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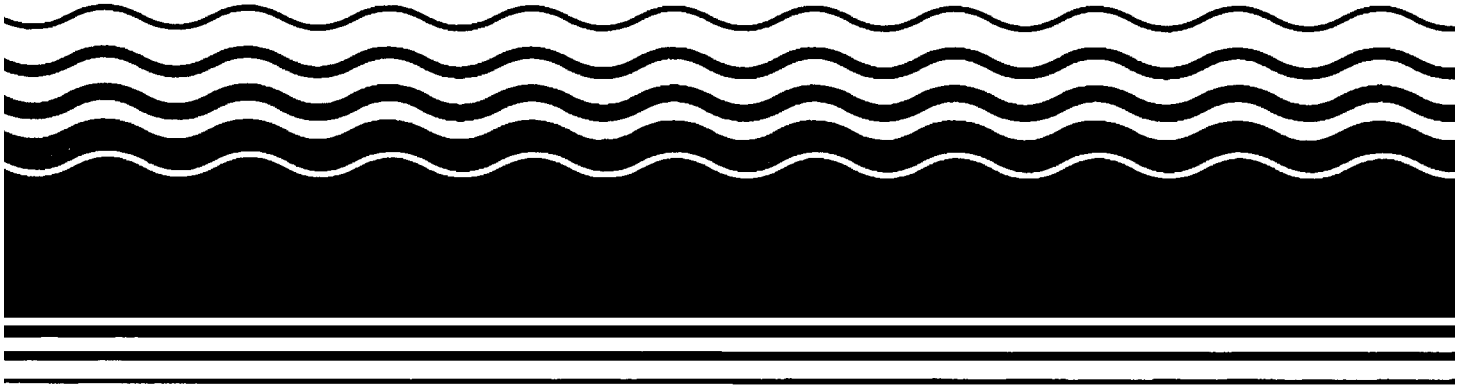
Superfund

Evaluation of the Likelihood of DNAPL Presence at NPL Sites

National Results



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EVALUATION OF THE LIKELIHOOD OF DNAPL PRESENCE AT NPL SITES

National Results

FINAL REPORT

Office of Emergency and Remedial Response
Hazardous Site Control Division
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Washington, D.C. 20460

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EXECUTIVE SUMMARY

This document presents the results of a survey undertaken by the U.S. Environmental Protection Agency's (EPA's) Office of Emergency and Remedial Response (Superfund). The survey was designed to estimate the proportion of National Priorities List (NPL) sites where Dense Nonaqueous Phase Liquids (DNAPLs) may be present. Earlier studies by OERR suggested that DNAPLs may be more common at hazardous waste sites than previously thought, and may act as a continuing source of contamination thus reducing the ability of pump-and-treat systems to attain cleanup goals within expected timeframes (Evaluation of Ground Water Extraction Remedies, Phase II, EPA 9355.4-05). This study represents the first systematic nation-wide review of NPL sites designed to estimate the extent of subsurface DNAPL contamination.

Superfund sites with DNAPL contaminants pose special problems and challenges with respect to site investigation and remediation because DNAPLs comprise a separate liquid phase whose behavior differs significantly from that of the dissolved phase. Unlike the transport of dissolved contaminants, DNAPL migration is gravity driven and relatively unaffected by ground water flow. DNAPL transport is strongly influenced by small-scale geological heterogeneities, and the resulting subsurface distribution of DNAPLs can be extremely complex. Further, DNAPLs can migrate vertically through fractures in rock or clay layers, and thus, can contaminate deep aquifer systems. Since many DNAPLs are clear liquids in their pure product form, they are difficult to recognize, even when directly encountered in the subsurface. As a result of these characteristics, conventional site investigation methods which are used successfully at non-DNAPL sites may produce misleading data when used at DNAPL sites, and in some cases may cause site conditions to worsen. Once they reach the saturated zone, DNAPLs constitute a major long-term source of dissolved-phase contamination that is difficult or, in some cases, impossible to remove with current technology. Indeed, because of their unique characteristics and behavior in the subsurface, DNAPLs pose a serious challenge to conventional site investigation and remediation techniques.

In summary, this study developed an estimate of the likelihood of DNAPL in ground water by re-evaluating existing site data at a large sample of NPL sites. The results of the study are intended to aid policy makers by serving as a basis for assessing ground water remediation policy and guidance in the Superfund program. The results of this study also suggest that the emphasis of future research efforts should be placed on chlorinated solvents and mixed solvents sites, as these represent the majority of sites having DNAPL-related compounds.

