturation ages—as a result of slow mass transfer into the soil microstructure, dissolution, and biodegradation—detection becomes even more difficult, yet the aged residual can still provide a significant source of contamination.

When subsurface DNAPLs are present at residual saturation, indirect means are generally necessary to determine their presence. Determination of chemical concentrations in water is the best indirect method (Cohen and Mercer, 1993). Concentrations near the solubility of the DNAPL compound are positive confirmation that DNAPLs are present. However, generally DNAPL compounds are detected at less than 10 percent of their aqueous solubility limit in ground water due to the effects of nonuniform ground water flow, variable DNAPL distribution, mixing of ground water in sampling wells, and reduced effective solubility of individual compounds in a multiliquid NAPL mixture (Feenstra et al., 1991). Field work has shown that contaminant concentrations of greater than 1 percent of the aqueous solubility limit are highly suggestive of NAPL presence. Concentrations of less than 1 percent, however, do not preclude the presence of NAPLs (Cohen and Mercer, 1993). The 1 percent rule is frequently used in site characterization studies, and, given the available characterization technologies, it is the best means for estimating the extent of DNAPLs in the subsurface.

At many sites where DNAPL presence is suspected, investigators are reluctant to define the vertical extent of contamination because they fear remobilizing the DNAPLs and inducing new downward migration. A recent EPA memorandum (Clay, 1992) states, "Drilling through DNAPL zones into deeper stratigraphic units should be avoided." Potential remobilization of DNAPLs is a concern, but it does not mean that drilling should be avoided. Field experience indicates that remobilizing DNAPLs by drilling is extremely uncommon, possibly because in many cases much of the DNAPL may be present at residual saturation rather than in pools. Avoiding defining the vertical extent of the DNAPL zones at these sites will in many cases make it impossible to design an appropriate remedy. At many sites, a lack of vertical defining will give the illusion that the DNAPL zone is much larger than it actually is.

At present, locating source areas consisting of metals that have precipitated as mineral phases is even more difficult than locating source areas containing DNAFLs. The experience with these types of sites is



Collection of a ground water sample from a well. Courtesy of Rice University, Department of Environmental Science and Engineering.

very limited compared to sites with DNAPLs, and therefore no rules of thumb have been developed. From a practical perspective, it is almost impossible to collect data prior to pumping and treating that would allow determination of whether a mineral phase is acting as a long-term contaminant source. At the United Chrome site listed in Appendix A, the conclusion that a mineral phase was controlling the cleanup rate was a hypothesis that was developed and tested after data from a pump-and-treat system indicated that concentrations were not changing with time. From a theoretical perspective, describing the processes controlling min eral phases is much more difficult than describing the processes controlling NAPLs because of the strong influence of ground water chemistry on the behavior of the mineral phase.

Hydrogeologic Setting

In the first phase of site characterization, a broad description of the hydrogeologic setting is required to estimate the site's restoration potential and to identify potential ground water receptors. The basic information required at this stage is a description of the stratigraphy, thickness, and continuity of the aquifers and the extent of preferential pathways such as fractures, buried stream beds, and solution cavities. In later phases of site characterization, data are required to determine the rates and direction of ground water flow, an understanding of which is necessary to design a cleanup system and to define the contaminated area. The subsurface properties required to determine rates and direction of ground water flow, which are discussed in detail in Chapter 2, include the following elements: the hydraulic properties of the contaminated region (e.g., hydraulic conductivity, porosity, and storage coefficient distributions); system stresses (e.g., recharge, discharge, pumping rates, and hydraulic gradient); and system geometry (e.g., physical and hydraulic boundaries, stratigraphy, lithology, structural geology, and heterogeneities).

A particularly difficult problem in characterizing ground water flow is heterogeneity in aquifer properties, especially permeability. Fractured rock settings comprise an extreme example. According to EPA guidance (EPA, 1991), a complete description of a contaminated fractured rock system would include the following data: (1) the dimensions of the system; (2) individual fracture lengths, aperture widths, locations, and orientations; (3) the hydraulic head throughout the system; (4) the porosity and permeability of the rock matrix; (5) the sources of water and contaminants; (6) the nature and concentrations of the contaminants throughout the system; and (7) the chemical interactions between the contaminants and the rock matrix. Presently, collection of such detailed information is neither technically possible nor economically feasible at the scale of most contaminated sites. In addition, this detailed information is generally not needed to design a pump-and-treat system to contain the contaminated ground water, which is likely the only realistic objective for extensively contaminated fractured rock environments.

Restoration Potential

Traditionally, site characterization studies have been conducted with the implicit understanding that sufficient information would be collected to design a pump-and-treat system capable of restoring the aquifer to certain standards, usually health based. As this report has documented, however, at many sites complete restoration to health-based standards is not possible with present technologies. Thus, an explicit step in the site characterization process should be to estimate the restoration potential of each subarea of the contaminated site.

Excavating a trench during installation of piping for a ground water monitoring system. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

Table 3-2, in Chapter 3, shows a method for estimating restoration potential developed by the committee. In this table, the relative ease of cleanup is a function of the hydrogeologic setting and the properties of the contaminants. At one extreme are sites in category 1: these sites have mobile dissolved contaminants and homogeneous geology; they can generally be restored to health-based standards. At the other extreme are sites in category 4: these sites have NAPLs and complex geologic conditions; restoration of such areas to health-based standards is highly unlikely with present technologies. In the middle are sites in categories 2 and 3: these sites may have sorbing contaminants and LNAPLs present under varying geologic conditions; restoration of some of these sites may be possible, but restoration of others will not. For most sites in categories 2 and 3, the only way to accurately estimate the restoration potential will be to evaluate the performance of an interim or pilot-scale remediation system. It may be necessary to operate such an interim system for long periods of time in order to estimate restoration potential, because removing several aquifer volumes of water from the area of interest may be necessary to fully understand the characteristics of the site.

As noted in Chapter 2, cleaning up any contaminated site is theoretically possible, provided the cleanup can continue for an infinitely long time period into the future. Therefore, evaluation of restoration potential often reduces to an evaluation of whether or not restoration can be achieved in a reasonable time period. Chapter 3 describes techniques for estimating cleanup time, using the data discussed above. However, as discussed in Chapter 3, these techniques generally produce estimates that have a large uncertainty associated with them and often have a bias toward underestimating cleanup times. As a result, usually the only way to accurately estimate the cleanup time is to evaluate the performance of an interim or pilot-scale remediation system.

In considering a site's restoration potential, the importance of distinguishing between dissolved plume areas and contaminant source areas cannot be overemphasized. Often, dissolved plume areas will have a high restoration potential, while source areas will not.

STAGES OF SITE CHARACTERIZATION AND MANAGEMENT

Almost all ground water remedies will be long-term actions, requiring much more than five years to complete. In fact, many ground water cleanups will last for decades, if not centuries. Because of the complexity of the subsurface environment and the long time frames required for ground water cleanup, site characterization must not be viewed as a onetime event—or even a several-time event—that ends when the final remedial investigation report is submitted. Hydrogeologic and water quality data will be collected throughout the life of a ground water cleanup system, and these data should be reviewed regularly to determine if the cleanup system is meeting its objectives and, if not, whether adjustments are needed.

Site characterization consists of several iterative stages, starting with investigation of the site's history and continuing throughout remediation. Figure 5-4 illustrates these stages. In the initial stage, the investigator reviews background information about the site and previously collected data to determine the likely original sources of contamination and what additional information is required. In the intermediate stages, the investigator collects sufficient information to define the volume of contaminated ground water and to design and implement a containment system. Also in the intermediate stages, the investigator defines potential long-term subsurface sources of contamination and collects sufficient

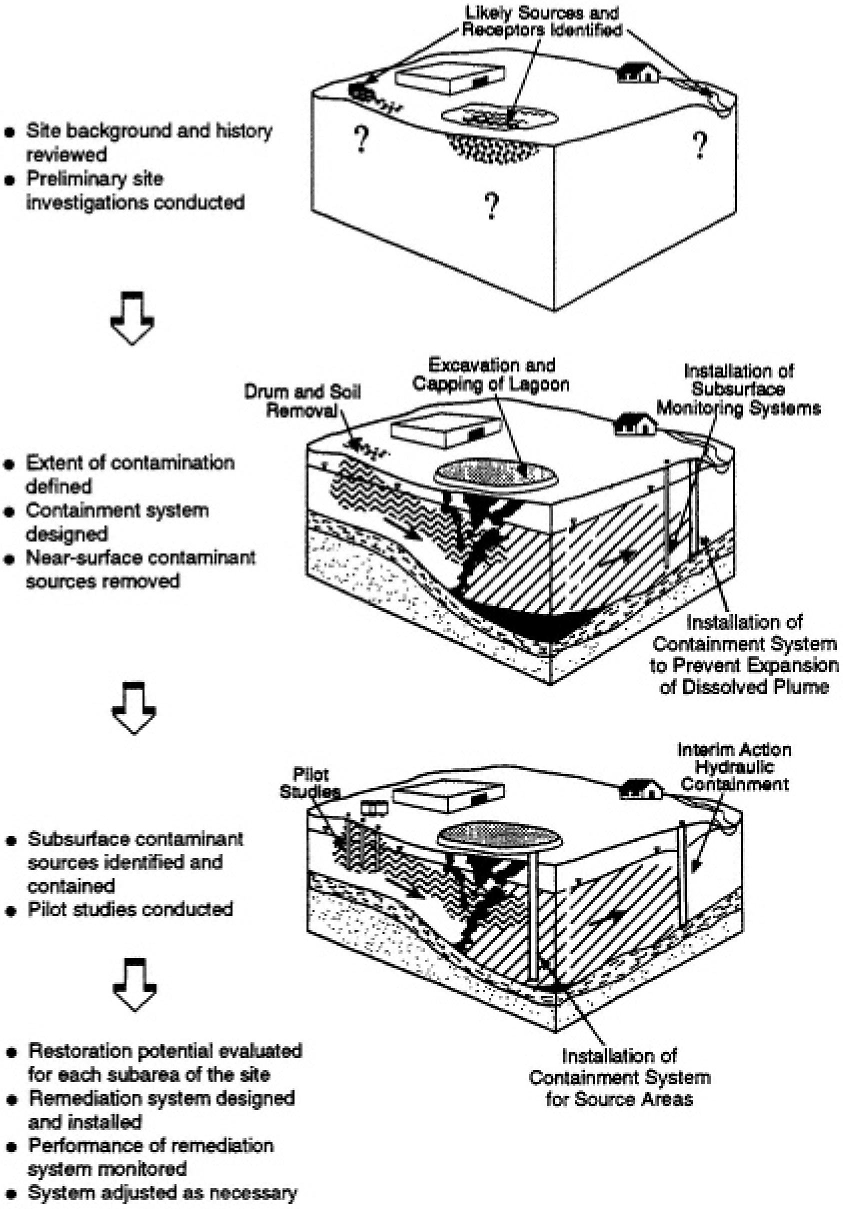


FIGURE 5-4 Iterative stages of site characterization (adapted from EPA, 1993b).

information to design and implement a remedial action to contain and/or remove these sources. In later stages, the investigator evaluates the restoration potential of each subarea of the site and collects sufficient information to design a system that will meet that potential. As the stages of site characterization proceed and as knowledge of the site becomes more complex and complete, the conceptual model may be represented in part by a mathematical model to provide a tool for analyzing remedial alternatives and for planning additional data collection.

Containment systems can generally be designed with the data gathered in the early stages of site investigation. However, in many situations (represented by categories 2 and 3 in Table 3-2) it is difficult, if not impossible, to collect the data required to determine the site's restoration potential in the early stages of investigation. In such situations, the data required for determining restoration potential and for designing a system to meet that potential can best be collected by stressing the system by pumping from contaminated locations and observing the response. The data collected from operating a containment system can provide one such indicator of the ground water system's response to stresses.

Ground water systems are dynamic and complex, and as a result some uncertainty will always remain regarding the performance of a remedial action. The data collection program should not be overdesigned in an attempt to eliminate all uncertainties, as this will be impossible. Rather, remedial designs should be robust, should include monitoring systems to detect failure, and should include contingency plans to make changes in remedial measures if failure occurs. Mistakes are inevitable, and thus it is essential that the remediation plan include a mechanism to detect and correct failure to control the contamination.

RESEARCH NEEDS

Site characterization is often a slow process, in part because of the long time required to conduct a thorough analysis with existing subsurface sampling technologies. Installation of remediation systems in the past has been delayed because of the limits on the ability to collect and analyze site data quickly; where containment systems were not installed, the contamination problem worsened with the passage of time while site characterization proceeded. Remediation efforts have also suffered from the inability of site characterization to accurately predict early on the restoration potential of the site and to quantify and locate subsurface sources of contamination. Research to improve the speed of site characterization and its ability to locate sources of contamination would greatly improve the ability to carry out effective ground water cleanups. At the same time, however, one must realize that even with improvements in site characterization technology, a complete picture of the subsurface will be impossible to obtain, and in many cases operation of a remediation system (whether pilot or full scale) will be the only way to accurately determine the site's restoration potential.

Research to address the following questions would help advance the site characterization process:

- How can the extent of ground water contamination be assessed rapidly?
- How can the location and mass of contaminants present in source areas, especially those with NAPLs, be more accurately quantified?
- How can the characterization process be improved to provide more reliable and timely estimates of the restoration potential of contaminated aquifers?
- What measures—technical and institutional—are needed to ensure the setting of realistic cleanup objectives and the optimal design of a cleanup system based on site characterization data?
- What measures—technical and institutional—are needed to ensure that knowledge about the site gained during the course of remediation will be considered in reassessing cleanup objectives and the design of the treatment system during long-term cleanup projects?

CONCLUSIONS

Based on a review of the processes for characterizing contaminated sites in order to design ground water cleanup systems, the committee reached the following conclusions:

- **The goal of site characterization studies should be the collection of sufficient data to select and design a remedial action**. Site characterization studies need not be designed to develop as complete a picture as possible of the subsurface environment. These types of characterization studies may be appropriate at research sites, but they are not needed at most sites. The subsurface environment is complex, and as a result, the committee has observed that the characterization process often drags out because the main goals of the characterization process are forgotten.
- **Site characterization studies should define early the parts of the site that can be considered source areas and the parts that can be considered dissolved plume areas**. Restoration of dissolved plume areas may be possible at many sites, while restoration of subsurface source areas may not be possible. At the same time, however, the restoration potential of the dissolved plume areas cannot be realized until the source areas are contained.
- **At many sites, operation of prototype systems will be necessary**

to obtain the data required to design and predict performance of full-scale remedies. Because of the complexity of many contaminated sites, predicting how the ground water system will respond to operation of the remediation system may not be possible without observing the effects of a prototype system.

- **Improved methods are needed for assessing the scope and distribution of contamination**. Existing site characterization techniques cannot always accurately locate subsurface sources of contamination and are often costly and slow.

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6

Setting Goals For Ground Water Cleanup

The preceding chapters provide clear evidence that a range of conditions and complexities exist at waste sites where ground water contamination has occurred. While the conventional and innovative technologies described in this report provide approaches for restoring these sites, there are limits to how completely and how quickly existing technologies can remove contamination from ground water.

Historically, the goal of ground water remediation in the United States has been to protect public health and the environment. If the levels of remediation required could be achieved rapidly and at low cost with existing technologies, no conflict would exist between technology's capabilities and society's goals. However, in a number of cases, existing ground water cleanup goals cannot be met with current technologies. In other cases, achieving these goals will require extraordinary amounts of time (decades to centuries) and money (tens of millions of dollars). Thus, a public policy decision must be made about whether the goals of ground water treatment should be changed to reflect what can be achieved today.

The Committee on Ground Water Cleanup Alternatives discussed several questions relating to the goals of ground water cleanup. Should existing goals (which are usually drinking water standards) be changed to be consistent with the highest level of treatment technically achievable today? Should the goals be maintained and the objective kept at meeting the goals, irrespective of technologic capability, time needed, and cost?

Should the goals be made stricter and more consistent with a nondegradation approach in order to restore ground water quality to its fullest? Should the Environmental Protection Agency (EPA), in setting goals, consider other factors such as cost, fairness to all stakeholders, and comparative risks of exposure to contaminants in ground water relative to involuntary and voluntary risks people take in everyday life?

In exploring these questions, the committee defined its role as one of compiling and reviewing information on risks, benefits, costs, and uncertainties that surround the evaluation of these issues, rather than undertaking and contributing original research. The committee's main mission was to consider the degree to which technologies can restore contaminated sites. Nevertheless, technology does not operate in a vacuum: cleanup goals will have a significant impact on the type of remediation technology selected, on the design of the system, and, ultimately, on whether the effort is perceived as a success or a failure. Therefore, any review of the capabilities of ground water cleanup technologies would be incomplete without an assessment of cleanup goals driving the selection of technologies and of factors driving the selection of cleanup goals.

This chapter begins with a review of current U.S. goals for ground water cleanup and a discussion of alternative goals suggested by various interest groups. Next, the chapter discusses the public health and ecological risks that currently drive selection of cleanup goals. It then discusses what is known and not known about the costs of various cleanup options. Finally, it summarizes the committee's assessment of whether changes in ground water cleanup goals are warranted to reflect the limits of technology.

CURRENT CLEANUP GOALS

The two primary federal laws governing ground water cleanup are the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, also known as the Superfund act because of the fund it established to clean up sites) and the Resource Conservation and Recovery Act (RCRA). Most commonly, ground water cleanup goals under CERCLA and RCRA are set at drinking water standards. However, although drinking water standards are the most commonly used cleanup goals, for any one chemical the cleanup goal may vary depending on the state in which the site is located and whether it is a CERCLA or a RCRA site. Table 6-1 shows a sampling of the range of concentrations that have been used as ground water cleanup goals under current policy.

Cleanup Goals Under CERCLA

Technically, CERCLA governs any site where there is a release or threatened release of a hazardous substance. However, the EPA generally uses it to order cleanup of closed or abandoned waste sites. The goal-setting process for cleaning up ground water at CERCLA sites is detailed in an EPA regulation known as the National Contingency Plan. Central to this plan (and to the statute itself) is that ground water cleanup goals should meet chemical-specific "applicable or relevant and appropriate requirements" from other regulations, known as ARARs. Ground water that could be used for drinking must meet federal requirements under the Safe Drinking Water Act (known as maximum contaminant levels, or MCLs; see Table 6-1) or state drinking water standards, whichever are more stringent. In addition to meeting drinking water requirements, ground water that directly discharges to surface water must meet federal requirements under the Clean Water Act or similar state requirements. Furthermore, if states have antidegradation laws that prohibit the contamination of ground water with certain chemicals, these laws also apply (see the third column in Table 6-1). For example, 24 states have established background levels as the goal of ground water remedial actions; for organic chemicals, the background level is usually zero (EPA, 1991a).

If no ARAR exists for a particular chemical, the ground water cleanup goal is based on a site-specific risk assessment. In general, cleanup goals based on risk assessments must result in a risk level of 10^{-4} to 10^{-6} for carcinogens (Table 6-1 shows a few examples of 10^{-4} to 10^{-6} risk levels) and a hazard index of less than 1 for noncarcinogens. A cancer risk of 10^{-4} indicates a 1-in-10,000 (or 0.01 percent) risk of contracting cancer from chronic exposure to a certain substance, while a cancer risk of 10^{-6} indicates a 1-in-1 million (or 0.0001 percent) risk. A hazard index of less than 1 indicates that the level of contamination is less than that known to cause harm. (The hazard index is the ratio of the dose received to the dose known to cause health problems.)

For any one chemical, different cleanup goals are possible under CERCLA. Cleanup goals may be higher than MCLs if the aquifer is not usable for drinking. The EPA defines such unusable aquifers as those that (1) cannot supply drinking water to a well or spring sufficient for the needs of an average family; (2) are saline (containing 10,000 mg/liter or more of total dissolved solids); or (3) are otherwise contaminated from other sources beyond restoration using reasonable techniques (EPA, 1986, 1990b). Cleanup goals may also exceed MCLs if they are based on protecting a surface water body to which the ground water discharges rather than on protecting the ground water. Cleanup goals may be lower than MCLs for individual contaminants if multiple contaminants are present

TABLE 6-1 Comparison of Potential Ground Water Cleanup Levels (parts per billion)

Contaminants	Federal Drinking Water Standards (MCLs)[a]	Representative Range of State Cleanup Standards[b]	RCRA Proposed Corrective Action Level[a]	Representative Examples of 10^{-4} to 10^{-6} Risk Range for Carcinogens or Reference Dose for Noncarcinogens[c]
Arsenic	50	BKG-50	50	0.046-4.6
Benzene	5	BKG-5	—	0.35-35
Benzo[a]pyrene/total polycyclic aromatic hydrocarbons	0.2	BKG-0.2	—	0.011-1.1
Cadmium	5	BKG-5	5	18
Carbon tetrachloride	5	BKG-5	0.3	0.2-20
Chromium VI	100	BKG-100	100	180
DDT	—	BKG-0.1	0.1	0.23-23
Ethylbenzene	700	BKG-700	4,000	1,300
Mercury	2	BKG-2	2	11
Methyl ethyl ketone	—	BKG-460	2,000	1,800
Pentachlorophenol	1	BKG-1	1,000	0.66-66
Phenol	—	BKG-6,000	20,000	22,000
Polychlorinated biphenyls	0.5	BKG-0.5	0.5	0.01-1
Tetrachloroethylene	5	BKG-5	0.7	1.3-130
1,1,1-Trichloroethane	200	BKG-200	3,000	1,300
Trichloroethylene	5	BKG-5	5	1.9-190
Vinyl chloride	2	BKG-2	—	0.023-2.3
Xylenes	10,000	BKG-10,000	70,000	12,000

[a] A "—" indicates that no standard has been established for this contaminant.