An additional goal of the project was to assess the usefulness of various indirect indicators of DNAPL presence associated with site historical activities and ground water contaminant information. The results of this study indicate that certain indirect indicators correlate well with DNAPL presence. This can benefit site managers by helping focus data

gathering efforts early in the site assessment and investigation phases.

This report does not detail all of the procedures that a site interpreter would use to determine the presence of DNAPLs at a specific site. There is no viable substitute for careful and thorough evaluation of all site data by an experienced site interpreter. However, the methodology used in this study to estimate the likelihood of DNAPL presence is quite similar to the method outlined in the Fact Sheet "Estimating the Potential for DNAPL Occurrence at Superfund Sites" (Appendix B, EPA/9355.4-07FS) and as such could be applied to any existing site where appropriate information exists. However, it is not intended to serve as a substitute for a complete and thorough site evaluation by an experienced site interpreter. The methodology used in this study will be used to revise and update the above-referenced Fact Sheet. For a detailed discussion of the scientific and technical issues associated with DNAPL compounds and their behavior in the subsurface environment please refer to the recently published technical guidance document "DNAPL Site Evaluation" (EPA 600/R-93-022).

The study included a screening level evaluation of 712 NPL sites (roughly 55% of all NPL sites, as of 1991) in Regions 1, 3, 5, 6, and 9. At forty-four of the 712 sites, DNAPLs were observed directly in the subsurface. The likelihood of DNAPL occurrence at the remainder of these sites was estimated based on more detailed analysis of a subset of 310 sites (25% of the NPL sites), including 40 of the sites where DNAPLs were observed directly. Finally, these results were then extrapolated to all NPL sites. Detailed information for each site studied was obtained from Remedial Investigation and other site characterization reports, direct discussions with Remedial Project Managers, and regional hydrogeologists. Nearly all major physiographic regions in the U.S. and virtually all categories of Superfund site types were covered by the study. The conclusions drawn in this report are based solely on the site historical information and site characterization information provided for review.

Two separate ranking systems were developed that, when applied to site information, would yield a relative ranking of low, medium, or high for the likelihood of subsurface DNAPL. The two ranking systems were based on site historical information and site contaminant information, respectively. These separate rankings for each site were then combined via a matrix table into a single estimate of the likely presence of DNAPL at that site. The sites where DNAPLs were observed directly were used to measure the applicability and effectiveness of the two ranking systems.

Three additional factors were evaluated in order to determine what influence they had on determining the likelihood of DNAPL presence. The three factors were: 1) hydrogeologic setting; 2) site use type; and 3) site contaminant type.

The results of this study provide the backdrop for a number of other important technical guidance documents and Fact Sheets. These include: "Evaluation of the Technical Impracticability of Ground Water Restoration"; "Presumptive Remedies: Strategies and

Treatment Technologies for CERCLA Sites with Ground Water Contamination" , "Site Characterization for DNAPLs"; and "Methods for DNAPL Extraction."

CONCLUSIONS

Extrapolation of the survey results to the current universe of NPL sites indicates that approximately 60% of all NPL sites exhibit a medium to high likelihood of having DNAPLs present as a source of subsurface contamination. A further breakdown yields the following: approximately 5% of the sites fall within the category where DNAPL presence is "definite or known"; 32% of sites have a "high potential" for DNAPL presence; 20% have a "medium potential"; 27% fall within the "low potential" category; and 16% are "unlikely" to have DNAPLs present. In some instances the lower likelihood of DNAPL presence may be the result of inadequate knowledge of past site activities and/or inadequate site characterization. Thus the results of this study suggest that the presence of DNAPLs should be considered carefully in planning site investigation and cleanup strategies for most Superfund sites.

The analysis of hydrogeologic setting on DNAPL occurrence indicated that there was no identifiable hydrogeologic setting that had a greater likelihood of exhibiting subsurface DNAPL than another. In addition, dissolved-phase DNAPL contamination was just as likely to be present in aquifers with a deep vadose zone as those with a shallow water table.

The relationship of site use to DNAPL occurrence was evaluated in order to determine if certain site uses (site types) exhibited a greater likelihood for subsurface DNAPL than others. The results indicated that indeed, certain site types continuously ranked "high" in likelihood of DNAPL presence. Site categories with the highest likelihood of having DNAPL include: wood-treating sites, general manufacturing sites, organic chemical productions sites, and industrial waste landfills. Sites within these categories should be assumed to have a medium to high likelihood of DNAPL presence and site managers should design site investigation and remediation activities accordingly. A more detailed list of site types falling under these four general categories is included in the main body of the report.

The relationship between site contaminants and DNAPL occurrence was evaluated in order to determine if there were certain suites of compounds present at concentration levels above their theoretical maximum solubilities that would exhibit a higher likelihood of subsurface DNAPLs than at sites where that situation does not exist. The results correlate well with the types of DNAPL compounds associated with specific site types. The contaminants most directly associated with DNAPL presence included: creosote compounds, coal tar compounds, Polychlorinated Biphenyls (PCBs), chlorinated solvents, and mixed solvents. However, even though creosote, coal tar, and PCB sites were easily linked with specific site uses, and have a relatively high likelihood of subsurface DNAPL, they represent only a very small proportion of the universe of NPL sites. The majority of NPL sites where

likelihood of DNAPLs is high exhibit chlorinated and mixed solvent contaminants in ground water.

The results of this study also suggest that the emphasis of future research efforts for ground water remediation should be placed on chlorinated solvents and mixed solvents sites, as these represent the majority of sites having DNAPL-related compounds present as a separate phase and as a source of dissolved-phase ground water contamination.

The site historical information ranking system correlated well with the information from the sites known to have DNAPLs present. The historical information focused on site use, past disposal practices and release of DNAPL compounds throughout the period of site operation. This information can yield important direct and indirect evidence that DNAPLs have been released. However, the lack of such information does not constitute evidence that DNAPLs were absent at a site.

The ground water contaminant ranking system (expressed as a per cent of maximum solubility) also correlated well with information from the sites known to have DNAPLs present. While the presence of a DNAPL-related compound dissolved in ground water is one of the best indirect indicators of the likelihood of DNAPL presence, the presence of dissolved-phase DNAPL does not confirm the presence of a pure-phase DNAPL source in the subsurface. However, certain concentrations are now generally accepted by the research community as indicating a high likelihood of a subsurface source of DNAPL across a wide range of site types (i.e. 1% or more of a compound's solubility). However, concentrations representing less than 1% of a compound's solubility does not indicate the absence of a subsurface DNAPL source.

CHAPTER 1
INTRODUCTION

Dense nonaqueous phase liquids (DNAPLs) are chemical compounds that are heavier than water in their pure form. Examples of such compounds are chlorinated solvents, which were associated with many site operations common at Superfund sites. By far, the largest group of DNAPL compounds encountered at Superfund sites consists of chlorinated organic solvents. Because of their unique characteristics and behavior in the subsurface, DNAPLs may pose a serious challenge to conventional site characterization and remediation techniques.

Superfund sites with DNAPL contaminants pose special problems and challenges with respect to site investigation and remediation (Cohen and Mercer, 1993; Huling and Weaver, 1991; Mackay and Cherry, 1989). DNAPLs comprise a separate liquid phase whose behavior differs significantly from that of the dissolved phase. DNAPL migration is gravity driven and relatively unaffected by ground water flow and often moves in a manner that is independent of ground water flow. DNAPL transport is strongly influenced by small-scale geological heterogeneities, and the ultimate subsurface distribution of DNAPLs can be extremely complex. DNAPLs can migrate vertically through fractures in rock or clay formations and thus, can contaminate deep aquifer systems. Once DNAPLs have entered the subsurface environment, they can act as a source of contamination for an extremely long period of time by releasing gas phase and aqueous phase chemicals to soil and ground water. Many DNAPLs are clear liquids in their pure product form and are therefore difficult to recognize, even when directly encountered in the subsurface. Conventional investigation methods which are used successfully at non-DNAPL sites may produce misleading data when used at DNAPL sites, or in some cases cause site conditions to worsen. Once they reach the saturated zone, DNAPLs constitute a major long-term source of dissolved-phase contamination that can be difficult or, in some cases, impossible to remove with current technology.

Scientific knowledge concerning the occurrence and behavior of DNAPLs in ground water was nearly non-existent in 1980 when the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) was enacted. As a result, many Superfund site investigations in the 1980s were carried out without regard for possible DNAPL presence. However, field data collected during these investigations include both direct observations of DNAPLs and indirect evidence of DNAPL sources. These data provide a valuable resource for understanding the impact of DNAPLs at Superfund sites and for guiding future efforts to define DNAPL contamination.