[b] BKG indicates the natural background level of the contaminant. This column is based on the summary of state cleanup goals in EPA 1991a, which indicates that goals range from background levels to drinking water standards or risk-based concentrations.

[c] The reference dose for noncarcinogens is the dose below which no adverse health effects are expected as reported in Smith, 1993. The risk ranges shown for carcinogens are from Smith, 1993, which regulators in EPA's Region III use as a risk-based screen for Superfund sites to determine whether further investigation is warranted. Smith's data are based on the assumption that a person drinks 1 liter of water per day from ages 1 to 6 years and 2 liters per day from ages 7 to 30 years.

SOURCES: Smith, 1993; EPA, 1991a.

and the cumulative risk from all of them exceeds 10^{-4} for carcinogens or a hazard index of 1 for noncarcinogens. Cleanup goals may also be lower than MCLs if the state in which the site is located has state-mandated MCLs or cleanup standards lower than the federal MCLs. As an example, between 1982 and 1991 the EPA selected a cleanup goal of 5 μg/liter (the MCL) for the chemical trichloroethylene (TCE) at 99 Superfund sites, lower concentrations at 23 Superfund sites, and higher concentrations at 13 sites; at 32 sites, the goals were based on risk levels in the 10^{-4} to 10^{-6} range.[1]

Although a range of cleanup goals is possible, as a practical matter federal drinking water standards serve as ceilings for ground water cleanup goals at most sites for the contaminants for which MCLs have been developed. Of the approximately 300 ground water remedial actions selected in the Superfund program between October 1, 1987, and September 30, 1991, the cleanup goal was to achieve drinking water standards through pumping and treating at 270 sites (EPA, 1992). At the remaining sites, the most common alternative to drinking water standards was the provision of alternative water supplies.

Cleanup Goals under RCRA

RCRA provides for cradle-to-grave management of hazardous wastes. The EPA uses the statute in part to require ground water and soil cleanup at operating hazardous waste treatment, storage, and disposal facilities and at closed facilities that once operated under the RCRA program. The primary EPA regulation for implementing ground water cleanups under RCRA is known as the Corrective Action Rule (EPA, 1990a).[2] The Corrective Action Rule has not yet been finalized, but the EPA is nevertheless using it to oversee ongoing work. More than two-thirds of the approximately 100 ground water cleanup remedies under the RCRA corrective action program have been finalized in the past two years (M. Hale, EPA, personal communication, 1994). There is therefore little basis upon which to evaluate the application of cleanup goals under this program.

Unlike cleanups governed by CERCLA, cleanups under the RCRA corrective action program have no requirement to meet ARARs from other laws. Nevertheless, the EPA intends that RCRA and CERCLA should establish a consistent approach for ground water cleanup. This internal consistency requirement is a key component of the EPA's long-term ground water strategy (EPA, 1991e). In keeping with the ground water strategy and with the proposed RCRA regulations, the agency anticipates that CERCLA and RCRA will arrive at similar solutions to similar environmental problems and that actions undertaken by one program will be adopted by the other program in cases where the programmatic responsibility for a site shifts from one to the other. Therefore, under RCRA the EPA generally sets cleanup levels at MCLs, even though the proposed corrective action regulations do not require that cleanup goals correspond to ARARs.

Exceptions to Goals Based on Drinking Water Standards

Although ground water cleanups under CERCLA and RCRA usually require attainment of drinking water standards, the laws have provisions for allowing waivers to these standards even for potential drinking water sources. Both statutes attempt to balance the desirability of meeting health-based cleanup standards wherever possible with the constraints posed by technologic capability and cost. The basis for dealing with these practical considerations differs for the two statutes.

Under CERCLA, the EPA may waive health-based cleanup requirements where achieving them is "technically impracticable from an engineering perspective." However, the EPA has been criticized for making minimum use of CERCLA's statutory waiver provisions. Of the 945 sites for which cleanup remedies were selected between 1982 and 1991, only 13 included technical impracticability waivers.[3]

Because RCRA cleanups need not meet ARARs, the RCRA program is generally more flexible than the CERCLA program in allowing cleanup goals other than MCLs. Under RCRA, those responsible for the cleanup may apply for an "alternate concentration limit" (ACL) in place of drinking water standards as the cleanup goal. The ACL is based on a site-specific risk assessment. The key factor that the EPA considers in granting an ACL is whether it will protect public health at the point of exposure, i.e., whether contaminant concentrations will be reduced to ensure adequate public health protection at the nearest drinking water well.

The EPA is increasingly recognizing that attaining drinking water standards is not feasible at certain types of sites and has drafted a guidance document to clarify the policy regarding technical impracticability of ground water cleanup at CERCLA and RCRA sites (EPA, 1993b). The guidance document, discussed in more detail in the next chapter, describes the types of data necessary to demonstrate that the original cleanup goals for a site should be waived because of technical limitations.

ALTERNATIVE CLEANUP GOALS

Whether the nation's current emphasis on restoring contaminated ground water to drinking water standards is appropriate is a matter of debate. On one hand, achieving MCLs may be impossible at many sites and may be extremely costly even when possible. On the other hand, even when strict cleanup goals are not technically achievable, their existence may provide an incentive against further pollution and may encourage development of cleanup technologies that better protect public health. In the debate over whether strict ground water cleanup goals are appropriate, given the limitations of technology and the high costs, various interest groups have advocated goals ranging from complete restoration to restricting use of the ground water, as shown on Figure 6-1 and explained below.

Unrestricted Use Goals

At the left end of the spectrum of possible goals in Figure 6-1 is cleanup to allow unrestricted use of the ground water. Many states have identified unrestricted use as the most beneficial use of ground water. Three possible cleanup goals that allow unrestricted use are (1) complete cleanup (i.e., cleanup to concentrations that may sometimes be below natural background levels), (2) cleanup to background levels measurable in uncontaminated areas (or to the detection limit for the contaminant), and (3) cleanup to health-based levels.

Complete Cleanup

Some groups have advocated complete cleanup—meaning removing the contaminants to zero concentration levels—as a ground water cleanup goal in order to keep the environment "pure" for ethical or moral reasons, to provide the private sector with a continuing incentive to exercise care in handling hazardous wastes, and to ensure that the most thorough cleanup possible occurs. However, the attainment of *zero* contaminant concentrations as an outcome for ground water remediation should be recognized as an unattainable goal no matter how far cleanup technologies advance in the future. Even pristine waters contain certain inorganic chemicals regarded as contaminants. In addition, it is impossible to prove zero concentrations, given limitations in analytical detection ability. Although the Safe Drinking Water Act established zero as the ultimate goal for carcinogens, the enforceable levels under the act are nonzero MCLs based on the capabilities of drinking water treatment technologies and the detection limits for the contaminants; the nonzero MCLs, rather than the ultimate goal of zero, serve as cleanup goals under Superfund and RCRA.

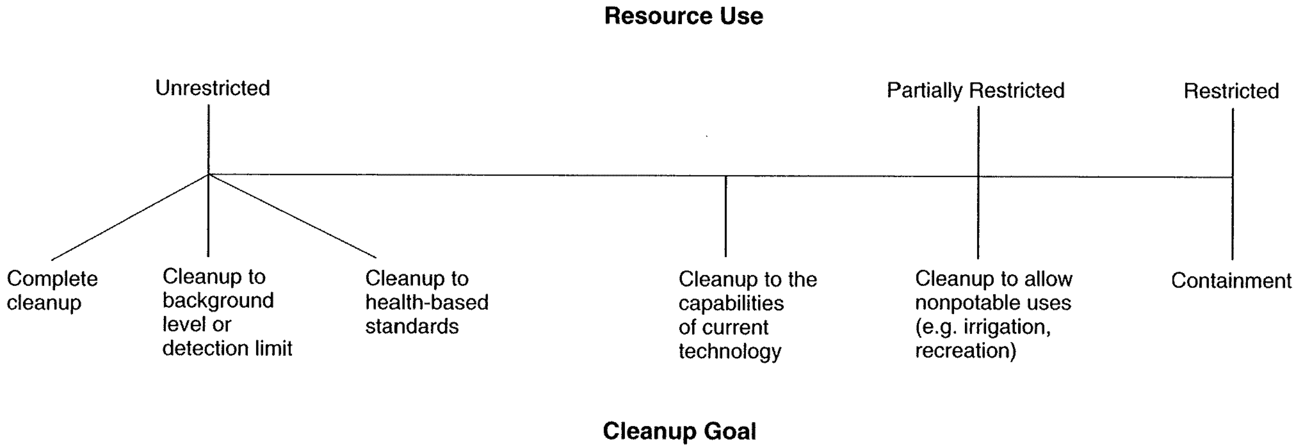

FIGURE 6-1 The range of possible ground water cleanup goals.

Cleanup to Background/Detection Limits

As a more feasible alternative to zero contaminant levels, some have advocated the use of background concentrations or analytical detection limits as ground water cleanup goals. For example, 24 states use detection limits or background levels as the only acceptable cleanup goal (EPA, 1991a). Cleanup to background levels may be selected in cases where there is a naturally occurring background concentration of a contaminant; otherwise, analytical detection limits serve as cleanup goals. One benefit of using detection limits or background levels as cleanup goals is the elimination of the need for government agencies to define explicitly an "acceptable" risk level. Rather, using detection limits or background levels implies that cleanup is accomplished to the fullest extent measurable with today's technologies. A drawback is the high cost that can be associated with such cleanups; it is possible that such goals will achieve only a small additional benefit—at substantially higher cost—compared with cleanup to specific health-based goals. Another drawback is that detection limits change over time as analytical capabilities improve, meaning that cleanup standards will become outdated as technology advances.

Cleanup to Health-Based Levels

As discussed above, cleanup to health-based standards is the most common type of goal used today. There are two possible mechanisms for setting health-based goals: (1) using predetermined standards, such as drinking water standards and the other ARARs used at Superfund sites, and (2) using risk assessments at each site.

The advantages of using predetermined standards versus using site-specific risk assessments include speed and ease of implementation, consistency in the treatment of similar sites, usefulness for initial screening of contamination to determine its significance, elimination of incentives for industry to locate in the most environmentally lenient states, and avoidance of a need for technical expertise on the part of regulators in order to address toxicological and risk assessment issues on a case-by-case basis (Siegrist, 1989). The use of predetermined standards, if established based on "worst-case" assumptions, will also ensure adequate margins of safety for all sites. However, using predetermined standards also has important drawbacks. The most significant drawback is the inability to account for site-specific exposure patterns, which may result in higher expenditures than are necessary to protect public health at a particular site.

In lieu of using previously established standards as health-based goals, formal risk assessments may be used to develop site-specific goals, as is done in some cases under the Superfund and RCRA corrective action programs. The site-specific approach allows flexibility in considering site conditions. It also ensures that the level of risk, which is based on exposure patterns as well as contaminant levels, will be the same at different sites. (When uniform cleanup standards are used, the level of risk may vary from site to site because of different exposure patterns, even if the contaminant concentrations are the same.) One major disadvantage of this approach is that it is time consuming and costly to implement. The site-specific approach requires that regulatory agencies have a technically trained staff large enough to evaluate individually the risk data for each site. Another major disadvantage is that by changing key exposure assumptions, the results can be easily manipulated.

It is important to realize that ground water remediation to assure a "safe" drinking water supply may not result in full restoration, because levels of contaminants may remain at concentrations greater than background levels. Further, contaminant levels designed to protect human health may not protect ecological receptors. Separate risk-based goals may be needed for ecosystem protection.

Partially Restricted Use Goals

Some who believe that the current ground water cleanup program is too costly have advocated using partially restricted use goals, shown in the middle of Figure 6-1. Under this scenario, cleanup goals would correspond to the expected use of the water. In some cases such goals are already used, such as when the goals are based on protecting a surface water body used for boating and fishing but not for drinking. Like health-based goals, partially restricted use goals can be based on predetermined standards, such as water quality criteria, or on site-specific risk assessments. The major drawback of such goals is that they may require institutional controls, such as well restrictions or fish advisories, to prevent excessive human exposure to the contamination. Some have expressed concern about whether it is possible to design policies and institutions capable of perpetually limiting people's use of contaminated water.

Technology-Based Goals

Many major environmental statutes applicable to media other than ground water use a technology-based approach to setting cleanup goals. For example, under the Clean Water Act municipal wastewater treatment plants are required to treat their effluent to a level achievable by what are known as "secondary treatment" systems (unless more strin gent treatment is necessary because of local water quality considerations). Technology-based goals, shown in the middle of Figure 6-1, specify a remedial action to be taken rather than a concentration to be reached. The protectiveness of technology-based goals relative to health-based goals varies because the use of technology-based goals may result in risks that are greater than or smaller than those associated with health-based goals. For example, the best available technology may be unable to achieve concentrations based on health risk or may achieve concentrations below those necessary for public health protection.

Among the various cleanup options, technology-based goals are the only goals that fully account for the capabilities and limitations of technology that this report has emphasized. The technology-based approach avoids raising false expectations about what level of cleanup is possible. On the other hand, some contend that this approach eliminates the incentive to develop technologies capable of reaching health-based goals. Another drawback is that the approach, if too rigidly applied, may overlook important site-specific factors that could affect both implementation risks of that technology (for example, air pollution risks associated with incinerating soils) and the ability of the technology to actually achieve the desired remediation at a particular site.

Restricted Use: Degradation with Containment

Many critics of the current approach to ground water remediation have suggested establishment of areas in which ground water is permitted to remain degraded, as long as measures are taken to contain the contamination or to prevent public exposure by other means. Restricted use goals are the least costly approach to managing contaminated ground water. Such goals also account for the fact that in some cases containment may be the only technologically feasible option, as discussed in Chapter 3.

The major drawback of restricted use goals, like partially restricted use goals, is the requirement for measures to ensure that the public is not exposed to contaminated water. Restricting ground water use is especially problematic when the contaminated water serves as a drinking water supply, which is the case at a significant number of sites. Data indicate that at nearly one-third of Superfund sites, existing private, community, and public drinking water supply wells have been closed or restricted because of contamination (Wells, 1992). Three options are possible to prevent exposure in these situations: wellhead treatment, point-of-use treatment, and development of alternative water supplies (see Box 6-1 and Box 6-2). Each of these options has limitations, and whether any one of them will be possible or appropriate depends on site-specific considerations such as the availability and size of a municipal water supply system, the number of residents affected, and the proximity to alternative water sources.

BOX 6-1 OPTIONS FOR SUPPLYING DRINKING WATER WHEN GROUND WATER CONTAMINATION REMAINS IN PLACE

- ***Wellhead Treatment*** Wellhead treatment involves upgrading the local drinking water treatment plant to remove contaminants from the water before it is distributed for drinking. Once contaminated water is pumped to the surface, treatment and removal of the contaminants prior to the water's distribution is generally possible. However, many water utilities in areas threatened by ground water contamination lack the specialized systems necessary to remove hazardous chemicals and would require an upgrade at substantial expense.
- ***Point-of-Use Treatment*** When citizens whose drinking water has been contaminated are served by private wells rather than by public utilities, installation of special treatment units in individual homes is necessary. An example of this approach is in Elkhart, Indiana (see Box 6-2), where in-home granular activated carbon units and in some cases air strippers are being used for private wells contaminated with a variety of industrial solvents (Lykins et al., 1992). Using home treatment units where health-based ground water cleanup goals cannot be reached has two problems: maintenance requirements and high cost when many homes are affected. For example, in the Elkhart case frequent replacement of the carbon filters was necessary to maintain water quality (see Box 6-2). In addition, city officials decided that installing new water mains would ultimately be less costly than installing 800 individual home units.
- ***Development of Alternative Water Supplies*****:** In the simplest cases, alternative water can be obtained from an existing public water supply through expansion of the existing water delivery system, as in the Elkhart, Indiana, case described in Box 6-2. However, where there is no readily available existing alternative supply of adequate capacity, alternative water sources must be developed. Important obstades may limit this option. In some cases no readily available alternative supply exists. More commonly, alternative water sources exist but are of poor quality due to factors such as high salinity or high levels of dissolved solids. Finally, in some areas of the country, especially in the arid West, alternative water sources may already be allocated for someone else's use.

Comparing the Alternatives

If the capability of technology were the most important factor to consider in establishing ground water cleanup goals, then society might easily agree on a technology-based approach to remediation. Unfortunately, the decision is not so simple. The selection of ground water cleanup goals from among the variety of options discussed above is a political process involving debates about several factors, summarized in Table 6-2.

BOX 6-2 POINT-OF-USE TREATMENT FOR TCE CONTAMINATION—ELKHART, INDIANA

In 1984, a private citizen on the eastern side of Elkhart, Indiana, had his well water tested and learned that the water contained more than 200 µg/liter of the solvent TCE. Use of TCE and other chlorinated solvents is widespread in the town's industries, which include manufacturers of pharmaceuticals, recreational vehicles, and plastics. The citizen notified the county health department, which then notified the EPA, and the EPA and health department proceeded with an extensive sampling program on the eastern side of town.

The samples revealed that 80 wells had TCE levels above 200 µg/liter, with 15 of the wells exceeding 1,500 µg/liter and one sample containing 19,380 µg/liter. Investigators also found dichloroethylene, perchloroethylene, trichloroethane, and carbon tetrachloride. TCE at the levels found in the wells constitutes an immediate health threat from consumption, dermal absorption, and vapor inhalation. Therefore, the EPA and county health department temporarily placed 800 residents on bottled water.

In deciding on a long-term solution to the well water contamination, the county government decided that connecting most of the affected homes to the municipal water system would be more cost effective than maintaining in-home treatment units. The county connected 301 homes and 7 businesses on the east side of town to the municipal system, 11 homes that were not adjacent to the water main and where the contamination was relatively minor were given point-of-use treatment units. However, this was not the end of the town's TCE contamination problem.

In 1986, a private citizen, this time on the west side of town, found 800 µg/liter of TCE and 488 µg/liter of carbon tetrachloride in his water supply. The EPA tested 88 wells on the west side of town and found carbon tetrachloride at concentrations up to 6,860 µg/liter and TCE at concentrations up to 4,870 µg/liter. The EPA decided to install in-home activated carbon filters in 76 homes.

EPA tests revealed that the standard design calculations for these filters were unreliable for predicting filter life. Filters generally lasted half as long as expected (treating 490,000 liters instead of 850,000 liters) before contaminant breakthrough occurred. Researchers attributed the early breakthrough to competitive adsorption from multiple contaminants, bacterial colonization, and high influent levels. If the home treatment systems had not been carefully monitored by the EPA and the filters had been replaced according to the manufacturer's instructions, the homeowners would have incurred a significant health risk from contaminant exposure after the filters had exceeded their capacity.

SOURCE: Lykins et al., 1992.

Most of these factors have received far more consideration in policy debates than the capabilities of technology. Of the factors shown in Table 6-2, health risks and costs have received the most attention. Increasingly, policymakers are also recognizing the ecological risks of contamination as an important consideration. The following discussions focus on health and ecological risks of ground water contamination and the costs and benefits of cleanup because these factors are at the center of national policy debates over cleanup goals. The chapter then addresses the question of whether current ground water cleanup goals should change, given the committee's conclusions about the capabilities of technology and the available evidence on health risks, ecological risks, and cleanup costs.

TABLE 6-2 Site-Specific Factors Raised in Debates About Ground Water Cleanup Goals

Factor	Questions Raised
Public health risk	What levels of contamination create a public health risk?
Ecological risk	What levels of contamination cause damage to ecosystems?
Cost versus benefit	Will the benefits of cleaning up the contamination equal or exceed the costs?
Capabilities of technology	Are existing technologies capable of reaching the cleanup goal?
Time to reach the goal	How long will it take to reach the cleanup goal?
Risks associated with the cleanup technologies	Does implementation of cleanup using these technologies pose risks, such as breathing of contaminant vapors or construction accidents?
Impact on community	What will be the magnitude and duration of the visual disruption, noise, and traffic generated by constructing a remediation system?
Fairness to all stakeholders	Is the goal fair to all stakeholders, including nearby residents, responsible parties, regulators, and future generations?

HEALTH RISKS OF CONTAMINATED GROUND WATER

Incidents such as that at Love Canal, in which homeowners were evacuated because the ground water and soil in their neighborhood were contaminated with hazardous wastes, have caused widespread public concern that subsurface contamination from hazardous waste sites poses serious risks to human health. Yet, determining the precise level of risk these sites pose—and what level of concern is warranted—is a task that is complicated by a high degree of uncertainty. Two general sources provide information on the potential for health effects from contaminated ground water: epidemiologic studies and animal studies. The evidence from each of these sources is uncertain and has been interpreted differently by different interest groups.

Evidence from Epidemiologic Studies

Epidemiologic studies determine health effects by examining specific populations exposed to the contaminants. These populations may be either occupational groups exposed through the workplace or residents near contaminated sites. Studies of people living near contaminated sites are the more relevant approach because occupational groups are usually exposed at higher levels and through different pathways than populations exposed through contaminated ground water. However, there are serious limitations to undertaking epidemiologic studies at hazardous waste sites, undermining their ability to answer questions about health hazards.