The primary goal of this study is to estimate the likelihood of occurrence of DNAPLs in ground water at Superfund sites nation-wide through the re-evaluation of existing site data. The results of this study are intended to provide a technical and scientific basis for refining ground water remediation policy and guidance in the Superfund program. Secondary goals of this project are to:

- assess the usefulness of various indirect indicators of DNAPL occurrence from existing Superfund site documents;

- raise awareness of DNAPL issues in the EPA regional offices and highlight specific sites at which DNAPLs occurrence is likely; and

- identify groups of Superfund sites that have similar DNAPL-related characteristics in order to provide a framework for long-term program planning and research.

This report is not a guidance document, however, the methodology used to estimate the likelihood of DNAPL presence is based slight modifications of the method outlined in the Fact Sheet "Estimating the Potential for DNAPL Occurrence at Superfund Sites" and could be applied to any existing site where appropriate information exist. The methodology used in this study will aid in refining and revising the above referenced Fact Sheet. Please refer to the guidance document "DNAPL Site Evaluation" (EPA 600/R-93-022) for a detailed discussion of the scientific and technical issues associated with DNAPL compounds and their behavior in the subsurface environment.

1.1 Background

The Superfund program specifically addresses sites where past, rather than current, activities have led to the contamination of soil and water resources. Contamination at many Superfund sites has been occurring over many years, or in some instances, several decades. Typically the contamination results from waste handling and disposal practices no longer allowed, and frequently involves contaminants that are resistant to rapid breakdown. Common among these contaminants are synthetic organic compounds, a category of compounds manufactured in large quantities since the second World War. Many of these synthetic organics, particularly the chlorinated solvents, are denser than water in their pure form.

The environmental media most commonly affected by contamination at Superfund sites are soil and ground water. A review of data collected from the current sites on the NPL indicates that 85% of the sites have ground water contamination and 72% have soil contamination (USEPA, 1991). An EPA report of Superfund Records of Decision (RODs) indicates that, of the 591 sites for which Records of Decision (RODs) have been signed address ground water contamination, 90% (535 sites) report ground water was contaminated with organic compounds. A central task of the Superfund program, then, is to address the contamination of ground water resources by organic compounds.

Ground water investigations differ from other kinds of environmental studies in that they involve a significant amount of inference. An understanding of potential sources and avenues for contaminant release generally id reconstructed from historical information on site practices. A three-dimensional site conceptual model of subsurface contamination

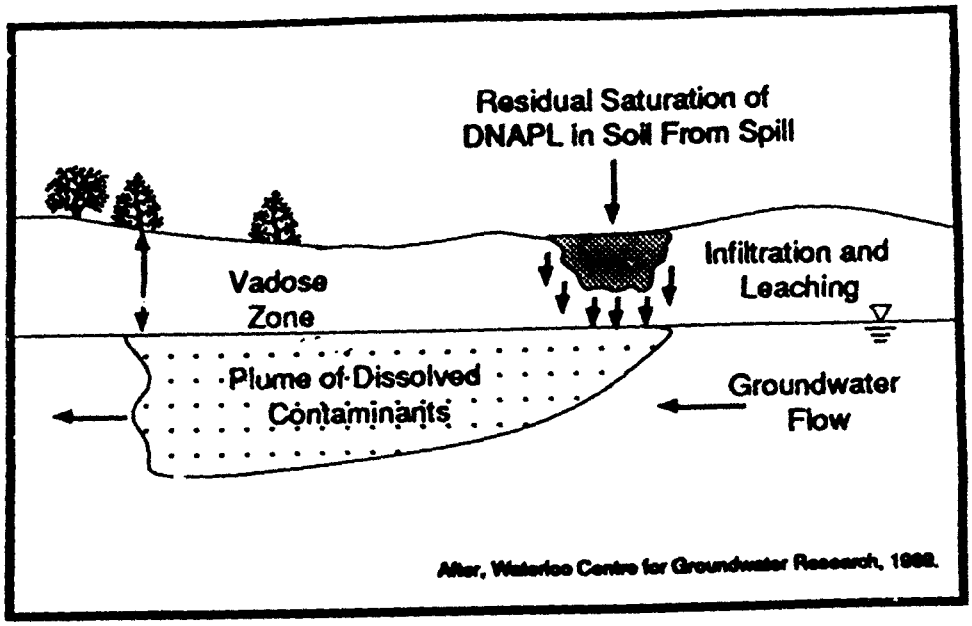
generally is developed using data from relatively sparsely placed soil and ground water sample locations, and contaminant behavior must be inferred from an understanding of the interactions of chemical properties and site hydrogeologic conditions.