Limitations of Epidemiologic Studies

The most important limitations of epidemiologic studies are the following:

- *Uncertain exposure*: Without question, the single most perplexing problem in developing human health data related to hazardous waste sites is the assessment of exposure experienced by the study population. In many epidemiologic studies, individual exposures to contaminants are unknown, limiting the ability to establish linkages between exposure and disease. Direct evidence of exposure, such as residues in human tissues or fluids, is seldom available. Exposure is most often estimated from surrogate data such as place of residence; answers to questionnaires; employment records; and results of air, water, and soil monitoring. Exposure of individuals may vary greatly within the geographic areas studied, resulting in the misclassification of exposure status of individuals. The magnitude of exposure may also change over time, and determining past exposures may be difficult. Variation in exposure within a geographic area is an especially perplexing problem when ground water contamination is involved because populations quite distant from the waste site may be exposed if the water is distributed through a municipal supply system, resulting in a much larger exposed population than investigators would presume based on residential patterns near the site.
- *Latency*: Frequently, the interval between exposure to a toxic chemical and the appearance of cancer or other chronic diseases is measured in decades. In the real world, however, epidemiologic studies frequently need to be undertaken before this latency period has elapsed. The likelihood of epidemiologic studies detecting adverse health effects is thus reduced.
- *Small size of study population:* The populations studied in epidemi

ologic investigations of hazardous waste sites are usually small, a situation that may result in risks going unobserved because the statistical power of the study is too low. While studying large populations would be preferable, communities surrounding waste sites are usually small. Loss of members of the population in the course of follow-up investigations adds to the difficulty of maintaining a large enough study population.

Example of a containment suit worn by cleanup crews at hazardous waste sites. Courtesy of U.S. Environmental Protection Agency, R. S. Kerr Environmental Research Laboratory.

- *Inadequate control over comparison groups:* To establish the baseline disease rate in the absence of contaminant exposure, an unexposed, or "reference," population is necessary. However, it is difficult or impossible to be certain that the reference groups are not exposed to the chemicals under scrutiny unless direct exposure data are available for both the exposed and unexposed groups. When reference groups have also been exposed to the contaminants, excess occurrences of disease in the population under study may be impossible to detect.
- *Uncertain health effects of the contaminant*: Epidemiologic studies

benefit from information about contaminant toxicity that can direct investigators toward specific types of toxic effects. Unfortunately, few measurable health effects are sufficiently specific to particular chemicals to allow establishment of a direct link between exposure and disease. In addition, toxicity data for many contaminants are limited, especially when these contaminants are not end products of a familiar commercial process but rather are residual, intermediate, or precursor substances from the process.

- *Presence of contaminant mixtures:* Even less is understood about the toxic effects of complex mixtures of chemicals than about individual chemicals. Exposure to multiple contaminants is the rule rather than the exception at hazardous waste sites. Simultaneous exposure to many chemicals substantially complicates the determination of causality.
- *Confounding factors and sources of bias:* The results of epidemiologic studies may be confounded by factors other than contaminant exposure that are themselves associated with the disease under study. For example, some hazardous waste sites may be located in industrialized and highly polluted areas. Individuals in the surrounding area may have been exposed to chemical pollutants while working for companies that created the waste, or they may have been exposed to air pollution from industrial or vehicular sources. In cases where waste sites are located in economically depressed areas, poor diet and absence of prenatal or other preventive medical care may also affect the study's outcome. In addition, population characteristics other than contaminant exposure that are linked with increased disease risks (for example, smoking) must be taken into account. Increased or differential recall of past health problems by residents near the site may also bias results of studies based on self-reported symptoms. For example, because they are concerned about possible exposure, residents near a site may be more likely to recall and report past problems than residents living in areas farther from the site. Conversely, residents near waste sites may be unwilling to disclose information about some types of medical problems, such as miscarriages.

Results from Existing Epidemiologic Studies

Isolated epidemiologic studies have provided positive links between exposure to ground water contaminants and certain diseases. One of the most notable studies was conducted in Hardeman County, Tennessee (Clark et al., 1982; Meyer, 1983; Harris et al., 1984). At this site, a chemical company buried pesticide production waste in unlined shallow trenches between 1964 and 1972. The location is rural, but many people built homes around the site in anticipation that the company would build a facility. By 1977, local residents were complaining of bad taste and odor in their well water, which originated from ground water that extended under the area where the disposal trenches were located. The water from private wells was highly contaminated with chemicals known to cause liver damage and liver cancer in both animals and humans. A health survey was conducted in 1977 to determine if liver dysfunction was present in exposed populations. Epidemiologists found a dose-response relationship between measured levels of chemicals in the household water and an increase in liver function enzymes, a biochemical method for quantifying the effect of exposure. In addition, there was a significant difference in the presence of an enlarged liver between the exposed and unexposed controls, based on a clinical examination performed by a physician.

The Hardeman County study is important from an epidemiologic perspective for two reasons. First, direct measurements were taken to determine exposure to chemicals in individual households. This enabled determination of which families were heavily exposed and which were less severely exposed. Second, the chemical compounds detected are specifically related to the outcomes found. For example, carbon tetra-chloride is known to cause enlargement of the liver and elevated enzyme levels in humans.

Unfortunately, the ability to conduct conclusive epidemiologic studies at hazardous waste sites such as that in Hardeman County is extremely rare. As a result, when one analyzes the existing body of epidemiologic evidence as a whole, the public health implications of ground water contamination from hazardous waste sites are unclear. Many researchers have reviewed the evidence from existing epidemiologic studies and have provided cautiously worded, but nevertheless inconsistent, conclusions regarding the magnitude of human health risk associated with hazardous waste sites. Grisham (1986) reviewed 29 studies and concluded that "none of the investigations surveyed has provided sufficient evidence to support the hypothesis that a causal link exists between exposure to chemicals at a disposal site and latent or delayed adverse health effects in the general populace." Marsh and Caplan (1987) reviewed studies of 15 hazardous waste sites and concluded that "the exposure-health outcome linkages that were examined are, for the most part, weak or inconclusive." In both of these reviews the majority of community health studies revealed no adverse effects attributable to waste chemical exposure; the reviewers regarded the minority of studies that did report exposure-disease associations as inconclusive because the studies failed to meet the scientific standards of research in epidemiology. Likewise, in a review of 16 published studies of 8 hazardous waste sites, Upton et al. (1989) concluded that "[o]f the studies published thus far, few have been sufficiently well designed and well conducted to yield meaningful re-suits."

A more recent review of health effects associated with hazardous waste sites by the National Research Council (1991) evaluated 22 published studies from 14 waste sites and concluded that the available epidemiologic literature on this subject is "scanty and not conclusive." Nevertheless, this report concluded that drinking water contaminated with certain chemicals is injurious to human health but that the magnitude of the risk is uncertain. As evidence, the report points to studies showing that trihalomethanes in surface drinking water are associated with an increased risk of bladder and other cancers (Cantor et al., 1987) and to a limited number of studies linking spontaneous abortion (Swan et al., 1989), low birth weight (Vianna and Polan, 1984), and birth defects to drinking water contamination.

Recent congressional testimony by the Agency for Toxic Substances and Disease Registry (ATSDR) describes studies by both the ATSDR and other researchers suggesting that reproductive problems may be associated with drinking contaminated water or living near hazardous waste sites (Johnson, 1993). Additional epidemiologic studies are under way to clarify these associations.

Evidence from Animal Studies

Regulators often lack sufficient data from epidemiologic studies of humans to determine the adverse consequences of ground water contamination. Therefore, in determining the human health risks of ground water contamination, regulators often must rely on animal studies. Animal studies provide estimates of the long-term human health effects of environmental contaminants based on the response of animals, usually rats and mice, to large doses of the contaminant over relatively short time periods (although the time period is long relative to the animal's life span). The use of animal studies is essential to a preventive approach to protecting public health because it avoids the ethically and medically unacceptable prospect of waiting for diseases to develop in human populations before taking action to protect public health.

Although essential in evaluating the health risks of exposure to ground water contamination, animal bioassays have several shortcomings. First, these studies must extrapolate effects observed in animals that are administered large doses of the contaminant to humans who will most likely receive much smaller doses. Second, different species may metabolize chemicals in different ways and therefore may be affected differently by chemical exposure. For example, a recent experimental study of the toxicity of mixtures of 25 ground water contaminants to rats and mice revealed health complications in the rats at sufficiently high exposure levels but no effects in the mice (National Toxicology Program, 1992). Third, most animal studies to date have focused on single contaminants rather than on the mixtures most likely to be found at waste sites.

Because of such limitations, some scientists question whether health risks predicated on studies involving animals accurately reflect the likely magnitude and type of health impact on humans (Kimbrough, 1990). Nevertheless, those responsible for assessing the risks of ground water or other environmental contamination must often rely on experimental animal data. Although observations in humans are more relevant for predictions of risk in human populations, toxicologic data from animal studies are essential in quantitative risk assessment in circumstances where direct human information is not available which is the situation at the majority of hazardous waste sites.

Evaluating the Evidence: Risk Assessment

Epidemiologic and animal studies provide information about the types of health problems that *may* occur from exposure to hazardous chemicals, but they may be insufficient to determine the likelihood that health problems *will* occur in a given exposed population. To determine this likelihood, environmental regulators use a process known as risk assessment.

Many human activities, such as driving a car, carry some degree of risk. Many risks are known with a high degree of accuracy because data have been collected on their historical occurrence. For example, the risk of death in motor vehicle accidents in a given year can be determined from roadway data. However, the risks associated with activities that do not cause immediately observable forms of injury or disease cannot be as easily quantified. Exposure to hazardous chemicals in ground water is one area where determining the degree of risk is an uncertain process.

In assessing risks from activities such as chemical exposure, the National Research Council in 1983 defined four basic steps in the risk assessment process, as follows:

- *Hazard identification* involves reviewing and critically evaluating data relevant to the toxicological properties of a substance and identifying the types of effects associated with exposure to the substance. For contaminated ground water, this step answers the question, "What types of health problems does chronic exposure to the contaminant cause?"
- *Dose-response evaluation* involves determining the relationship between the magnitude of exposure and the probability that the adverse effects will occur. For contaminated ground water, this step answers the

question, "How is the probability of contracting health problems affected by a change in the dose of contamination received from ground water?"

Monitoring total hydrocarbons in the air for worker protection at a contaminated site. A network of pumping wells is visible in the background. Courtesy of the Johns Hopkins University, Department of Geography and Environmental Engineering.

- *Exposure evaluation* involves identifying human populations that may be exposed to the substance and determining the potential magnitude and duration of the exposure. For contaminated ground water, this step answers the questions, "Who was exposed to the contaminants in the water, how frequently were they or might they be exposed, and for how long?"
- *Risk characterization* involves integrating information on hazard, dose-response, and exposure to develop quantitative estimates of risk and of the uncertainties associated with the risk estimate. For contaminated ground water, this step answers the question, "What is the increased risk of health problems in a given population from exposure to the contaminants in the ground water?"

Table 6-3 shows the connection between the above four steps of the risk assessment process and information from epidemiologic research, animal studies, and field measurements.

Risk assessments of ground water contamination have several limitations. As discussed above, they often rely on hazard and dose-response information obtained from studies in experimental animals, which is then extrapolated to human populations. The general lack of information on human exposures to chemicals is another limitation. In addition, risk may vary with age at exposure. For example, the National Research Council (1993) recently concluded that infants and children have markedly different risks from exposure to pesticide residues than do adults. Despite these limitations, risk assessment has formed the methodological basis for much public policy related to the regulation of ground water contamination (and other environmental problems) in the United States. For example, as discussed in this chapter, for chemicals for which no drinking water standard exists, cleanup goals at Superfund sites are based on a site-specific risk assessment.

TABLE 6-3 Major Elements of Risk Assessment

Research Phase	Risk Assessment Phase
Observations from epidemiologic and toxicologic studies	**Hazard Identification:** What types of health problems does chronic exposure to the contaminant cause?
Information on methods for extrapolating from high to low contaminant dose, small to large animals, and animals to humans	**Dose-Response Assessment:** How is the probability of contracting health problems affected by a change in the dose of contamination received from ground water?
Field measurements of contaminant transport and estimated human exposures; characterization of exposed populations	**Exposure Assessment:** Who was exposed to the contaminants in the ground water, how frequently were they or might they be exposed, and for how long?
	Risk Characterization: What is the increased risk of health problems in a given population from exposure to the contaminants in the ground water?

Ideally, the characterization of risk (risk assessment) is separate from the subsequent process of deciding whether risks are sufficiently high to justify regulatory action and, if so, the types of action necessary (risk management). Risk management decisions are reached not solely on the basis of risk assessment but also on the basis of relevant statutory requirements, policy precedents, and societal values. For example, the decision that a 10^{-4} to 10^{-6} risk level is acceptable at Superfund sites is specified in the National Contingency Plan. Some argue that separation of risk assessment from risk management is difficult to achieve in prac tice and that the increasing complexity of the advancing science of risk assessment has lowered public confidence in risk assessment (Silbergeld, 1993). Nevertheless, risk assessment remains an important tool in the regulatory process. In fact, the EPA is exploring the concept of "comparative risk assessment"—in which environmental problems would be ranked according to their relative risk—as a method for helping to establish environmental cleanup priorities (EPA, 1987; Science Advisory Board, 1990).

Uncertainty in the Evidence of Health Risks

In sum, existing evidence is insufficient to provide clear conclusions about the level of health risk posed by ground water and soil contamination from hazardous waste sites. Nevertheless, the absence of documentation of health risks cannot be used as proof that exposure and adverse health effects have not occurred. Given the scientific uncertainties associated with epidemiology and risk assessment, public policymakers should err on the side of caution in setting ground water cleanup goals.

ECOLOGICAL RISKS OF GROUND WATER CONTAMINATION

Until recently, ground water contamination was widely viewed as primarily a public health threat rather than a threat to ecosystems. Nevertheless, in recent years more attention has focused on this issue as regulators and the public have realized that ground water contamination can alter ecosystems in important ways. For example, at the Munisport landfill in Florida, the EPA required a $6.2 million remedial action because of a significant threat to aquatic organisms in an adjacent state mangrove preserve (EPA, 1990c). Because of salt water intrusion, the local ground water was not suitable for drinking; therefore, the cleanup goal was based on ecosystem protection rather than on human health protection.

Ground water contamination can damage three types of ecological receptors: organisms living in ground water and in the zones where streams connect with ground water; terrestrial plants that take up contaminated ground water through their roots; and organisms in surface waters that receive ground water discharges.

Impacts on Organisms in Ground Water

Ground water can support a diverse microbial community that functions as a biological filter for certain organic materials. Contaminated ground water can adversely affect natural microbial communities by making the environment anaerobic and/or by direct chemical toxicity to the microbes. Studies of microbial adaptation and in situ biodegradation of contaminants in ground water are the primary sources of information on such effects (Madsen et al., 1991). There is also evidence that ground water contamination can damage the ecology of the hyporheic zone—the subsurface location near streams where the ground water and surface water are hydrologically connected. Hyporheic zones, which can extend as deep as 10 meters and as wide as several kilometers from the stream channel, in some locations serve as a refuge for important aquatic species of bacteria and benthos during drought or stress and consequently play an important role in the recovery of stressed systems (J. Stanford, University of Montana, personal communication, 1992).

Contamination may also affect organisms in limestone karst or conduit systems, such as areas of underground sinks, caverns, and streams that can be inhabited by fish, amphibians, and invertebrates (such as the cave crayfish). While these ecosystems represent only a fraction of a percent of the ground water in the United States, they are nonetheless important. Karst systems concentrate ground water flows and are therefore very important in influencing migration of ground water contamination.

Impacts on Terrestrial Plants

Contaminated ground water has been an issue of concern for some time in arid regions such as southern California, where ground water is used for crop irrigation. Highly saline and otherwise degraded sources of ground water can damage crops. There are also limited examples of phytotoxicity from ground water sources outside the context of irrigation. For example, researchers have reported that contaminated ground water has affected tree growth downslope from seepage basins at the Department of Energy's Savannah River site (LeBlanc and Loehle, 1990; Greenwood et al., 1990). At this site, trees in wetlands along Four Mile Creek began to show localized stress and mortality in the late 1970s. The researchers concluded that alteration of soil acidity and of soil aluminum, sodium, and heavy metal concentrations caused by ground water contamination likely predisposed trees to deteriorate, with severe drought acting as the final trigger for deterioration and tree death. In another example, involving a wetland, researchers observed direct and severe ecological effects as a result of ground water contamination with a highly alkaline leachate from an on-site lagoon at a Massachusetts hazardous waste facility. Impacts included decreased species diversity and productivity, stunted growth, and altered life cycles of the wetland vegetation downgradient of the lagoon (EPA, 1989).

Impacts on Organisms in Surface Water

Contaminated ground water can discharge into surface water and can be a significant source of contaminant loading (EPA, 1991c). For example, the EPA and the New York State Department of Environmental Conservation estimated that in the late 1980s as much as 315 kg per day of toxic chemicals were migrating or had the potential to migrate into the Niagara River from ground water on the U.S. side and that 30 kg per day were migrating from the Canadian side (EPA and New York State Department of Environmental Conservation, 1993). In 1987, Canada and the United States signed an agreement to reduce these loadings, with the United States committing to cut its contribution to 4 kg per day by 1996 (EPA and New York State Department of Environmental Conservation, 1993).

Field reports have indicated that contaminants discharging from ground water can cause significant ecological damage to surface water. One example is the 64-ha South Macomb Disposal Superfund site in Michigan, which contains two inactive municipal landfills (EPA, 1991f). A small stream, the McBride Drain, runs along the western and southern boundaries of the site. Landfill leachate contaminated the ground water with benzene, toluene, phenols, arsenic, and chromium. Fish kills reported in the stream were attributed to landfill leachate seeping into the stream via ground water transport.

Probably the most comprehensive review of the ecological impacts of ground water contamination on surface water ecosystems is an EPA analysis of the nature and extent of ecological risks at Superfund sites (EPA, 1989). Of 52 Superfund sites evaluated, 30 (including 14 landfills and 16 surface impoundment lagoons) had seepage to ground water that discharged to surface water (EPA, 1989). Using a combination of laboratory tests of samples collected at the sites, in situ field tests, and correlations between chemical and biological monitoring programs, the EPA identified ground water contamination of surface waters (and wetlands) as a potential contributor to fish and shellfish kills, increased disease incidence, behavioral changes, reduced floral and faunal species diversity, and reduced aquatic productivity. The EPA determined that approximately 10 percent of the sites posed serious ecosystem threats and 10 percent represented minor threats, with the rest involving moderate threats typically confined to small areas.

Importance of Ecological Impacts

In summary, at certain sites the ecological risks of ground water contamination can be significant. Given that nearly 60 percent of Superfund sites are located adjacent to a stream and 52 percent are adjacent to a river (EPA, 1991d), the ecological effects of ground water contaminants must be considered when alternative ground water cleanup goals are analyzed.

ECONOMICS OF GROUND WATER CLEANUP

In the debate over ground water cleanup goals, many have emphasized the high costs of attempting to reach health-based cleanup levels as a reason for making the goals less stringent. Changing cleanup goals can have a significant impact on cleanup costs. However, like the health and ecological risks of various levels of ground water contamination, the costs of reaching various cleanup goals are highly uncertain at both the national and site levels.[4]

National Cleanup Costs

A widely cited national study published by the University of Tennessee in 1991 concluded that the costs of cleaning up all hazardous waste sites nationwide could drop by approximately one-third if cleanup goals are made less stringent or could increase by approximately one-half if cleanup goals are made more stringent (Russell et al., 1991; Abelson, 1992). According to this study, the "best-guess" cost of cleaning up all hazardous waste sites nationwide under current policy will be $752 billion over the next 30 years. If cleanup goals become less stringent, shifting toward containment and isolation of wastes rather than full cleanup, the cost would decrease to approximately $484 billion. If cleanup goals become more stringent, minimizing the amount of contamination left in place, the cost would increase to approximately $1,177 billion.

The University of Tennessee report has been critiqued for presenting costs as raw cumulative values, not as present values (Congressional Budget Office, 1994). Table 6-4, developed by the committee, shows the cost estimates from the University of Tennessee study adjusted to present values by estimating a profile of annual costs over the 30-year time horizon used in the study and by converting these annual costs to present values. The table includes best-guess estimates of cleanup costs based on the Tennessee study, as well as upper and lower bounds, also based on the Tennessee study. As the table shows, the best-guess cost in present value terms under current policy is $280 billion. With more stringent cleanup goals, the cost in present value terms increases to $440 billion. With less stringent cleanup goals, the cost decreases to $180 billion.

TABLE 6-4 Costs of Various National Policies for Hazardous Waste Site Remediation

	Present Value of Resource Cost (billions of 1991 U.S. dollars)		
National Policy	Lower Bound	Best Guess	Upper Bound
Current policy[a]	180	280	390
Less stringent policy[b]	140	180	260
More stringent policy[c]	360	440	630

NOTE: This table is based on data from Russell et al. (1991). It converts the figures in Russell et al. to present value by assuming that costs are prorated equally each year for a 30-year time horizon and that the discount rate is 4 percent.

[a] According to Russell et al. (1991), current policy, means "the set of principles and practices for hazardous waste remediation that are inferred to be in place in the period 1988-91 when the experience base and data for this study were collected."

[b] According to Russell et al. (1991), less stringent policy means relying more on containment and less on full cleanup.

[c] According to Russell et al. (1991), more stringent policy means application of more intensive treatment technologies and reduced burden on future generations.

The University of Tennessee estimate encompasses all facets of hazardous waste site cleanup, including cleanup of media other than ground water (such as sediments and sludge) and cleanup of sites where the ground water is not contaminated. According to the EPA (1993a), an estimated 20 percent of CERCLA sites do not have contaminated ground water. Furthermore, at sites with contaminated ground water, not all of the costs are for ground water cleanup. Therefore, ground water cleanup costs account for less than 80 percent of the figures presented in Table 6-4. If one presumes that 70 percent of the total cost of hazardous waste site remediation represents ground water cleanup, then the best-guess cost in present value terms is $200 billion under current policy. If one presumes that 50 percent of the cost applies to ground water cleanup, then the best-guess cost is $140 billion under current policy.

Many assumptions underlie the cost estimates in the University of Tennessee report. As a result, some critics have argued that the estimates are too high, while others have argued that they are too low (Congressional Budget Office, 1994). Nevertheless, comparisons with other sources of information about cleanup costs indicate that the study probably provides a reasonable estimate of the order of magnitude of likely clean up costs over the next 30 years. For example, in 1991 Carlin et al. (1991, 1992) estimated that in that year the nation would spend $29.7 billion complying with requirements under RCRA and CERCLA and that the level of spending would increase into the future. For comparison's sake, $30 billion per year for 30 years at a 4 percent discount rate yields a present value of approximately $520 billion, which is substantially above the $390 billion upper bound for current policy from the Tennessee study. Given the different approaches taken in the two studies[5] and given that there are substantial uncertainties in both, these estimates should be viewed as only illustrative of the magnitude of cleanup costs.

Site-Level Cleanup Costs

Simple computations for a hypothetical site provide further indication of how changes in cleanup goals can affect cleanup costs. For this hypothetical illustration, consider an aquifer containing a 190-million-liter plume of the common contaminant TCE at an average concentration of 1,000 µg/liter.[6] If the site will be cleaned Up using a conventional pump-and-treat system that will treat the effluent with an air stripper and a granular activated carbon filter, then Table 6-5 shows estimates for the time and cost required to achieve various cleanup goals, ranging from 80 to 99.99 percent TCE removal. As the table illustrates, the present worth cost of cleaning up the site increases substantially as the cleanup goal becomes more stringent—going from $2.8 million for 80 percent removal to $6.0 million for 99.99 percent removal. It is important to realize, however, that when a significant amount of contamination remains in place, additional costs will be incurred to construct and maintain a containment system, decreasing the cost differences shown in the table. The magnitude of the cost of the containment system is highly site specific, depending on factors such as the nearest sensitive receptor as well as on local hydrogeologic conditions.

Figure 6-2 compares present worth costs for various cleanup goals using different assumptions about discount rates. As can be seen, increasing requirements from 80 percent TCE removal to 99.99 percent removal would increase the present worth cost by approximately a factor of three for the low discount rate case. In contrast, using a higher discount rate such as the EPA uses in its cost estimates, the cost increase is substantially less.

Because this example is hypothetical and because the methods used to estimate cleanup cost are subject to substantial uncertainties, the numbers in Table 6-5 should not be cited as accurate values but rather as approximations of how changes in cleanup goals can affect cleanup costs. Further, while this example shows the general trend of how cleanup goals can influence site-level costs, it is important to realize that costs vary widely depending on numerous factors at each site. Part of the variation in cleanup costs is due to local factors such as local construction costs, the types of equipment available, and whether extracted ground water can be discharged to publicly owned treatment works (which results in significantly lower treatment costs). At least as important, however, are the hydrogeologic conditions at the site and the treatment technology or sequence of technologies chosen.

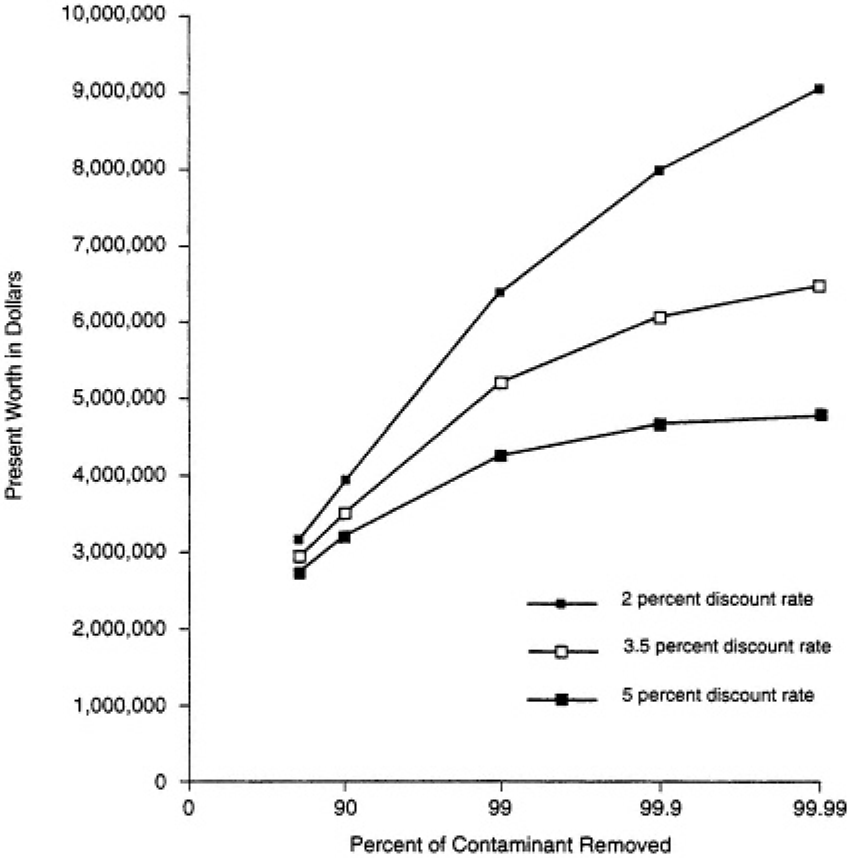

FIGURE 6-2 Cost of operating a pump-and-treat system as a function of the cleanup goal. The curves begin at a goal of 80 percent contaminant removal. As the figure demonstrates, increasing the removal efficiency to 99.99 percent substantially increases cleanup costs.

As an illustration of how hydrogeologic conditions affect cleanup

TABLE 6-5 Impact of Cleanup Goal on Cost of a Conventional Pump-and-Treat System

Percent Removal Required	Calculated Years to Achieve	Present Worth
80	15	$ 2,800,000
90	21	$ 3,250,000
99	42	$ 4,750,000
99.9	63	$ 5,600,000
99.99	84	$ 6,000,000

NOTE: The following assumptions were made: the plume volume is 190 million liters; the pumping rate is 380 liters per minute; 1.05 pore volumes are pumped per year; the retardation factor for TCE is 4.8; the air stripper influent concentration for TCE is 1,000 μg/liter; the air stripper effluent concentration for TCE is 5 μg/liter; and the discount rate is 4 percent. The estimates include capital, operation, and maintenance costs. They were prepared using the Cost of Remedial Action software package (EPA, 1991b).

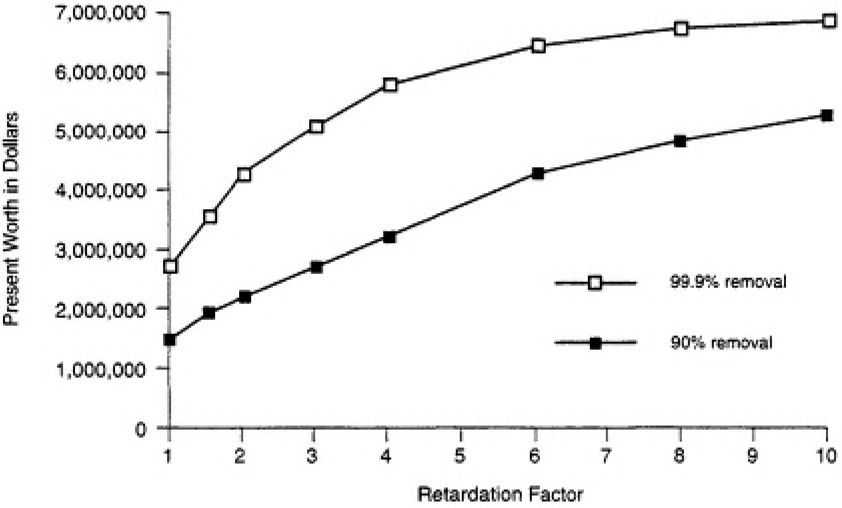

FIGURE 6-3 Cost of operating a pump-and-treat system as a function of the contaminant's retardation factor, which indicates its tendency to sorb to solid material in the aquifer. The figure illustrates that cleanup costs can increase substantially when contaminants sorb. This example assumes a pumping rate of 1 pore volume per year, initial capital costs of $650,000, initial operation and maintenance costs of $180,000, a 3.5 percent discount rate (reflecting 7.5 and 4 percent interest and inflation rates), and complete replacement of equipment every 25 years.

costs, Figure 6-3 shows the cost of cleaning up the TCE plume in the hypothetical example as a function of the tendency of soils at the site to sorb the TCE. In the figure, sorptive capacity is indicated by the retardation factor—the ratio of the total contaminant mass in the aquifer to the contaminant mass dissolved in the ground water. The greater the tendency of the contaminant to sorb (indicated by large retardation factors), the higher will be the cleanup costs, as illustrated by the figure. The cost difference between requiring 90 percent contaminant removal and requiring 99.9 percent removal ranges from approximately $1 million to more than $2 million, depending on the retardation factor.

TABLE 6-6 Comparison of Costs for a Conventional Pump-and-Treat System and an In Situ Bioremediation System for Benzene Removal

	Present Worth	
Removal Efficiency	In Situ Bioremediation	Conventional Pump-and-Treat
90	$2,460,000	$3,200,000
99	$3,000,000	$5,020,000

NOTE: The assumptions for the conventional pump-and-treat system in this example are the same as those used in Table 6-5 except that the contaminant is benzene, for which the required effluent concentration is 1 μg/ liter and the retardation factor is 3.6. The hypothetical bioremediation system pumps at 190 liters per minute to supply oxygen and nutrients to stimulate biodegradation.

As an illustration of how the cleanup technology chosen affects cleanup cost, Table 6-6 compares costs for a conventional pump-and-treat system and an in situ bioremediation system for benzene removal. As shown in the table, for 90 percent benzene removal, in situ bioremediation provides a substantial savings compared to the conventional pump-and-treat system. Increasing the percent removal to 99 percent, if this were achievable, would provide an even greater cost advantage for in situ bioremediation. (It is important to note that if the in situ bioremediation system cannot reach the required cleanup goal in the predicted time, its life cycle costs may increase to the point where the costs are similar to those associated with conventional pump-and-treat systems.)

These hypothetical computations show that changing ground water cleanup goals from 80 or 90 percent contaminant removal to nearly 100 percent contaminant removal can have a substantial effect on cleanup costs at the site level. However, the magnitude of the effect is influenced by local economic conditions, site hydrogeology, and the cleanup tech nology chosen. Furthermore, it may be partially offset by the need to build and maintain containment systems when a significant quantity of contamination remains in place.

Benefits of Ground Water Cleanup

In considering costs for ground water cleanup under various scenarios, one must recognize that spending on cleanup yields benefits that have economic value. Benefits include reduced health risks, increased property values for uncontaminated land, and the knowledge that the ground water will be available for unrestricted use in the future. No studies have attempted to compare differences in the dollar value of benefits received for different national ground water cleanup goals. Further, at the time this report was prepared only one study assessing the total national economic benefits of restoring ground water was available, and this study was controversial. The study was carried out for the EPA by McClelland et al. (1992) at the University of Colorado as part of an effort to assess the economic impact of the proposed RCRA regulations.[7] The study was controversial because it used an economic analysis method known as contingent valuation to estimate the benefits of clean ground water, and it was criticized by the EPA's Science Advisory Board (1993).

Contingent valuation is a method used to estimate what are known as the nonuse values of ground water. Nonuse values are those that individuals place on water unrelated to their own need to use it in the present or the future—values such as desiring to preserve the resource for future generations and desiring to preserve it because it is a unique natural asset. In contrast, use values are those that individuals place on the water to use it today or to have the option of using it for themselves in the future. While most use values can be approximated based on current water prices, nonuse values cannot be determined from observation of actual marketplace transactions. Consequently, economists devised the contingent valuation method to assign monetary worth to non-use values for natural resources. The method estimates nonmarket values by conducting surveys to ask individuals what they are willing to pay to maintain the resource (or what compensation they are willing to accept for its loss). In the EPA study, researchers surveyed a national sample of 900 people and asked, "What would a *complete cleanup program* be worth to your household, if you faced the hypothetical problem of 40 percent of your water supply coming from contaminated ground water as we have described?"[8]

The contingent valuation technique is controversial in part because of its short scientific life span and because flaws in the method are still being worked out. The first contingent valuation study of nonmarket goods was completed by Robert K. Davis in the early 1960s (Davis, 1963). During the early 1970s, economists studied the method intensively for valuing atmospheric visibility in the Four Comers region of the southwest, but little research was carried out on its use for valuing other resources (Randall et al., 1975; Rowe et al., 1980). The studies of the 1970s showed that different contingent valuation studies with different designs yielded similar results, leading researchers to believe that the technique might be a useful approach for valuing nonmarket commodities in general (Rowe et al., 1980). However, the research also revealed distinct flaws in the method, including the following:

- Results may vary depending on experimental design factors, such as whether individuals are surveyed over the telephone or in person and the amount and type of information the researcher provides to the individual (Rowe et al., 1980).
- The fact that individuals are not actually required to pay their bid may affect the result of the study, although where there are well-defined related markets the magnitude of this bias seems small (Brookshire and Coursey, 1987).
- Individuals may offer the same bid for cleaning up one hazardous waste site, all related hazardous waste sites, or all hazardous waste sites in a region (Kahneman and Knetsch, 1992), although some researchers have suggested that this problem can be overcome if the contingent valuation analysis is done correctly (Smith, 1992).

Despite these and other flaws, many economists believe the contingent valuation method shows promise. For example, Mitchell and Carson (1989) have said that the contingent valuation method may be "a powerful and versatile tool" for measuring the economic benefits of the provision of nonmarketed goods. More importantly, a recent panel convened by the National Oceanic and Atmospheric Administration and chaired by two Nobel Prize-winning economists concluded that the method may be used as a starting point for legal evaluation of nonuse values, as long as sufficient and elaborate scientific safeguards are taken (Arrow et al., 1993). However, other economists caution that the method has not reached a stage of scientific maturity sufficient to place confidence in the reliability and accuracy of the estimates it provides. In a recent general review, Cummings and Harrison (1992) concluded that "the present state of the art of the CVM [contingent valuation method] leads us to what we believe is an unavoidable conclusion: for uses that require that the term 'value' will imply some nexus with real economic commitments of people, it has yet to be demonstrated that the CVM as currently applied is up to the task." A National Research Council committee is currently review ing this method to determine whether it is appropriate for assessing the future value of ground water.

TABLE 6-7 National Benefits of Ground Water Cleanup of U.S. dollars)

	Present Value of National Benefits of Ground Water Cleanup (billions of U.S. dollars)	
Discount Rate (real rate, percent)	10-year Time Horizon	Indefinite Time Horizon
2	76	420
4	69	210
6	63	140
8	57	110
10	52	85

NOTE: If the amount paid per year were assumed to continue indefinitely rather than stopping in 10 years, the present value of benefits would equal the amount in the second column. There is some evidence that respondents cannot differentiate between a 10-year payoff and an indefinite payoff date. This illustrates how sensitive contingent valuation measures are to exact specifications of the commodity.

SOURCE: McClelland et al., 1992.

In the EPA study of the national benefits of ground water cleanup, the 900 survey respondents indicated that, on average, they would be willing to add $7.08 to their monthly water bills for the next 10 years to clean up ground water.[9] With approximately 100 million households in the United States, this estimate indicates an aggregate willingness to pay $8 billion per year for 10 years. Table 6-7 shows the present value of this annual willingness to pay using various discount rates for a 10-year period. Because there is some evidence that respondents cannot differentiate between a 10-year payoff date and an indefinite payoff date, also shown in Table 6-7 are present worth values assuming that people are willing to pay the $7.08 indefinitely. As shown in Table 6-7, based on the EPA study the benefits of ground water cleanup, like the costs, may range up to hundreds of billions of dollars.

Because of questions about the validity of the EPA study, one must view Table 6-7 with caution. The Science Advisory Board criticized the study because board members believed that the commodity "ground water cleanup" was not sufficiently well defined to allow a single interpretation of the respondents' answers to the survey. Whether this criticism is valid can only be proved or disproved by further scientific analyses. As an example of the study's possible limitations, the survey indicated a nonuse value component for ground water of $49.44 per household per year—close to the nonuse values estimated for preserving visibility in the Grand Canyon and for cleaning up hazardous waste sites in Colorado as determined in other contingent valuation studies (Rahmatian, 1987; Energy Resource Consultants, 1986). That the value survey respondents placed on this "good cause" is similar to the measured values for other "good causes" may signal problems. The sum of values people express in independent studies of willingness to pay for all good causes may exceed the disposable income of any one respondent (Kahneman and Knetsch, 1992).

THE COMPLEXITY OF SELECTING CLEANUP GOALS

Selecting ground water cleanup goals is not a simple matter: it involves consideration of health risks, ecological risks, costs versus benefits, and a variety of other factors—all of which are difficult to quantify with certainty. Different people interpret this uncertainty in different ways. For example, some view the uncertainty in the health risks of ground water contamination as an indication that the risks are insignificant, while others view it merely as an indication that science is limited in its ability to quantify what they perceive as a major risk. Similarly, some view the inability to place a precise dollar value on the economic damage caused by ground water contamination as proof that the economic damage is not significant, while others view it as proof only of the limitations of economics to adequately value important resources. Thus, some view existing ground water cleanup programs as having high cost while providing society with little benefit, while others view the programs as barely adequate to address an important environmental problem. The national policy debate over ground water cleanup goals must resolve these two conflicting extremes.

The task of selecting ground water cleanup goals would be difficult enough without technologic constraints. However, as this report documents, present technologies will be unable to restore portions of a large number of sites. The limitations of technology, in the view of some people, provide added reason to reconsider whether current ground water cleanup goals are appropriate. Given the high level of uncertainty in the risks and economic damage created by ground water contamination, the committee believes that whether changes are needed in the policies for setting long-term cleanup goals can only be decided through policy debates; science can influence these debates, but value judgments must be the deciding factors. At the same time, however, the committee strongly believes that because existing ground water cleanup goals cannot be at tained at a large number of sites, short-term objectives should be established at these sites to temporarily supersede long-term goals.

Under the scenario the committee envisions, short-term objectives would be set based on the capabilities of current technologies at sites where long-term cleanup goals cannot be reached for the full site with current technology but the ability to reach them in the future cannot be ruled out. Access to portions of sites where contamination remains would be restricted or partially restricted. Periodically, the EPA would review whether technology had advanced to the point that the interim objective could be moved closer to the long-term goal. Short-term objectives would not be needed for the sites at which cleanup goals can be reached with current technology. In addition, short-term objectives might not be needed for another group of extremely complex contaminated sites where cleanup is highly unlikely even with new technologies; at such sites, technical impracticability waivers might be used to waive cleanup goals, as is done under current policy in the Superfund program. The next chapter explains the details of how policymakers would decide which sites should have interim objectives in addition to long-term goals.

The setting of short-term objectives in situations where long-term cleanup goals cannot currently be achieved has precedence in existing environmental policy. For example, the Clean Water Act set an unenforceable national goal of "zero discharge" of pollutants for surface water but used "interim" enforceable objectives that recognized that achieving zero discharge was not technically feasible at the time the act was passed. In the Clean Water Act and under the scenario the committee envisions for ground water cleanup programs, the long-term goal provides the vision for national policy, while the interim objectives reflect the reality that there may be technical constraints to reaching the goal. The committee believes that interim objectives prevent the expenditure of resources trying to reach goals that are not achievable with current technology and more accurately communicate to the public what is possible with current technologies. At the same time, interim objectives do not rule out the possibility that at some future time new technological breakthroughs may enable the achievement of existing cleanup goals. They preserve the values that public policymakers believed were important when the nation's ground water cleanup programs were first implemented.

CONCLUSIONS

Based on an assessment of current ground water cleanup goals in light of the capabilities of ground water cleanup technologies, along with a review of the risks, costs, and benefits associated with ground water contamination and cleanup, the committee reached the following conclusions:

- **Interim ground water cleanup objectives may be needed for portions of sites where health-based cleanup goals cannot be achieved with existing technology**. The establishment of policies for setting long-term cleanup goals at sites requires consideration of many factors other than the capabilities of technology, including health risks, ecological risks, costs, benefits, and people's values. Changes in long-term cleanup goals therefore require debate in public policy arenas. However, the committee strongly advises setting short-term, technology-based objectives to temporarily supersede long-term goals at portions of sites where achieving the long-term, health-based goals is not possible with current technologies.
- **The health risks of ground water contamination from hazardous waste sites are uncertain, but this uncertainty does not provide justification for changing long-term cleanup goals**. The inadequate documentation of health risks derives from the general absence of information on human exposure to contaminated ground water and lack of information on the adverse effects of ground water contamination on humans. Given this lack of information, the relative degree of public health protection offered by one ground water cleanup goal, such as drinking water standards, in comparison to another goal, such as contaminant levels higher or lower than drinking water standards, cannot be quantified with accuracy.
- **Ground water contamination can cause significant ecological damage at certain sites**. Ground water remediation has generally focused on public health concerns. However, given the increasing evidence that ground water contamination can also damage important ecosystems, the ecological effects of unremediated contaminant plumes are important to consider when choosing a long-term ground water cleanup goal.
- **At the site level, ground water cleanup goals can substantially affect cleanup costs**. Removing 80 or 90 percent of the contamination generally costs much less than attempting to remove all or nearly all of the contamination. The magnitude of the cost difference depends on local economic factors, site characteristics, the cleanup technology chosen, and whether a containment system will be necessary if contamination remains in place.
- **At the national level, the total benefits and the costs of existing ground water cleanup policies are both likely to be in the tens to hundreds of billions of dollars range—but these figures are highly uncertain**. Many assumptions underlie existing estimates of benefits and costs,

and there is no consensus on these estimates in the economics community. As a result, direct comparisons of the costs and benefits of various ground water cleanup policies must be used with caution.

NOTES

1. These numbers are based on the committee's analysis of the EPA's Record of Decision data base.

2. Similar but separate regulations apply to the correction of leaks from landfills.

3. This figure is based on a key word computer search of the EPA's data base containing Records of Decision issued from 1982 to fiscal year 1991.

4. Uncertainty increases substantially when one aggregates cleanup costs from the site level to state, regional, and national levels.

5. The Carlin et al. estimate excludes sites outside the Superfund and RCRA programs, while the University of Tennessee estimate includes all waste sites. On the other hand, the Carlin et al. estimate includes costs under Superfund and RCRA unrelated to ground water cleanup, such as waste disposal costs.

6. The plume volume is defined as the volume of ground water containing dissolved TCE at concentrations above the detection limit (0.5 μg/liter). For this example, all of the TCE is either dissolved or adsorbed to solid materials in the aquifer; none is present as a dense nonaqueous-phase liquid.

7. Under the Reagan administration, the Office of Management and Budget required economic analyses of all proposed new regulations.

8. In the hypothetical situation described in this survey, the contamination originated from a leaking public landfill. "Complete cleanup" refers to building a concrete wall around the landfill down to the rock layer beneath it and pumping and treating the water outside the containment zone.

9. The researchers who carried out this survey attributed $4.12 of the $7.08 to nonuse values.

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7

Policy Implications of a Technical Problem

The overriding question that this report has ad-dressed—whether there are technological limits to attaining health-based ground water cleanup goals—is a classic example of a technical issue with significant policy ramifications. At the passage of the Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) in 1980, in the 1984 expansion of the Resource Conservation and Recovery Act (RCRA) corrective action program, and when Congress reauthorized and expanded CERCLA in 1986, the technical limitations to remediating contaminated ground water were poorly understood. Now that the United States has spent more than a decade trying to meet the public demand to clean up contaminated sites, limitations in the ability of technology to meet society's desires are apparent.

This chapter reviews existing national ground water cleanup policies and recommends changes to reflect the limitations of technology. The term "policy" encompasses not just the laws Congress has passed requiring cleanup of contaminated ground water but also the variety of government documents issued to implement these laws. The chapter begins with a broad overview of the components of ground water cleanup policy in the United States. It then reviews the key evolving policies relevant to sites where technical limitations prevent the achievement of ground water cleanup goals. Finally, the chapter summarizes the committee's recommendations for improving ground water cleanup policies to reflect the limits of technology.

COMPONENTS OF GROUND WATER CLEANUP POLICY

CERCLA and RCRA set overarching national ground water cleanup policy by prescribing priorities and decision frameworks. Most states also have their own versions of these laws, which often can be more prescriptive or more stringent than the federal laws. It is up to public sector managers—primarily in the Environmental Protection Agency (EPA) and its state-level equivalents—to implement the sometimes vague mandates contained in these laws. Courts grant public agencies great deference in developing policy, recognizing the interaction between scientific limitations, economic factors, and sometimes conflicting statutory requirements.

Based on the broad statutory mandates of CERCLA and RCRA, the EPA has developed specific requirements for ground water cleanup made binding through regulations. The National Contingency Plan specifies the detailed mechanisms for implementing CERCLA. The proposed Corrective Action Rule provides the mechanisms for implementing site clean-ups under RCRA.[1]

Regulations are further implemented by guidance documents explaining how to make the many decisions required by the regulations, such as how to determine the necessary frequency of ground water sampling or how to test for the presence of certain contaminants. Unlike regulations, guidance documents are not legally enforceable and thus are not subject to legal challenge. However, regulators can make provisions of guidance documents legally enforceable by including them in enforceable documents such as permits or consent decrees.

In addition to regulations and guidance documents, another important set of mechanisms for the development of ground water cleanup policy is the issuance of policy statements by EPA officials. Policy statements are often directed at how work is performed within the government bureaucracy but can have wide-ranging impacts on the substance of the ultimate rules. A key example of a policy statement pertaining to ground water cleanup is a 1992 memorandum directing EPA employees on how to manage sites where dense nonaqueous-phase liquid (DNAPL) contaminants are preventing the achievement of ground water cleanup goals (Clay, 1992).

KEY POLICIES ADDRESSING THE TECHNICAL UNCERTAINTY OF GROUND WATER CLEANUP

Both CERCLA and RCRA contain provisions for modifying ground water cleanup goals when health-based standards are not technically achievable, as explained in Chapter 6. However, although CERCLA and RCRA contain references to the technical uncertainty of achieving cleanup goals, the causes of the uncertainty are only recently being recognized. Consequently, the policies for regulating sites where health-based cleanup goals may be unachievable are still evolving and have not yet been uniformly applied.

The EPA has four types of policies addressing, at least in part, the possibility that existing technology may be unable to achieve current goals for ground water cleanup. These policies, reviewed in detail below, address the following problems: (1) how to implement a site cleanup program early, even while insufficient data are available to determine the design of the final cleanup system; (2) how to manage sites with DNAPL contaminants; (3) how to document that achieving health-based cleanup goals is not possible; and (4) how to encourage development and use of innovative technologies.

Early Action Policy

The EPA has been heavily criticized for the slow pace of cleanups at CERCLA sites, with some contending that the growing backlog of unremediated sites may overwhelm the program (Guerrero, 1991). In response, the EPA has developed the Superfund Accelerated Cleanup Model and accompanying documents to guide site managers in expediting the cleanup process (EPA, 1992a,b,c,e,f,g). The accelerated cleanup model encourages immediate actions to reduce hazards and prevent the further spreading of contamination even before the parties agree on the final cleanup plan for the site. The guidance documents issued as part of this program recommend installation of a prototype pump-and-treat system to contain the contaminant plume as early as possible and collection of data and redesign of the prototype to meet long-term goals. Data collected during operation of the prototype system have the potential to substantially reduce the technical uncertainties associated with designing the full-scale remedy. Thus, the EPA's early action policies are an important component of its efforts to address the technical uncertainties of cleaning up hazardous waste sites.

The committee strongly endorses the EPA's emphasis on early actions to contain contamination while site investigation and design of the full-scale cleanup system are under way. As this report has documented, the longer contamination remains underground and the further it spreads, the more difficult it is to clean up. Therefore, early action increases the likelihood of successful cleanup. The committee believes it is especially important to emphasize monitoring of early actions because monitoring data can reduce many technical uncertainties.

The committee sees no technical constraints to immediate initiation of early actions. However, institutional, policy, and regulatory barriers may slow implementation. For example, some groups representing companies responsible for cleanup have identified as a key barrier the EPA's policy of requiring that private parties agree to implement the entire cleanup remedy all at once rather than allowing them to agree to the early action before agreeing to the full remedy (Diamond, 1991). These groups have suggested allowing responsible parties to agree to implement ground water remedial actions in phases, without a legally binding commitment to implement the later phases. A phased approach would encourage companies to agree to the early action without legal challenge because the amount of up-front resources involved would be smaller than for the full remedy. A phased approach would also allow time to identify all of the potentially responsible parties before any one party must agree to the final remedy. A possible drawback of such a phased approach is that it would increase the number of times site plans would have to be reviewed and approved, potentially increasing the burden on regulators and transaction costs for the government and private parties. Pilot tests would be necessary to determine the feasibility of a phased approach to deciding on cleanup remedies.

DNAPL Policy

As explained in Chapters 2 and 3, one site characteristic that interferes with reaching health-based cleanup goals is the presence of DNAPL contaminants. Because many of the most common contaminants are DNAPLs, the EPA focused on the DNAPL problem before it addressed other site complexities and has developed a specific technical policy to address sites with DNAPLs. The policy is not explicitly reflected in either the law or regulations but rather appears in recent EPA policy statements and guidance documents (Clay, 1992; EPA, 1991a,b). Through these documents, the EPA explicitly recognizes that attaining health-based standards may currently be infeasible at certain types of CERCLA and RCRA sites with DNAPL contaminants.

The EPA's policy on sites with DNAPLs is supported to a great extent by the committee's technical review. The policy acknowledges the difficulty inherent in cleaning up DNAPL sites and the critical importance of proper site characterization and early action to stop contaminant migration. It also recognizes that it may not be possible to restore all ground water at sites with DNAPLs and that separate approaches may be needed for the dissolved plume emanating from the DNAPLs, which can be cleaned up in some situations, and the DNAPLs themselves, which generally cannot be cleaned up with current technology. However, although the EPA's DNAPL policy is generally sound, the committee has three concerns about this policy.

The first concern is that the DNAPL guidance documents do not adequately acknowledge the difficulty of locating DNAPLs. The agency's guidance states that "if planned from the beginning, collection of this information can be combined with other efforts such that investigation costs and time frames should not be greater than current levels, for most sites" (Clay, 1992). However, the committee believes that DNAPL investigations may require more time and effort, depending on the cleanup goals for the site, because they may require more subsurface sampling and more analysis of the samples. Despite this concern, the committee supports the EPA's decision to require expanded DNAPL investigations because the additional information will facilitate selection of an appropriate remedial action. What level of investigation is appropriate depends on the complexity of the site and the objectives for the treatment system. The committee supports the EPA's effort to develop rules of thumb based on site records and types of contaminants to estimate the likelihood of DNAPL contamination (see, for example, Cohen and Mercer, 1993).

The committee's second concern is that the DNAPL policy is not sufficiently explicit in addressing the issue of cleanup time. Current methods for predicting cleanup time are likely to underestimate the time because they typically rely on chemical fate and transport assumptions that do not apply in DNAPL situations, as explained in Chapter 3. Although the additional information gathered during DNAPL investigations may provide a more reliable basis for estimating cleanup time, the committee believes that the state-of-the-art of time prediction is still inadequate and is unlikely to be accurate. Agency guidance should explicitly state these uncertainties and, if possible, whether the uncertainties are likely to re-suit in overestimated or underestimated cleanup times.

The committee's third and most important concern relates to the approach used to demonstrate technical impracticability at sites with DNAPLs. In practice, EPA regulators generally require an attempt to achieve health-based cleanup goals and allow establishment of less stringent cleanup goals only after the implemented system fails to achieve the initial cleanup goals. This was perhaps the most difficult area of the application of existing DNAPL policy for the committee to evaluate. Although the committee sees value in ensuring that best possible efforts are employed to address DNAPL contamination, a requirement that a remedial action be designed to achieve the impossible (based on current technology) is counterproductive.

Technical Impracticability Policy

As result of the growing evidence that reaching health-based ground water cleanup standards may be technically impracticable at a large number of sites, in 1993 the EPA developed a guidance document specifying how to apply for waivers to ground water cleanup goals at CERCLA and RCRA sites (EPA, 1993b). The guidance document applies to all types of CERCLA and RCRA sites, not just those with DNAPLs. It outlines in detail the specific types of data that must be provided in a technical impracticability waiver application. According to the guidance document, the EPA anticipates that it will consider most technical impracticability applications only after operation of an interim or full-scale remediation system provides sufficient data to show that reaching the cleanup goals is not possible. In the committee's view, this guidance document represents an important step in addressing how to oversee sites where limitations of present technologies prevent the full achievement of ground water cleanup goals. However, the committee foresees major problems with implementing the guidance.

First and most important, the guidance document is likely to create a regulatory log jam. The EPA estimates that 60 percent of Superfund sites have a medium to high likelihood of containing DNAPLs (EPA, 1993a). Because of the difficulty of cleaning up DNAPLs and because other site complexities in addition to DNAPLs may prevent achievement of health-based ground water cleanup goals, more than half of the sites in the Superfund program might be eligible for technical impracticability waivers. Each site will require a highly detailed evaluation by EPA staff. More important, at most sites regulators require construction and operation of cleanup systems designed to reach technically infeasible goals before granting a waiver, a practice that is likely to significantly slow progress in the CERCLA and RCRA corrective action programs.

Second, the guidance document is both too restrictive and not restrictive enough in its consideration of appropriate cleanup goals. It will deny any interim goal modification for the large majority of sites where present technology cannot achieve health-based standards. Rather, owners of these sites may expend large sums proving that they cannot achieve the health-based standards with present technology. On the other hand, once the money is spent to define the limits of today's technology, the goal is waived. Even if technology capable of meeting the health-based goals is developed in the future, there are no explicit requirements to apply the new technology. This situation creates a disincentive to develop improved technology that could lead to the denial of future impracticability waivers.

The problems with the technical impracticability policy arise from inadequate recognition of the large number of sites where technical limitations may prevent complete cleanup within the foreseeable future. The current policy appears to rest on the assumption that there will be a small number of sites where cleanup is impracticable and that the majority of sites will not require a detailed technical impracticability evaluation. It thus divides sites into two groups: those that can be cleaned up and those for which cleanup is infeasible. To address the problems the committee foresees with this policy, the committee recommends a new model including three—rather than two—groups of sites. Table 7-1, adapted from Chapter 3, shows these three groupings, which are as follows:

- *Group A*: At sites in group A, full-scale cleanup systems would be installed to reach health-based goals. Cleaning up these sites should be relatively straightforward, and consideration of technical impracticability should not be required. An example of this type of site is one contaminated with gasoline components released through a very small leak in an underground storage tank. As shown in Table 7-1, sites in this group have rating of I for difficulty of cleanup according to the system used in Chapter 3.
- *Group B*: At sites in group B, cleanup may or may not be possible, and whether health-based goals can be reached should be established in phases. In the first phase, the sources of contamination should be contained and the plume of dissolved contaminants should be cleaned up. In the second phase, the possibility of removing some of the contaminant mass from source areas should be considered (although the committee does not view maximizing the pumping rate to remove mass from source areas as an efficient removal method). In the third phase, data should be gathered to determine whether attainment of ground water cleanup goals is feasible with existing technology. If not, interim cleanup objectives should be established for the site, prior to implementation of a full-scale remedy. These interim objectives should supersede the long-term, health-based cleanup goals and should be based on the capabilities of technology. Periodically, the EPA should assess whether a new technology could attain the health-based goals. As shown in Table 7-1, sites in group B have a rating of 2 or 3 for difficulty of cleanup according to the system used in Chapter 3.
- *Group C*: At sites in group C, cleanup will most likely be infeasible with current technology. These sites warrant immediate consideration for infeasibility waivers with the concomitant selection of a new protective long-term goal. At these sites, the plume of dissolved contaminants should be cleaned up, contaminant mass should be removed from source areas to the extent practicable, and remaining contaminant sources should be contained. However, the requirement to clean source areas to health-

TABLE 7-1 Categories of Sites for Technical Infeasibility Determinations

	Contaminant Chemistry					
Hydrogeology	Mobile, Dissolved (degrades/ volatilizes)	Mobile, Dissolved	Strongly Sorbed, Dissolved (degrades/ volatilizes)	Strongly Sorbed, Dissolved	Separate Phase LNAPL	Separate Phase DNAPL
Homogeneous, single layer	A (1)	A (1-2)	B (2)	B (2-3)	B (2-3)	B (3)
Homogeneous, multiple layers	A (1)	A (1-2)	B (2)	B (2-3)	B (2-3)	B (3)
Heterogeneous, single layer	B (2)	B (2)	B (3)	B (3)	B (3)	C (4)
Heterogeneous, multiple layers	B (2)	B (2)	B (3)	B (3)	B (3)	C (4)
Fractured	B (3)	B (3)	B (3)	B (3)	C (4)	C (4)

NOTE: Shaded boxes at the left end (group A) represent types of sites for which cleanup of the full site to health-based standards should be feasible with current technology. Shaded boxes at the right end (group C) represent types of sites for which full cleanup of the source areas to health-based standards will likely be technically infeasible. The unshaded boxes in the middle (group B) represent sites for which the technical feasibility of complete cleanup is likely to be uncertain. The numerical ratings indicate the relative ease of cleanup, where 1 is easiest and 4 is most difficult.

- based standards should be permanently waived. An example of this type of site is one where large amounts of chlorinated solvents have lodged in fractured bedrock. As shown in Table 7-1, sites in this group have a rating of 4 according to the system used in Chapter 3.

The classification scheme shown in Table 7-1 is one approach to dividing sites into the three groups. The committee recognizes that it is not a perfect scheme. For example, continued observation of some sites in group B might indicate that they, like sites in group C, warrant consideration for technical impracticability waivers. On the other hand, at other sites in group B, continued observation may show that reaching cleanup goals is feasible, just as at sites in group A. In a more detailed scheme additional factors, as well as a broader range of classifications, might be considered. The committee leaves to the appropriate agencies, private sector, public interest community, and consensus standard setting groups the determination of an optimal classification scheme for identifying the types of sites that should be included in each of the three groups.

Finally, the committee believes strongly that one cannot prescribe an absolute rule concerning the infeasibility of attaining ground water cleanup goals given the wide range of conditions and cleanup objectives that exist at different sites. Such classification schemes, although useful, cannot be rigidly or mechanically applied. Classification schemes must retain considerable flexibility and still must be applied on a site-by-site basis using sound scientific judgment. Nevertheless, the committee believes that a classification scheme such as the one proposed above is technically justified and would significantly improve the degree to which ground water cleanup policy reflects the capabilities and limitations of technology.

Programs For Innovative Technology Development

As explained in Chapter 4, numerous barriers have discouraged the development and use of innovative ground water cleanup technologies. These barriers are interfering with the ability to increase the likelihood of reaching health-based cleanup goals. Although the EPA and other agencies are implementing programs to develop innovative technologies, the committee believes that strong economic incentives are needed to encourage innovation.

To create economic incentives to use innovative technologies, the committee suggests pilot testing the concept of requiring an annual "infeasibility fee" at every site where the requirement to attain health-based cleanup goals has been deferred or waived. The fee would be paid by responsible parties at the sites. The annual cost it would create would encourage development and use of new and more effective technologies that would eliminate the need to pay the fee. The fee could be proportional to the size of the unmitigated problem, or it could be a fixed fee per responsible party per site, or it could be determined in some other fashion. In any case, the fee must be large enough to encourage innovative technology development while being lower than the cost of pumping and treating at a high rate.

The funds collected from the infeasibility fee could be pooled into an applied ground water research fund. One portion of the fund could be used for field research, and the other portion could be used to create an economic incentive for implementing innovative technologies. Responsible parties often hesitate to use innovative technologies because they are still responsible for implementing—and paying for—a conventional pump-and-treat system as a backup if the innovation fails. If responsible parties could recoup some of these losses through the infeasibility fund, they would have a greater incentive to try new technologies. Responsible parties could apply to a special ground water advisory panel (discussed later in this chapter) for approval to use the innovative technology fund. The advisory panel would approve use of the technology only if it was likely to achieve the specified cleanup objective. If the technology failed to achieve the goals, the responsible party would receive money to cover its research costs. If the technology worked, the responsible party would not receive payment but would receive the benefit of having its liability for the site eliminated because the site would be cleaned up.

The infeasibility fee approach has several advantages. First, it is consistent with the "polluter pays" principle, without being punitive or requiring restoration of ground water that cannot be cleaned up using existing technology. It makes more explicit the cost of actions that contaminate ground water and would therefore foster better corporate decisionmaking. Second, even if there is disagreement over the appropriate goal for ground water cleanup or with the imposition of a fee on industry, in the long run such an approach provides benefits to the private sector. Over time, the applied ground water research that the fund would support is likely to lower the cost of ground water remedial actions at all sites. Third, the approach offers a cost-effective mechanism for pooling industry's resources. The use of federal, state, and private sector partnerships would add to the cost-effectiveness of this method of funding applied ground water research.

The committee analyzed only the broadest outlines of this scenario. Detailed economic analyses would be needed prior to the creation of an infeasibility fee for sites where ground water cleanup is technically impracticable.

IMPLEMENTATION OF POLICIES

The four types of EPA policies described above, although literally applicable only to CERCLA and RCRA sites, are likely to guide other parts of the EPA, other government agencies, and private companies in making similar determinations. Therefore, it is extremely important for the long-term effectiveness of the nation's ground water cleanup programs that these policies present a manageable approach for addressing all types of site complexities documented in this report. In addition to the specific suggestions for improving the policies described above, the committee has additional suggestions related to the broad implementation of policies for managing sites where the ability to achieve health-based ground water cleanup goals is uncertain.

Broad And Equivalent Application of Policies To All Sites

The committee is concerned about inconsistencies in the application of ground water cleanup policies at different sites. Such inconsistencies can occur because policy implementation is not closely monitored and is highly dependent on the knowledge of the personnel overseeing the site. Inconsistencies can also occur because of the different statutes, regulations, and guidance documents governing different sites. For example, some state agencies have adopted background contaminant levels as the goal of all ground water remedial actions, while other states use drinking water standards. Regardless of who manages the site, and regardless of the statutes and regulations involved, the approach to addressing the impracticability of attaining cleanup goals should be consistent from site to site.

Vigorous Efforts to Ensure That New Guidance is Applied at The Site Level

Once EPA headquarters issues a new guidance document, a determined effort must be maintained to ensure that site-level project managers are aware of it and that there are no hidden disincentives to implementing it. This type of effort might include meetings and training courses. It might also require revising performance criteria for the personnel overseeing the sites. For example, if there are time limits for completing remedial investigations that make it difficult to characterize a site adequately, it is unlikely that revisions to the remedial investigation guidance calling for more complete site investigations will change staff personnel behavior. The EPA is already making progress in this area, for example by presenting technical seminars to explain the guidance document on demonstrating technical impracticability of achieving cleanup goals. Such efforts should continue.

Continuous Program Evaluation

Additional effort is needed to evaluate the successes and failures of ground water cleanup under the various programs. Although the EPA's 1992 review of 24 pump-and-treat systems (see Chapters 1 and 3) was a good start at evaluation, a larger data base of sites is needed to assess the success of cleanup programs. Continuous evaluation of sites where clean-ups are under way would require a more rigorous program for implementation oversight. The results of the oversight would allow the EPA to continuously improve its implementation guidance documents, its reference case examples, and its training programs. Such a program evaluation process should involve input from EPA program managers, expert scientists, and stakeholders at the site (including citizens and responsible parties).

Routine Use of Scientific Experts

The availability of interdisciplinary scientific expertise within the EPA and other agencies is currently insufficient to evaluate the multitude of complex hazardous waste sites. Decisions at complex sites could benefit from additional scientific expertise. While not a substitute for hiring and retaining technically trained staff, the technical expertise available to the agencies could be enhanced by creating several independent multi-disciplinary scientific ground water advisory panels. The panels could provide advice at CERCLA, RCRA, federal facility, state, and possibly private sector sites.

The details of how to organize such advisory panels would need to be carefully worked out. Several advisory panels could be created on a regional basis, based on the number of complex sites in the region. Alternatively, the panels could be set up on a national level. Inclusion of experts from outside the EPA in addition to top EPA technical staff would enhance public confidence in the panels as providers of unbiased advice. Panels could include experts from other federal and state agencies, academia, and private consulting firms. The EPA could select panelists using criteria similar to those used to select the agency's Science Advisory Board. The members would need to possess special expertise (as opposed to the more general qualifications of the typical cleanup project manager). Strict adherence to conflict-of-interest rules would be necessary.

These advisory panels would be consulted as early as possible, preferably during the field investigation stage. The same panel would be consulted throughout implementation of the remedy and could answer questions concerning the feasibility of achieving technical goals. Panels could also provide advice for sites where cleanup is currently under way and significant difficulties have been encountered. The panelists' advice would be limited to technical issues, as opposed to policy or risk management issues. For example, the panel might confirm the validity of a proposed conceptual model of the site, whether DNAPLs are present, the likelihood that an exposure pathway exists, the feasibility of attaining a specific cleanup goal, whether a remedial action alternative is effective, whether cost estimates of a remedial alternative are credible, and whether the design of the monitoring plan is effective. The types of policy-related issues that would not be addressed by the advisory panel include questions such as what ground water remedial action goal should be selected or what remedy should be selected. The panels might also be used for technical "appeals" by responsible parties or local citizens who disagree with the regulatory technical staff. [2]

Development of A Mechanism For Long-Term Site Management

Currently the nation lacks institutional mechanisms for long-term management of sites where health-based cleanup goals cannot be achieved with existing technologies. This report has shown that cleanup at many sites will not occur until new technologies are developed, if ever. The threat posed by the potential of exposure to ground water contamination will remain for a very long time at many sites, even with use of the best available technology. Therefore, a lasting institutional structure is necessary to monitor the long-term performance of the containment systems that will be needed to prevent contaminant migration and to restrict public access to the contaminated water until new technologies emerge for cleaning up the sites. The long-term effectiveness of any technical impracticability policy will depend on an institutional maintenance mechanism.

SUMMARY OF POLICY RECOMMENDATIONS

In summary, the committee believes that the EPA is making considerable progress in developing policies to address the fact that existing technologies may be unable to achieve current ground water cleanup goals at many sites. Nevertheless, improvements are needed in these policies to manage the large number of sites where technical limitations may present problems, to encourage wider use of innovative technologies, to assure consistent application of the policies, and to provide greater understanding of the factors preventing achievement of cleanup goals. Following are the committee's specific policy recommendations, developed from the committee's review of the policies discussed in this chapter in light of the technical limitations documented throughout this report.

Recommendation 1: **The committee recommends that in evaluating whether ground water cleanup is technically feasible, the EPA (and other agencies) categorize contaminated sites into three groupings corresponding to the complexity of the site.**

For sites in the first group (group A in Table 7-1), health-based ground water cleanup goals should be achievable with current technology. For sites in the second group (group B in Table 7-1), attainment of health-based goals may be difficult or unlikely with current technology but not necessarily impossible over the long term. Sites in this group would require an interim infeasibility process in which the long-term cleanup goal would be temporarily replaced—prior to construction of a full-scale cleanup system—with interim objectives reflecting the capabilities of existing technologies. On a regular basis, these sites would be reviewed to determine whether improved technology could achieve the long-term health-based goals. For sites in the third group (group C in Table 7-1), restoration to health-based standards is highly unlikely in reasonable time frames (decades). These sites would likely warrant permanent infeasibility waivers with the concomitant selection of a new protective long-term goal.

At sites that receive infeasibility waivers or interim cleanup objectives, it is extremely important to recognize that cleanup of part of the contaminated area may be possible with existing technologies. The technical limitations often apply only to limited areas, such as those where significant quantifies of contaminants are present as nonaqueous-phase liquids or as metal precipitates. Thus, the waiver or the interim objectives must account for the different levels of cleanup possible in different zones of the site.

Recommendation 2: **Although the committee recognizes that different agencies must operate under different authorities, all regulatory agencies should recognize that ground water restoration to health-based goals is impracticable with existing technologies at a large number of sites.**

The EPA and other regulatory agencies should work cooperatively to establish consistent mechanisms for deciding when cleanup is technically impracticable, whether revised long-term goals are warranted, and whether a phased cleanup process is appropriate. The complexities and limitations described in this report are a function of the nature of the contaminants and the hydrogeology of the site, not the identity of the agency or private party attempting to address the problem or the statutory authority or regulatory agencies involved.

Recommendation 3: **The committee recommends that the EPA prepare new guidance documents that will lead to improved optimization of the hazardous waste site characterization process and explicitly address factors that will determine whether health-based cleanup goals are practicable.**

The EPA should revise existing site characterization guidance for the Superfund and RCRA programs to ensure that factors influencing whether cleanup goals are achievable are addressed as early as possible. If the complexities of a site are not taken into account in the earliest stages of site investigation (for example, during the remedial investigation and feasibility study stages), the remedy selected could be inadequate, contaminant containment could be delayed or not achieved, and/or significant investigation and remedial costs could be wasted.

Recommendation 4: **For complex sites, the committee recommends that government and private entities use expert panels to evaluate site characterization, remedy selection, and remedy performance.**

At present, federal and state regulatory agencies have an insufficient number of technically trained staff to address the multitude of complex sites. While not a substitute for hiring and retaining technically trained staff, ground water advisory panels could provide guidance in addressing the often difficult technical choices at these sites. Funding for the advisory panels could come from Super fund or from the new infeasibility fee fund discussed in Recommendation 7, below. The EPA could also establish a user fee system to cover advisory panel involvement. The EPA or the lead regulatory agency would decide when to convene an advisory panel. However, interested private parties or the public could request help from or technical appeal to a panel.

Recommendation 5: **The committee recommends that the EPA establish a standardized, centralized, broadly accessible repository for site information.**

At present, it is virtually impossible to access the large amount of existing site data from completed and ongoing ground water remediation projects. The committee was confronted with this dilemma as it tried to examine existing data in order to identify patterns of behavior and potential recommendations. The committee believes that the EPA can facilitate a solution in two ways. First, the EPA could develop suggested formats for collection and analysis of site-specific information. The current lack of standard formats often leads to inadequate monitoring at sites because it is unclear what information is necessary to document problems or progress. Second, the EPA could establish an easily used, publicly accessible repository for site data. Such a data base would greatly facilitate the agency's own analyses and would enhance the public debate concerning ground water cleanup. The committee is not recommending the inclusion of all data from each site in a single data base; rather, the committee recommends that the data base include a brief description, data summary, and contact person for each site.

Recommendation 6: **The committee recommends that the EPA systematically evaluate its experience in cleaning up sites to improve understanding of factors that prevent achievement of health-based cleanup goals.**

Given its relatively long history compared to other ground water cleanup programs, the Superfund program has the potential to provide valuable centralized data on the performance of existing systems under a wide range of conditions. However, since its inception, Superfund has been implemented in a decentralized manner through the ten EPA regional offices. Consequently, data are not systematically collected across regions for review and evaluation. Because site-specific cleanup experience is rarely submitted for publication in peer-reviewed technical journals, it is especially important for the EPA to take the lead in gathering, assessing, and summarizing the information being generated at Super-fund sites to better understand current capabilities of ground water cleanup systems and to identify key areas for future research. While there are several ways to centralize data collection, the committee suggests that each EPA project manager develop a summary similar to those in the agency's recent study of pump-and-treat systems at 24 sites (EPA, 1992d). The project manager would update the summary as needed. On a regular basis, the EPA could publish technical findings developed from a careful review of all the summaries.

Recommendation 7: **The committee recommends that Congress investigate the possibility of charging an annual "infeasibility fee" to public and private responsible parties at sites where attaining health-based standards is not presently feasible.**

Congress could investigate various options for appropriating the funds collected from this fee. The committee sees two options as having special merit. One possibility is to use part of the funds to create an applied ground water research fund to pay for a strong research program for improved ground water cleanup techniques. The other possibility is to use some of the funds to encourage use of innovative cleanup technologies by reimbursing responsible parties for testing these technologies in certain circumstances. Under this scheme, the expert panel responsible for providing technical guidance at the site (see Recommendation 4) would approve use of an innovative technology. In the event that the innovative technology fails to achieve its intended goal and the responsible party is required to construct a backup technology, the responsible party would be able to recoup some or all of its losses from the infeasibility fee fund. If the innovative technology worked, the fund would not subsidize the project. Initially the fund might apply only to Superfund sites, but if successful it might be extended to other types of sites.

Recommendation 8: **The committee recommends that the EPA expand its efforts to inform the public about the limitations of existing technologies and the ability of innovative technologies to improve cleanup efforts.**

From the perspective of the affected public, the Superfund program has had limited success in responding to community concerns at many sites. This problem can in part be attributed to inadequate explanations about fundamental physical limitations of cleanup as well as unfounded optimistic promises about the likely pace or extent of site cleanup. Although the ground water cleanup problem is technically complex, the implications of site complexities as well as the promise that innovative technology holds to improve cleanups can and should be readily explainable to the general public. If the public is honestly informed of current capabilities and limitations of technology, it is more likely to participate as a constructive participant in subsequent site cleanup decisions. The committee believes that early site-specific public meetings, perhaps during initial scoping sessions, could provide key information to the public. The EPA should include expanded efforts at community relations within the technical impracticability waiver process or should revise its Super-fund community relations guidance documents to address issues of technical impracticability.

Recommendation 9: **The committee recommends that the EPA and other agencies identify and eliminate disincentives to early implementation of ground water remedial actions.**

An example of a policy that might eliminate disincentives to early action is one that would allow responsible parties to commit to only one phase of cleanup at a time instead of requiring them to agree to the entire remedy all at once. Such a policy might encourage more responsible parties to agree to early actions and might eliminate some of the legal battles that often ensue during the remedy selection phase. However, it might also increase transaction costs. The EPA should pilot test this concept to determine whether it results in faster cleanups or whether it slows the process because of the added regulatory burden.

Recommendation 10: **The committee recommends that the EPA assess and develop guidance on institutional strategies for preventing public exposure to contamination over the long term at sites where reaching health-based cleanup goals is infeasible with present technologies.**

An institutional structure capable of lasting for several generations will be needed to oversee the large number of sites at which complete cleanup is infeasible with current technologies. This institutional structure must include two components: (1) a long-term "memory" to ensure that the public remains aware of the risk posed by the site and (2) a long-term scheme for monitoring the site to ensure that the contamination is not spreading. While offering specific guidance on an approach for long-term maintenance is beyond the scope of this report, the importance of long-term maintenance to prevent public exposure to contamination in the future cannot be overemphasized.

NOTES

1. The Corrective Action Rule has not yet been finalized, primarily because of a presidential executive order issued during the Reagan administration requiring the EPA to assess economic impacts of all major regulations. However, RCRA site cleanups are being implemented today through the permit and enforcement order provisions of RCRA.

2. The EPA's current appeals process essentially consists of appealing to the supervisor of the person with whom one disagrees.

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Appendixes

A

Summary of Pump-and-Treat Systems Reviewed in this Study

Site	Contaminants
A [service station, location confidential] E	Gasoline
Advanced Micro Devices (Monolithic Mere.) [Sunnyvale, CA]A	Ethylbenzene; 1,2-DCE; PCE
Advanced Micro Devices (Bldg. 915) [Sunnyvale, CA]A	TCE; 1,2-DCE; TCA
Advanced Micro Devices (Bldgs. 901 & 902) [Sunnyvale, CA]A	TCE; 1,2-DCE
Ampex [Sunnyvale, CA]A	TCE; 1,2-DCE
Amphenol Corp. [Sidney, NY]B,C	Chloroform; TCE; PCE
Anacomp, Inc. (XIDEX) [Sunnyvale, CA]A	2-Methoxy ethanol; 1-methoxy 2-propanol; methylene chloride
Anacomp (Dysan Corp.) [Santa Clara, CA]A	MEK; isopropyl alcohol
Applied Materials (Bldg. 1) [Santa Clara, CA]A	TCA; 1,1-DCE; 1,1-DCA
Avantek [Santa Clara, CA]A	VC; TCE; 1,2-DCA
B [service station, location confidential] E	Unleaded gasoline
Black & Decker [Brockport, NY]B	VC; TCA; 1,2-DCE; TCE

				Results	
Site	Rank[1]	Flow Rate[2] (liters/ min)	Year Initiated	Containment Achieved	Cleanup Goals Achieved
2	140	1988	Uncertain	Yes	
4	160	1985	Yes	No	
4	270	1983	Yes	Partial[4]	
4	76	1983	Yes	No	
3	27	1985	Yes	No	
2	980	1987	Yes	No	
2	11	1987	Yes	No	
2	NP	1986	Yes[3]	Yes[5]	
4	80	1985	Uncertain	No	
3 or 4	19	1985	Uncertain	No	
3	23	1987	No	Yes	
4	38-57	1988	No	No	

Site	Contaminants
C [service station, location confidential][E]	Unleaded gasoline
CTS Printex, Inc. [Mountain View, CA][A]	TCE; TCA
D [service station, location confidential][E]	Unleaded gasoline
Des Moines TCE [Des Moines, IA][B,C]	VC; t-1,2-DCE; TCE
DuPont-Mobile [Axis, AL][B]	VOCs; pesticides
E [service station, location confidential][E]	Gasoline
Emerson Electric [Altamonte Springs, FL][B]	VOCs; MEK; MIBK; toluene
F [service station, location confidential][E]	Gasoline
Fairchild Semiconductor Corp. (NSC; Miranda Ave.) [Palo Alto, CA][A]	1,2-DCE; TCE; PCE
Fairchild Semiconductor [San Jose, CA][A,B]	TCA; 1,1-DCE; Freon; acetone
FEI Microwave, Inc. (TRW Microwave, Inc.) [Sunnyvale, CA][A]	VC; 1,2-DCE; TCE
Firestone Tire and Rubber [Salinas, CA][D]	TCA; 1,1-DCE; other VOCs
G [service station, location confidential][E]	Gasoline
General Mills [Minneapolis, MN][B,C]	TCA; TCE; PCE
GenRad Corp. (E. plume) [Bolton, MA][B,C]	TCE; other VOCs
Great Western/Stinnes-Western Chemical Corp. [Milpitas, CA][A]	TCE; TCA; PCE
H [service station, location confidential][E]	Gasoline
Harris Corp. [Palm Bay, FL][B,C]	VOCs
Hewlett-Packard (3500 Deer Creek Rd.) [Palo Alto, CA][A]	1,2-DCE; TCE
Hewlett-Packard (East Arques) [Sunnyvale, CA][A]	1,2-DCE; TCE
I [service station, location confidential][E]	Unleaded gasoline
IBM-Dayton [Dayton, NJ][B,C]	1,1-DCA; TCA; 1,1-DCE; TCE; PCE
IBM-San Jose [San Jose, CA][A,B,C]	TCA; 1,1-DCE; TCE; Freon 113; oil
INTEL Corp. (Middlefield-Ellis-Whisman plume) [Mountain View, CA][A]	VC; TCE; xylene

				Results	
Site	Rank[1]	Flow Rate[2] (liters/ rain)	Year Initiated	Containment Achieved	Cleanup Goals Achieved
2	19	1986	No	No	
4	210	1987	Yes	Partial[4]	
1	27	1986	Uncertain	No	
3	4,900	1987	Yes	No	
4	680	1985	No	NCG	
3	38	1985	Uncertain	NA	
2	110	1984	Yes	Yes[6]	
1	95	1986	Yes	Yes	
4	1	1985	Uncertain	No	
4	36,000B	1982	Yes	Partial[4]	
4	80	1985	Yes	No	
2 or 3	2,800	1986	Yes	Partial[7]	
3	120	1986	Yes	Yes	
4	1,400	1985	No	No	
2	150	1987	Yes	No	
4	110	1986	Yes	No	
3	53	1992	Uncertain	Yes	
2	1,200	1984	No	No	
4	42	1985	Yes	No	
4	30	1986	Uncertain	No	
3	76	1986	Yes	No	
3	3,800	1978	NA	No	
4	23,000B	1982	Yes	No	
4	2	1982	Yes[8]	No	

	Contaminants
INTEL Corp. (Facility III) [Santa Clara, CA][A]	TCA; TCE; Freon 113
Intersil/Siemens (Tantau Ave.) [Cupertino,CA][A]	TCA; TCE; Freon 113
J [pipeline leak, location confidential][E]	Gasoline; diesel; fuel oil
Jones Chemical [Milpitas, CA][A]	TCA; TCE; PCE
K [oil field brine site, location confidential][E]	Brine (8% chloride)
KTI Chemicals, Inc. [Sunnyvale, CA][A]	Odorless mineral spirits
L [refinery, location confidential][E]	Refined products
M [refinery, location confidential][E]	Refined products; lube oils; asphalt
Magnetics Peripherals, Inc. [Santa Clara, CA][A]	TCE; Freon
Memorex [Santa Clara, CA][A]	MEK; xylene; isopropyl alcohol
Micrel Wafer Fab, Inc./Litronix, Inc. [Sunnyvale, CA][A]	TCE
Micro Storage/INTEL Magnetics[Santa Clara, CA][A]	TCA; TCE
Mid-South Wood Products [Mana, AR][B]	PCP; PAHs; Cr; Cu
National Semiconductor [Santa Clara, CA][A]	1,1-DCE; TCA; TCE
Nichols Eng. [Hillsborough Township, NJ][B,C]	VOCs; CS2
Occidental Chemical [Lathtop, CA][B]	EDB; DBCP; other pesticides
Olin Corp. [Brandenburg, KY][B]	DCEE; DCIPE
Ponders Comer [Tacoma, WA][B,C]	t-1,2-DCE; TCE; PCE
Precision Monolithic Inc. [Santa Clara, CA][A]	1,2-DCE; TCE; Freon
River Park/Lincoln Prop. [San Jose, CA][A]	1,2-DCE; TCE; PCE
Signetics (811 E. Arques) [Sunnyvale, CA][A]	DCE; TCA; TCE
Savannah River Plant [Aiken, SC][B,C]	TCA; TCE; PCE
Sharpe Army Depot [Lathtop, CA][C]	TCE
Site A [cleaning compound manufacturing facility, south Florida; location confidential][B]	VC; t-1,2-DCE; benzene; 1,4-DCB; chlorobenzene
Solvent Service, Inc. [San Jose, CA][A]	1,2-DCE; TCE; acetone
Sylvester/Gilson Rd. [Nashua, NH][B,C]	Metals; VOCs; semivolatiles

				Results	
Site	Rank[1]	Flow Rate[2] (liters/ min)	Year Initiated	Containment Achieved	Cleanup Goals Achieved
3 or 4	38	1985	Yes	Partial[4]	
4	190	1987	Yes	No	
3	1,300	1988	No	No	
4	420	1987	Uncertain	No	
2	83	1989	Yes	No	
3	34	1985	Yes	No	
3	6,100	1988	Uncertain	NA	
3	4,500	1984	Uncertain	NA	
3 or 4	19	1985	Yes	Partial[4]	
3	110	1986	Yes	Partial[4]	
4	110	1986	Yes	No	
3 or 4	30	1984	Yes	No	
4	160	1985	No	Partial[4]	
4	580	1985	Uncertain	No	
3	250	1988	NA	No	
3	2,300	1982	No	No	
3	24,000	1974	Yes	NCG	
2	7,600	1984	No	No	
3 or 4	310	1985	No	Partial[4]	
3 or 4	1,200	1988	Yes	No	
4	340	1982	Yes	No	
4	2,100	1985	No	NCG	
3	760	1988(?)[9]	Yes	No	
2	190	1988	NA	Partial[4]	
4	4	1985	Yes	No	
4	1,100	1981	No	No	

Site	Contaminants
Synertek Bldg. 1 (Honeywell) [Santa Clara, CA]^{A}	1,1-DCE; TCA; TCE
Synertek Bldg. 3 (Honeywell) [Santa Clara, CA]^{A}	Acetone; xylenes; TCA
Technical Coatings [Santa Clara, CA]^{A}	Toluene; xylene; MIBK
Teledyne Semiconductor/Spectra Physics [Mountain View, CA]^{A}	TCE
Twin Cities AAP [New Brighton, MN]^{C}	TCE
Tyson's Dump [King of Prussia, PA]^{B}	Trichloropropane; other VOCs; ethyl benzene; toluene; xylene
United Chrome [Corvallis, OR]^{C}	Cr(VI)
Utah Power & Light [Idaho Falls, ID]^{B}	Creosote
Van Waters & Rogers, Inc. [San Jose, CA]^{A}	TCA; PCE; 1,2-DCE
Varian Associates (Palo Alto) [Palo Alto, CA]^{A}	1,2-DCE; TCA; TCE
Varian Associates (Santa Clara) [Santa Clara, CA]^{A}	TCA
Verona Well Field [Battle Creek, MI]^{B,C}	VOCs
Ville Mercier [Quebec, Canada]^{B}	Organics
Western Processing [Kent, WA]^{B}	Metals; organics
Wurtsmith AFB [Wurtsmith, MI]^{C}	TCE; t-1,2-DCE

NOTES AND ABBREVIATIONS

1. Rank is based on the criteria presented in Table 3-2.
2. Flow rates are based on first-quarter 1992 monitoring data for A sites and on maximum pumping rates for B, C, D, and E sites.
3. Not pumping; pumps shut off in February 1991. Containment was achieved when pumping.
4. Selected contaminants have been cleaned up; other contaminants remain above cleanup levels.
5. Pending final review by the San Francisco Bay Regional Water Quality Control Board.
6. Site has been dosed by the state regulatory agency, but no new monitoring data exist to verify cleanup.
7. Cleanup goals reached everywhere except in a small off-site area.
8. On-site area only; plume is commingled off site.
9. A "?" indicates that the "year initiated" has been estimated.

				Results	
Site	Rank[1]	Flow Rate[2] (liters/ min)	Year Initiated	Containment Achieved	Cleanup Goals Achieved
3 or 4	45	1987	Yes	No	
2	4	1987	Yes	Yes	
3	8	1987	Uncertain	No	
4	810	1986	Yes	No	
4	10,000	1988(?)[9]	Yes	No	
4	450	1988	No	NCG	
3	64	1988(?)[9]	NA	No	
4	760	1985	No	NCG	
4	42	1986	No	No	
4	95	1987	Yes	No	
3 or 4	61	1985	Yes	Partial[4]	
4	9,100	1984	No	No	
4	2,800	1983	NA	NA	
4	830	1988	No	NA	
2 or 3	1,100	1978	NA	No	
	5,500	1982			

NA - data not available
NCG - plume containment was the remedial goal.
NP - not pumping
Uncertain - may indicate either a poorly designed monitoring well network or a lack of water level data.

Site References

A. Sites reviewed in the San Francisco Bay Regional Water Quality Control Board's study.
B. Sites reviewed in the EPA's 24-site study.
C. Sites reviewed in the University of Tennessee's study.
D. Site not reviewed in any formal study.
E. Sites reviewed in the American Petroleum Institute's study.

Chemical Names

Cr	chromium
CS_2	carbon disulfide
Cu	copper
DBCP	dibromochloropropane
1,1-DCA	1,1-dichloroethane
1,4-DCB	1,4-dichlorobenzene
DCE	dichloroethene (unspecified isomer)
1,1-DCE	1,1-dichloroethene
1,2-DCE	1,2-dichloroethene
t-1,2-DCE	trans-1,2-dichloroethene
DCEE	dichloroethyl ether
DCIPE	dichloroisopropyl ether
EDB	ethylene dibromide
Freon 113	1,1,2-trichlorotrifluoroethane
MEK	methyl ethyl ketone
MIBK	methyl isobutyl ketone
PAH	polynuclear aromatic hydrocarbon
PCE	tetrachloroethene
PCP	pentachlorophenol
TCA	1,1,1-trichloroethane
TCE	trichloroethene
VC	vinyl chloride
VOC	volatile organic chemical

B

Glossary

Abiotic	Refers to chemical transformations that occur without the aid of microorganisms.
Adsorption	The adherence of ions or molecules in solution to the surface of solids.
Advection	The process whereby solutes are transported by the bulk mass of flowing fluid.
Aerobic biodegradation	The degradation of compounds by microorganisms in the presence of oxygen. In aerobic biodegradation, microorganisms convert oxygen to water in the process of transforming other compounds to simpler products.
Air sparging	The injection of air below the water table to strip volatile contaminants from the saturated zone and to promote contaminant biodegradation.
Aliphatic hydrocarbons	A class of compounds built from carbon and hydrogen joined in open chains.
Alkane	A chemical composed of a straight chain of carbon atoms bonded on all sides by hydrogen atoms and containing no double bonds between carbon atoms. The simplest alkane is methane.
Alkene	A chemical composed of a straight chain of carbon and hydrogen atoms containing at least one double bond between carbon atoms. The simplest alkene is ethene (also known as ethylene).
Amphiphilic	A compound, such as a surfactant, that has an end with

	an affinity for water and an end with an affinity for substances that lack an affinity for water.
Anaerobic biodegradation	The degradation of compounds by microorganisms in the absence of oxygen.
Analytical model	A model that can be solved using classical mathematical tools, such as differential equations.
Anoxic	Describes an environment without oxygen.
Aquifer	An underground geologic unit that stores ground water.
Aquitard	A bed of subsurface materials that retards but does not prevent the flow of water from an upper aquifer to a lower aquifer.
Area of attainment	The area in which cleanup standards are to be achieved.
Aromatic hydrocarbon	A chemical formed from benzene rings, originally called "aromatic" because of its distinctive aroma.
Bedding plane	A plane that separates layers in the subsurface.
Bioavailability	The availability of a compound for biodegradation, influenced by the compound's location relative to microorganisms and its ability to dissolve in water.
Biodegradation	The biologically mediated conversion of a compound to simpler products.
Bioremediation	Exploiting the metabolic activity of microorganisms to transform or destroy contaminants.
Biotransformation	Chemical alteration of organic compounds brought about by microorganisms.
Bioventing	The process of passing air through the soil to stimulate biodegradation of organic contaminants. The goal is to maximize aerobic biodegradation while minimizing volatilization.
BTEX	An acronym for benzene, toluene, ethylbenzene, and xylenes, which are volatile, monocyclic aromatic compounds present in coal tar, petroleum products, and various organic chemical product formulations.
Buffering capacity	The capacity of water in a specific location to maintain its pH by neutralizing added acids or bases.
Capillary force	A force that draws a fluid into the small interstices in the subsurface.
Capillary fringe zone	The zone immediately above the water table.
Carbonate	A rock formed primarily from carbonate minerals, such as limestone and dolomite.
CERCLA	See "Comprehensive Environmental Response, Compensation, and Liability Act of 1980."

Chemotaxis	The movement of bacteria toward a chemical that they may use as an energy source.
Chlorinated solvent	A solvent containing at least one chlorine atom in its chemical structure. Typically, these compounds are used to dissolve substances that do not dissolve easily in water. Because they are used for a wide variety of purposes—from manufacturing, to degreasing, to dry cleaning—chlorinated solvents are common ground water contaminants.
Colloid	A particle that has a diameter in the range of 10^{-8} to 10^{-5} meters. The small size of colloids tends to keep them in suspension for long time periods.
Cometabolism	The simultaneous metabolism of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate). For example, in the process of degrading methane, some bacteria can degrade hazardous chlorinated solvents that they would otherwise be unable to attack.
Complexation	A reaction in which a metal ion and one or more anionic ligands chemically bond. Complexes often prevent the precipitation of metals.
Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA)	A law that established a national program to respond to past releases of hazardous substances into the environment. CERCLA created the "Superfund" for financing remedial work not undertaken by responsible parties. Approximately 1,200 sites are scheduled for cleanup under the CERCLA program.
Confined aquifer	An aquifer bounded above and below by units of distinctly lower hydraulic conductivity and in which the pore water pressure is greater than atmospheric pressure.
Confining bed	A subsurface layer that inhibits the downward flow of water.
Conservative solute	A chemical that does not react with the soil or ground water or undergo biological, chemical, or radioactive decay.
Containment	Refers to systems that prevent the further spread of contamination. These systems control the ground water flow direction around the contaminated site by using pumps, injection wells, and cutoff walls placed at strategic locations.
Conventional pump-and-treat systems	Systems that extract contaminated ground water and treat it at the surface.
Cosolvent	A compound that enhances the water solubility of organic contaminants.
Cyclic hydrocarbon	A chemical composed of carbon and hydrogen atoms bonded in ring structures.

Darcy's Law	A formula used to describe fluid flow in the subsurface. The law states that the velocity of flow through a porous medium is directly proportional to the hydraulic gradient (assuming that the flow is laminar and that inertial forces can be neglected).
Dechlorination	A process whereby chlorine atoms are removed from a compound. Complete dechlorination makes compounds less toxic and easier to biodegrade.
Denitrification	The conversion of nitrate to nitrogen gas by microorganisms. Denitrification can be an important process in the subsurface, because when oxygen is absent, denitrifying bacteria can use nitrate to degrade hazardous compounds in the same way that they would ordinarily use oxygen.
Density	The mass per unit volume of a substance.
Desorption	The release of sorbed molecules from the solid into solution (the reverse of sorption).
Diffusion	Contaminant movement caused by the random motion of molecules. Contaminants diffuse from areas of high concentration to areas of low concentration.
Dispersion	The spreading and mixing of chemical constituents in ground water. Dispersion is caused by diffusion and mixing due to microscopic variations in velocities within and between pores as well as by macroscopic velocity variations among zones of differing hydraulic conductivity.
Dissolution	The process by which solid or nonaqueous-phase liquid components of a contaminant dissolve in infiltration water and form a ground water contaminant plume. The duration of remediation measures (either cleanup or long-term containment) is determined by the rate of dissolution that can be achieved in the field and the mass of soluble contaminants.
DNAPL	An acronym for denser-than-water nonaqueous-phase liquid— an organic liquid, composed of one or more contaminants, that does not mix with water and is denser than water. The most common DNAPL contaminants in ground water are chlorinated solvents.
Electron acceptor substrate	See "Substrate."
Electron donor substrate	See "Substrate."
Enhanced oil recovery	Processes (such as cosolvent or steam flooding) for recovering additional oil (or other nonaqueous-phase liquids) from the subsurface.
Enzyme	A protein that a living organism uses in the process of degrading a specific compound. The protein serves as a catalyst in the compound's biochemical transformation.

Extraction well	A well used to remove contaminated ground water from the subsurface.
Facultative anaerobe	A type of bacteria that can function with or without oxygen. Because the oxygen supply in ground water is often limited, these bacteria can be important players in degrading subsurface contaminants.
Feasibility study	A study carried out at a hazardous waste site covered under the Comprehensive Environmental Response, Compensation, and Liability Act to determine possible remedies for contamination at the site.
Fiber spectroscopy	A remote method for determining contaminant presence or concentration in water by sending a light pulse down a light-transmitting fiber whose end is submerged in the water (for example, through a well) and interpreting a signal returned via that or another fiber.
Fixation	Mixing of contaminated soils with a chemical stabilizer, usually a cementatious grout compound.
Fixed-film reactor	A laboratory vessel used to simulate microbial activity in the subsurface. The vessel is filled with a granular material, such as sand, with films of bacteria attached to the surfaces of the material.
Fraction of organic carbon	A soil's organic carbon content, expressed as a mass fraction of the dry soil.
Fractured medium	A large subsurface rock or clay formation that is mostly solid but contains cracks that can transmit or store water.
Free liquid diffusivity	The diffusion coefficient for a solute in a dilute aqueous solution.
Functional group	A reactional component of a chemical compound.
Gas chromatograph	An instrument used to identify volatilizable chemical contaminants in water.
Geomorphology	The features of the earth's surface.
Halogenated compound	A compound in which one or more hydrogen atoms have been replaced by a halogen atom, such as fluorine, chlorine, or bromine. Examples include chlorinated solvents (such as 1,1,1-trichloroethane, trichloroethylene, and tetrachloroethylene), which have been widely used in cleaning and degreasing operations in some fumigant pesticides. Many halogenated compounds are DNAPLs.
Henry's Law constant	The equilibrium ratio of the partial pressure of a compound in air to the concentration of the compound in water at a

	reference temperature. It is sometimes referred to as the air-water partition coefficient.
Heterogeneity	Refers to nonuniformity in properties of a subsurface porous medium.
Homogeneity	Refers to subsurface media that are relatively uniform.
Horizontal well	A well placed horizontally in the subsurface, through which water may be injected or extracted or air may be injected to aid the volatilization of contaminants.
Humic substance	A macromolecular organic substance formed from the decomposition of plant or animal material.
Hydraulic barrier	A barrier to flow caused by system hydraulics, such as a line of ground water discharge caused by extraction wells.
Hydraulic conductivity	A measure of the volume of water at the existing kinematic viscosity that will move in a unit time under a unit hydraulic gradient through a unit area of medium measured at right angles to the direction of flow.
Hydraulic containment	See "Containment."
Hydraulic gradient	The change in head per unit distance in a given direction, typically in the principal flow direction.
Hydrolysis	A chemical reaction that involves splitting one chemical bond and adding the elements of water.
Hydrophilic	"Water loving"; refers to compounds that are highly water soluble.
Hydrophobic	"Water fearing"; refers to substances that are relatively insoluble in water.
Igneous rock	A rock that solidified from molten material. "Igneous" is one of the three categories (igneous, metamorphic, and sedimentary) into which all rocks are divided.
Immunoassay	A method used to detect whether contaminants are present based on their ability to bind to antibodies produced by a living organism in response to the contaminant.
In situ	In place, i.e., within the contaminated aquifer itself.
In situ vitrification	The heating of the subsurface to extremely high temperatures to destroy organic contaminants. Upon cooling, the subsurface solidifies, incorporating inorganic contaminants and ash.
Infiltration gallery	A trench, basin, or sprinkler system used to add nutrients and energy sources to the subsurface to stimulate the growth of bacteria that can degrade hazardous compounds.
Injection well	A well through which fluids (water or air) are injected into the subsurface.
Interfacial tension	A measure of the forces at the interface between two fluids.

Interphase mass transfer	The net transfer of chemical compounds between two or more phases.
Interstitial velocity	A measure of the speed at which water travels through pores and other openings underground. More precisely, it is the rate of discharge of ground water per unit area of the geologic medium per percentage volume of the medium occupied by voids measured at right angles to the direction of flow.
Intrinsic permeability	A measure of the relative ease with which a porous medium can transmit a liquid under a potential gradient. Intrinsic permeability is a property of the medium and is dependent on the shape and size of the openings through which the liquid moves.
Ion	A molecule that has a positive or negative electric charge.
Ion exchange	The exchange of ions between a solution and a solid while maintaining charge balance. Through ion exchange, charged molecules that are naturally part of the subsurface soil may be replaced by contaminant molecules.
Isotherm	An equation that relates the mass of contaminant sorbed to a solid to the concentration of the contaminant in solution at equilibrium.
Isotope Refers	to the fact that a chemical element in the periodic table may have two or more species that behave nearly identically chemically but have different atomic masses and physical properties.
Kinetic	Refers to the speed of a process.
Kriging	A statistical procedure that geologists use to characterize the subsurface; kriging maximizes the information obtained from a given number of samples.
Leachate	The liquid that leaks from a contaminant source as water percolates through the source area and leaches chemicals from the waste.
Lens	A geologic deposit bounded by converging surfaces, in a shape similar to a convex lens.
Lenticular	Layered.
Lithology	A description of the rocks beneath the ground at a site.
LNAPL	An acronym for less-dense-than-water nonaqueous-phase liquid. LNAPLs do not mix well with water and are less dense than water. Gasoline and fuel oil are common LNAPLs.
Mass balance	An attempt to determine the fate of a compound in a unit of space by evaluating all possible sources and sinks of the compound in the space, applying the principle of mass conservation.
Mass spectrometer	An instrument used to identify the chemical composition of a fluid.

Mass transfer	The transfer of contaminant mass from one medium to another. Mass transfer from an undissolved contaminant pool to water occurs through dissolution; mass transfer from a contaminant pool or water to air occurs through volatilization.
Maximum contaminant level (MCL)	The maximum amount of a compound allowed in drinking water under the Safe Drinking Water Act. MCLs are set by considering both health effects of the compound and technical feasibility of removing the compound from the water supply.
Maximum contaminant levels goal (MCLG)	Nonenforceable health goals established under the Safe Drinking Water Act intended to protect against known and anticipated adverse human health effects with an adequate margin of safety. Technical feasibility is not considered in setting MCLGs.
Metabolism	The chemical reactions in living cells that convert food sources to energy and new cell mass.
Metamorphic rock	A rock created from preexisting rocks in response to changes in temperature, pressure, shearing stress, or chemical environment.
Methanogenesis	The production of methane by bacteria. Because they thrive without oxygen, methanogenic bacteria can be important players in the subsurface, where oxygen is often absent.
Methanotrophic bacteria	Bacteria that grow using methane as their primary energy source. Methanotrophic bacteria may be important in cleaning up ground water, because in the process of degrading methane, they may also metabolize hazardous contaminants that are ordinarily resistant to biodegradation.
Micelie	A colloidal aggregate of amphiphilic molecules. The interior of micelles is hydrophobic and can dissolve hydrophobic contaminants.
Mineralization	The complete conversion of an organic compound to inorganic products.
Miscibility	The ability of two liquids, such as alcohol and water, to mix without splitting into separate phases.
Model	An attempt to represent processes, such as water and contaminant flow, by mathematical equations.
Monitoring well	A tube or pipe, open to the atmosphere at the top and to water at the bottom, used for taking ground water samples.
Monomer	A molecule that can combine with like molecules to form a polymer.
NAPL	An acronym for nonaqueous-p hase liquid, a liquid consisting of organic compounds that are not completely miscible with water (see also "DNAPL" and "LNAPL").
National Oil and Hazardous Substances Pollution Contingency Plan (NCP)	The regulation describing how the mandates from Congress specified in the Comprehensive Environmental Response, Compensation, and Liability Act will be carried out in practice.

Numerical model	A model whose solution must be approximated by varying the values of controlling parameters and using computers to solve approximate forms of the model's governing equations.
Octanol-water partition coefficient	A measure that indicates the extent to which a compound is attracted to an organic phase (for which octanol is a proxy) and hence the compound's tendency to sorb to subsurface materials. It is computed by dividing the amount that will dissolve in octanol by the amount that will dissolve in water. The greater the value, the greater the tendency to sorb in the subsurface.
Olefin	Synonymous with "alkene."
Organic carbon partition coefficient	A measure that indicates the extent to which a compound will sorb to the solid organic content of geologic media in the subsurface. It is computed as the ratio of the amount of chemical sorbed per unit weight of organic carbon in the soil to the concentration of the chemical in solution at equilibrium.
Oxic	Describes an environment that contains oxygen.
Oxidation reaction	The transfer of electrons away from a compound to another compound. Oxidation reactions are important in the destruction of contaminants. They may occur spontaneously when the appropriate chemicals are mixed, or they may be catalyzed by microorganisms. For example, when microbes degrade organic compounds, they may transfer electrons away from the compound, converting the compound to carbon dioxide and deriving energy from the electron transfer process.
Partition coefficient	A term used to describe the relative amount of a substance partitioned between two different phases, such as a solid and a liquid. It is the ratio of the chemical's concentration in one phase to its concentration in the other phase.
Partitioning	A chemical equilibrium condition in which a chemical's concentration is apportioned between two different phases according to the partition coefficient.
Permeability	A measure of the relative ease with which fluids will flow through subsurface materials.
Pleistocene	A geologic time period associated with the Ice Age.
Plume	A zone containing predominantly dissolved contaminants and sorbed contaminants in equilibrium with the dissolved contaminants. A plume usually will originate from the contaminant source areas

	and extend downgradient for some distance, depending on site hydrogeologic and chemical conditions.
Polar molecule	A molecule that has a center of positive charge and a center of negative charge; polar compounds are usually hydrophilic.
Polychlorinated biphenyl (PCB)	A type of contaminant built from two benzene rings and chlorine atoms. PCBs are very stable, resisting both chemical and biological degradation, and are toxic to many species. At one time, they were used commonly in electrical transformers as heat insulators.
Polycyclic aromatic hydrocarbon (PAH)	A compound built from two or more benzene rings. Sources of PAHs include fossil fuels and incomplete combustion of organic matter (in auto engines, incinerators, and even forest fires).
Pore	A small pace between the grains of sand, soil, or rock in the subsurface. Ground water is stored and transmitted in pores.
Pore volume	The total volume in the pores in a given section of the subsurface. This term often is used to describe the volume of water that is contained within a contaminant plume.
Porosity	The volume of open spaces in the subsurface.
Porous medium	A subsurface zone composed of small rocks or sand particles with pores that can transmit or store water.
Primary substrate	A substance that can supply microorganisms with energy for growth and reproduction.
Pulsed pumping	An enhancement to a pump-and-treat system in which extraction wells are periodically not pumped. This method theoretically allows contaminant concentrations in the readily extracted ground water to increase by contaminant mass transfer from various subsurface zones in which the contaminants are retained.
Rate-limiting step	The step in a process that limits the speed at which the process can occur.
RCRA	See "Resource Conservation and Recovery Act."
Recharge	The replenishment of water beneath the earth's surface, usually through percolation through soils or connection to surface water bodies.
Record of Decision	A document issued by the Environmental Protection Agency specifying the remedy for contamination at a site covered under the Comprehensive Environmental Response, Compensation, and Liability Act.
Redox potential	Describes the distribution of oxidized and reduced species in a solution at equilibrium. Redox potential is important for predicting the likelihood that metals will precipitate from ground water upon pumping, for estimating the capacity of microorganisms

to degrade contaminants, and for predicting other subsurface reactions.

Reduction reaction	The transfer of electrons to a compound from another compound (see also "oxidation reaction"). Oxidation-reduction reactions are important in the destruction of contaminants. They may occur spontaneously, when the appropriate chemicals are combined, or they may be catalyzed by microorganisms. For example, when microbes degrade organic compounds, they may transfer electrons from the compound to oxygen, converting the oxygen to water.
Reductive dechlorination	A process whereby bacteria remove a chlorine atom from a chlorinated compound and replace it with a hydrogen atom.
Refractory	Resistant to biodegradation.
Remedial action objective	A description of remedial goals for each medium of concern at a site, expressed in terms of the contaminant(s) of concern, exposure route(s) and receptor(s), and maximum acceptable exposure level(s).
Remedial investigation (RI)	A study carried out at a hazardous waste site covered under the Comprehensive Environmental Response, Compensation, and Liability Act to determine the extent of contamination and the risk it poses.
Residence time	The average amount of time a fluid spends during transport through a unit volume of subsurface or a laboratory vessel.
Residual saturation	The ratio of the volume of contaminant trapped in subsurface pore spaces to the total volume of pore spaces. If the level of contaminants trapped in the pore spaces is below residual saturation, the contaminants will not drain from the pores. For example, as oil moves through soil, it leaves oil trapped in the soil pores at residual saturation.
Resource Conservation and Recovery Act (RCRA)	A law that regulates monitoring, investigation, and corrective action at operating hazardous treatment, storage, and disposal facilities. RCRA will provide the framework for environmental investigations and cleanup at an estimated 5,000 operating facilities.
Retardation	The movement of a solute through a geologic medium at a velocity less than that of the ground water. Retardation is caused by sorption and other phenomena that separate a fraction of the solute mass from the bulk ground water.
Retardation coefficient	A measure of how quickly a contaminant moves through the ground compared to water. It is computed as the ratio of the total contaminant mass in a unit aquifer volume to the contaminant mass in solution.

Risk assessment	An evaluation of the potential for exposure to contaminants and the associated hazard.
Risk-based concentration	A contaminant concentration determined from an evaluation of the compound's overall risk to human health.
Safe Drinking Water Act	The law, passed in 1974, that required the setting of standards to protect the public from exposure to contaminants in drinking water.
Saturated zone	The part of the subsurface that is beneath the water table and is saturated with water.
Second Law of Thermodynamics	A physical law that determines the direction of energy flow, such as the flow of heat from a warm body to a cooler body, or the irreversible conversion of work into heat caused by friction.
Secondary substrate	A substance that can be metabolized or transformed by microorganisms but that yields little or no energy for the organisms.
Sedimentary rock	A rock created from the consolidation of loose sediment that has accumulated in layers.
Site characterization	An attempt to identify the types and sources of contaminants present at a site and the site's hydrogeologic characteristics.
Slurry wall	A barrier constructed in the subsurface to prevent the spread of contaminants.
Soil flushing	The forced circulation (e.g., by use of injection and extraction wells) of water, steam, cosolvents, surfactants, or other fluids to enhance the recovery of contaminants (i.e., immiscible, dissolved, or adsorbed) from soil.
Solidification/stabilization	Processes that use cementing agents to mechanically bind subsurface contaminants and thereby reduce their rate of release.
Sorption	Refers to processes that remove solutes from the fluid phase and concentrate them on the solid phase of a medium.
Source area	The area at a contaminated site containing waste remaining in place. The source area may stretch beyond the original contaminant spill site; included in the committee's definition of source area are regions along the contaminant flow path where contaminants are present in precipitated or nonaqueous-phase liquid form.
Source control	A set of processes designed to prevent the spread of contaminants from the areas where the contaminants were originally spilled or areas where migrating contaminants have accumulated.
Source of contamination	A reservoir of contamination existing in a separate phase from water. The primary source of contamination is near

the site where the contaminant was originally spilled. However, some types of contaminants may travel long distances as separate phases from the water or may precipitate in mineral form at considerable distances from the original spill site.

Specific gravity	The density of a liquid divided by the density of water.
Steam stripping	The use of steam to heat the subsurface and aid contaminant volatilization.
Storage coefficient	The volume of water released by pressure changes per unit area during pumping in a confined aquifer. This property influences the quantity of water that can be obtained by pumping.
Stratigraphy	The arrangement of rock strata in the subsurface.
Substrate	A substance metabolized or transformed by microorganisms. An "electron donor substrate" may be thought of as a food source; the microbes degrade it to provide energy for cell growth. An "electron acceptor substrate" is oxygen or another substance that microbes use in the process of digesting the electron donor substrate; the organisms transfer electrons from the electron donor to oxygen (or another electron acceptor), obtaining energy from the transfer.
Sulfate reduction	The conversion of sulfate to hydrogen sulfide by microorganisms. Because they can degrade hazardous compounds without using oxygen, sulfate-reducing bacteria can be important players in the subsurface, where the oxygen supply is often limited.
Surface tension	The tension at the surface between a liquid and its own vapor.
Surfactant	Soap or a similar amphiphilic substance that bonds to oil and other immiscible compounds to aid their transport in water.
Surficial aquifer	An aquifer near the earth's surface, in the most recent of geologic deposits.
Tailing	The slow, nearly asymptotic decrease in contaminant concentration in water flushed through contaminated geologic material.
Tracer test	A method used to determine the flow of ground water or other fluids in the subsurface. It is conducted by injecting a nonreactive "tracer" chemical in the subsurface and monitoring its migration.
Treatment train	The combination of several remedial actions, such as a pump-and-treat system for ground water contamination combined with vacuum extraction for soil contamination.
Unsaturated zone	The soil above the water table, where pores are partially (or largely) filled with air.

Vacuum extraction	A method for removing volatile contaminants from the soil above the water table.
Vadose zone	The subsurface zone that extends between the ground surface and the water table and includes the capillary fringe overlying the water table.
Vapor extraction	See "Vacuum extraction."
Viscosity	An indicator of the ease with which a fluid will flow. The less viscous a fluid, the more easily it will flow.
Volatile organic compound (VOC)	An organic chemical that volatilizes (evaporates) relatively easily when exposed to air.
Volatilization	The transfer of a chemical from the liquid to the gas phase.
Water table	The "top" of the subsurface zone that is saturated with ground water. More precisely, it is the surface in an aquifer at which pore water pressure is equal to atmospheric pressure.
Water-table aquifer	An aquifer in which the water table forms the upper boundary.
Wellhead treatment	Treatment of extracted water to remove chemicals prior to the water's distribution for drinking. This differs from complete cleanup of an aquifer, because only the water that will be used for drinking—not all the water at the contaminated site—is treated.
Wettability	The ability of a liquid traveling through the subsurface to form a film on the solid material in the subsurface.
Zone of capture	The area surrounding a pumping well that encompasses all areas or features that supply ground water recharge to the well.
Zone of influence	The area surrounding a pumping or recharging well within which the water table or potentiometric surface has been changed due to the well's pumping or recharge.

C

Biographical Sketches of Committee Members and Staff

Committee Members

MICHAEL C. KAVANAUGH, who chaired the committee, is currently a principal with ENVIRON Corporation in Emeryville, California. During the study, he was senior vice president of the consulting firm Montgomery-Watson, Inc., and director of the Environmental Management Division of Montgomery-Watson, Ltd., located in the United Kingdom. He is a chemical and environmental engineer with more than 23 years of experience in all aspects of environmental engineering, including technical and managerial responsibility for more than 50 sites requiring soil or ground water remediation. He is also a consulting professor of environmental engineering at Stanford University. Prior to chairing this committee, he chaired the Water Science and Technology Board. He received a Ph.D. in sanitary engineering in 1974 from the University of California, Berkeley.

JAMES W. MERCER, who served as vice-chair of the committee, is a hydrogeologist and president of GeoTrans, Inc., which specializes in analysis of hydrogeologic transport, including ground water flow and solute transport in porous media. Previously a hydrologist with the U.S. Geological Survey's Water Resources Division, he has served on an advisory panel on national ground water contamination for the Office of Technology Assessment and on National Research Council committees on ground water contamination and ground water models. He received a Ph.D. in geology from the University of Illinois in 1973.

LINDA M. ABRIOLA, associate professor in the Department of Civil and Environmental Engineering at the University of Michigan, researches processes that influence aquifer remediation. Currently, she is investigating organic vapor transport mechanisms, entrapped organic liquid residual partitioning and mobilization, and bioremediation of solute plumes. In 1985, she received a National Science Foundation Presidential Young Investigator award. Dr. Abriola earned a Ph.D. in civil engineering from Princeton University.

CHARLES B. ANDREWS, president of S. S. Papadopulos & Associates, directs projects involving quantitative ground water hydrology. His areas of expertise include formulation of ground water projects, modification and development of numerical simulation models for adaptation to specific field projects, and evaluation of contaminant and energy transport in ground water systems. His current interests include developing techniques for quantifying the risk associated with a given level of ground water contamination when only limited data are available. Dr. Andrews previously served as senior project hydrologist with Woodward-Clyde Consultants, where he worked on projects that included managing cleanup of Superfund sites. He earned a Ph.D. in geology from the University of Wisconsin.

MARY JO BAEDECKER is a research chemist for the U.S. Geological Survey's Water Resources Division. Her research interests include the degradation of organic chemicals in shallow aquifers. In 1988, she received the U.S. Geological Survey's Special Achievement and Superior Service awards. She received an M.S. in chemistry from the University of Kentucky in 1967 and a Ph.D. in geochemistry from George Washington University in 1985.

EDWARD J. BOUWER is a professor of environmental engineering at Johns Hopkins University. His research interests include biodegradation of hazardous organic chemicals in the subsurface, biofilm kinetics, water and waste treatment processes, and transport and fate of bacteria in porous media. He is on the board of directors for the Association of Environmental Engineering Professors and serves on the editorial boards for *The Journal of Contaminant Hydrology* and *Biodegradation* . He received a Ph.D. in environmental engineering and science from Stanford University in 1982.

PATRICIA A. BUFFLER is dean and professor of epidemiology at the School of Public Health at the University of California, Berkeley. Before 1992, she was professor and director of the Epidemiology Research Unit and Southwest Center for Occupational and Environmental Health at the University of Texas Health Sciences Center in Houston. She has extensively researched the health effects of environmental and workplace exposure to contaminants, focusing specifically on cancer, pulmonary dis eases, and reproductive outcomes. She is currently president of the International Society for Environmental Epidemiology. She received a Ph.D. in epidemiology from the University of California, Berkeley.

ROBERT E. CONNICK is professor emeritus at the University of California, Berkeley. A pioneer in the investigation of plutonium's fundamental properties, his expertise is in physical chemistry. From 1943 until 1946, he worked as a research associate on the Manhattan Project. In 1945, he began his term as a professor of chemistry at the University of California, serving as department chair from 1958 until 1960, as college of chemistry dean from 1960 until 1965, and as university vice chancellor from 1969 until 1971. He was elected to the National Academy of Sciences in 1963. He received a Ph.D. in chemistry from the University of California in 1942.

RICHARD A. CONWAY is a senior corporate fellow at Union Carbide Corporation. His areas of expertise include petrochemical wastewater treatment, hazardous and solid waste management, and environmental risk analysis of chemical products. He chairs the Environmental Engineering Committee of the Environmental Protection Agency's Science Advisory Board, currently serves as a member of the National Research Council's Commission on Engineering and Technical Systems, and was elected to the National Academy of Engineering in 1986. He received a B.S. in public health in 1953 from the University of Massachusetts and an M.S. in sanitary engineering from the Massachusetts Institute of Technology in 1957.

RALPH C. D'ARGE is John S. Bugas Distinguished Professor of Economics at the University of Wyoming, where he researches environmental economics. His areas of expertise include the valuation of natural resources and the interactions between pollution and economic growth. Dr. d'Arge has served on the National Research Council's Environmental Studies Board and on several Research Council committees. He was a founding editor of the *Journal of Environmental Economics and Management*. He received a Ph.D. in economics from Cornell University in 1969.

LINDA E. GREER, senior project scientist for the Natural Resources Defense Council (NRDC), directs technical work and policy analysis related to toxic chemicals and hazardous wastes. She coauthored *Dumpsite Clean-Ups: A Citizens Guide to the Superfund Program*, published by the Environmental Defense Fund. Before joining NRDC, she worked for several years as a private consultant on hazardous waste technical and policy issues for the Environmental Protection Agency, CH2M Hill, and law firms. She served on the National Research Council's Committee on Hazardous Wastes in Highway Rights-of-Way. She received an M.S. in public health from the University of North Carolina's Environmental Sciences and En gineering Department and a Ph.D. in environmental toxicology from the University of Maryland.

JOSEPH H. HIGHLAND is director of ENVIRON Corporation, an environmental consulting firm. He has more than 15 years of experience assessing the effects on humans and the environment from exposure to toxic chemicals and hazardous waste. Before founding ENVIRON, Dr. Highland served as codirector of Princeton University's Hazardous Waste Research Program, chairman of the Environmental Defense Fund's Toxic Chemicals Program, and staff fellow at the National Cancer Institute. He received a Ph.D. in biochemistry from the University of Minnesota School of Medicine in 1971.

DOUGLAS M. MACKAY is an adjunct professor at the University of Waterloo's Centre for Groundwater Research. He conducts field work and laboratory experiments related to chemical transport in surface and ground waters and ground water decontamination technologies. He served as an environmental engineer for the Environmental Protection Agency in the 1970s and as an assistant professor in the University of California, Los Angeles, Program on Environmental Science and Engineering in the 1980s. He received a B.S. in engineering and an M.S. and Ph.D. in environmental engineering from Stanford University in 1970, 1973, and 1981, respectively.

GLENN PAULSON, research professor in the Pritzker Department of Environmental Engineering at the Illinois Institute of Technology, has been involved in hazardous and radioactive waste cleanup for more than 20 years, holding a series of positions in both state government and environmental and hazardous waste cleanup organizations, including assistant commissioner of the New Jersey Department of Environmental Protection, vice president of Clean Sites, Inc., and senior vice president of the National Audubon Society. He has served as an advisor to the Environmental Protection Agency and Department of Energy and has participated in several cleanup studies conducted by Congress's Office of Technology Assessment. In addition to serving on the National Research Council's Board on Radioactive Waste Management, he is a member of several National Research Council committees. He earned a B.A. in chemistry from Northwestern University and a Ph.D. in environmental science and ecology from Rockefeller University.

LYNNE M. PRESLO, vice president for the earth science practice of ICF-Kaiser Engineers, has more than 12 years of environmental consulting experience related to ground water cleanup. During the last seven years, she has served as the principal hydrogeologist and project director on five major ground water remediation projects in California and coauthored a book on in situ and ex situ remedial technologies. She also served on an expert advisory panel regarding ground water and soil cleanup policies, perspectives, and future trends for the Environmental Protection Agency's Office of Research and Development. She received a B.S. in applied earth sciences in 1979 and an M.S. in hydrogeology in 1980 from Stanford University.

PAUL V. ROBERTS, a professor of environmental engineering at Stanford University, researches contaminant transport in porous media. Previously, he headed the Engineering Department of the Swiss Federal Institute of Water Supply and Water Pollution Control. He has also worked as a research engineer at Stanford Research Institute and as a process engineer at Chevron Research Company. He received a B.S. in chemical engineering from Princeton University in 1960, a Ph.D. in chemical engineering from Cornell University in 1966, and an M.S. in environmental engineering from Stanford University in 1971.

WILLIAM J. WALSH has practiced environmental law as a partner at Pepper, Hamilton & Scheetz since 1986. Prior to 1986, he served as lead attorney for the Environmental Protection Agency in the Love Canal litigation, which involved four large hazardous waste landfills in Niagara Falls, New York. He is a member of the New York Academy of Sciences. He earned a B.S. in physics from Manhattan College and a J.D. from George Washington University.

C. HERB WARD, Foyt Family Chair of Engineering, directs the Environmental Science and Engineering Department at Rice University, where he is also professor of environmental science and engineering and ecology and evolutionary biology. His research interests include the microbial ecology of hazardous waste sites, biodegradation by natural microbial populations, microbial processes for aquifer restoration, and microbial transport and fate. He has served on the National Research Council's Committee on Multimedia Approaches to Pollution Control and Advisory Committee on Multiagency Hazardous Wastes Research. He received a Ph.D. in plant pathology, genetics, and physiology from Cornell University and an M.P.H. in environmental health from the University of Texas.

MARCIA E. WILLIAMS is president of Williams and Vanino, Inc., a consulting firm that works with clients to establish cost-effective, proactive environmental management programs and business strategies. Prior to establishing Williams and Vanino in 1991, Williams was divisional vice president at Browning Ferris Industries, where she cochaired the company's Environmental Policy Committee and managed its federal regulatory program. From 1970 to 1988, she worked for the Environmental Protection Agency, from 1985 to 1988 as director of the Office of Solid Waste. She received a B.S. in math and physics, *summa cure laude*, from Dickinson College in 1968.

Committee Staff

JACQUELINE A. MACDONALD, program officer at the National Research Council's Water Science and Technology Board, served as study director and managing editor for the Committee on Ground Water Cleanup Alternatives. She earned an M.S. in environmental science in civil engineering from the University of Illinois and a B.A., *magna cum laude*, in mathematics from Bryn Mawr College.

GREGORY K. NYCE, senior project assistant at the National Research Council's Water Science and Technology Board, managed logistical arrangements for meetings of the Committee on Ground Water Cleanup Alternatives, managed finances, and helped prepare early drafts of the committee's report. He received a B.S. in psychology from Eastern Mennonite College in 1991.

ANGELA F. BRUBAKER, project assistant at the National Research Council's Water Science and Technology Board, prepared the report of the Committee on Ground Water Cleanup Alternatives for publication and assisted with editing the final draft. She received a B.A. in liberal arts from Eastern Mennonite College in 1990.

GREICY AMJADIVALA, project assistant at the National Research Council's Water Science and Technology Board until January 1993, managed committee travel and meeting logistics during the early stages of the study.

GEORGE Z. HORNBERGER, summer intern at the National Research Council's Water Science and Technology Board in 1992, assisted with committee meeting planning. He is now involved in ground water modeling activities with the U.S. Geological Survey's National Research Program. He received a B.A. in mathematics from the University of Vermont in 1993.

GINO BIANCHI-MOSQUERA is a senior geochemist at Geomatrix Consultants. He provided technical assistance to the committee in reviewing the performance of pump-and-treat systems at the sites described in this report. His current work focuses on the fate and transport of organic compounds in the subsurface and on the design and evaluation of new aquifer remediation techniques. He received a B.A. in geochemistry from Occidental College in 1982, an M.S. in geochemistry from Pennsylvania State University in 1986, and a Ph.D. in environmental science and engineering from the University of California, Los Angeles, in 1993.

CINDY F. KLEIMAN provided technical assistance to the committee in assessing the risks of ground water contamination and various alternative ground water cleanup goals. Senior consultant at ENVIRON Corporation in Princeton, New Jersey, she has more than 10 years of experience in human health risk assessment, toxicology, occupational health and safety, and environmental epidemiology. Prior to joining ENVIRON, she was an occupational safety officer at a New York City medical center. She received a B.S. from Cornell University in 1978 and an M.P.H. from Yale University in 1981 with a specialization in environmental health.

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