Historically, for many Superfund investigations, the site conceptual model has assumed that the sources of ground water contaminants lie primarily in the unsaturated zone, near the ground surface. Also, contaminants are generally considered to have been released to the environment as part of an aqueous solution rather than in their pure liquid form. Under this conceptual model, rainwater infiltration through the unsaturated zone is considered to be the major mechanism of contaminant transport from the surface to ground water; and all contaminants in the saturated zone are either dissolved in ground water or sorbed to aquifer material.

This site conceptual model has driven nearly all Superfund site investigations through the 1980s and early 1990s. Perceiving a site in this manner affects the kinds of data collected at a site as well as the remedial actions selected. A revised conceptual model, where subsurface DNAPL is a source of dissolved-phase contamination should influence both the site investigation techniques and the options for ground water remediation.

Potential differences between a non-DNAPL site and a DNAPL site are illustrated in Figures 1-1 and 1-2. Figure 1-1 shows a plan view and cross sectional diagram of a site at which the source of contamination is an unlined hazardous waste lagoon that received trichloroethylene (TCE) waste over a twenty year period, all in the form of an aqueous solution. In this case, the TCE is transported through the unsaturated zone in dissolved form, reaching the water table and forming a plume of dissolved TCE in the upper aquifer. The plume migrates in the direction of ground water flow. In contrast, Figure 1-2 shows a site at which TCE was discharged into the lagoon over a similar active period as a separate immiscible liquid. For this second case, the pure TCE has migrated into the subsurface, where it acts as a source of dissolved contamination. The TCE DNAPL has traveled out the base of the lagoon through the upper sand, leaving behind immobile blobs (residual) trapped in the pore spaces of the sand. The first clay layer has not acted as a barrier to contaminant migration. Since DNAPL transport is gravity driven, the TCE pooled on depressions on the clay surface and penetrated fractures or rootholes in the clay, where it then entered the second aquifer. Both diagrams depict the same hydrogeological setting, with massive sand units interbedded with clay layers. These figures represent simplifications of actual subsurface conditions which may be encountered at Superfund sites.

Figure 1-1. Schematic cross section of a site at which TCE has been discharged to a waste lagoon over a 20 year period as part of an aqueous solution.



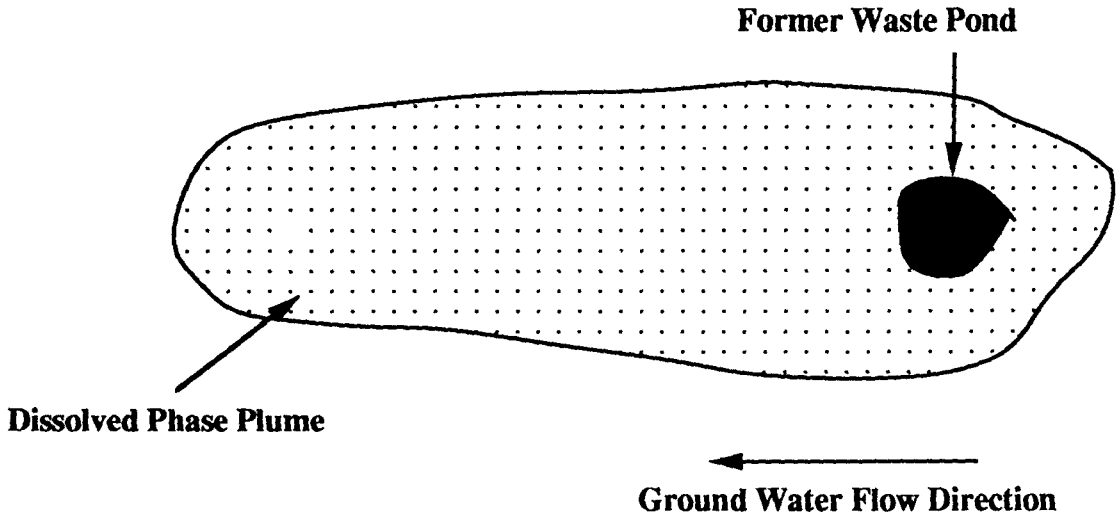
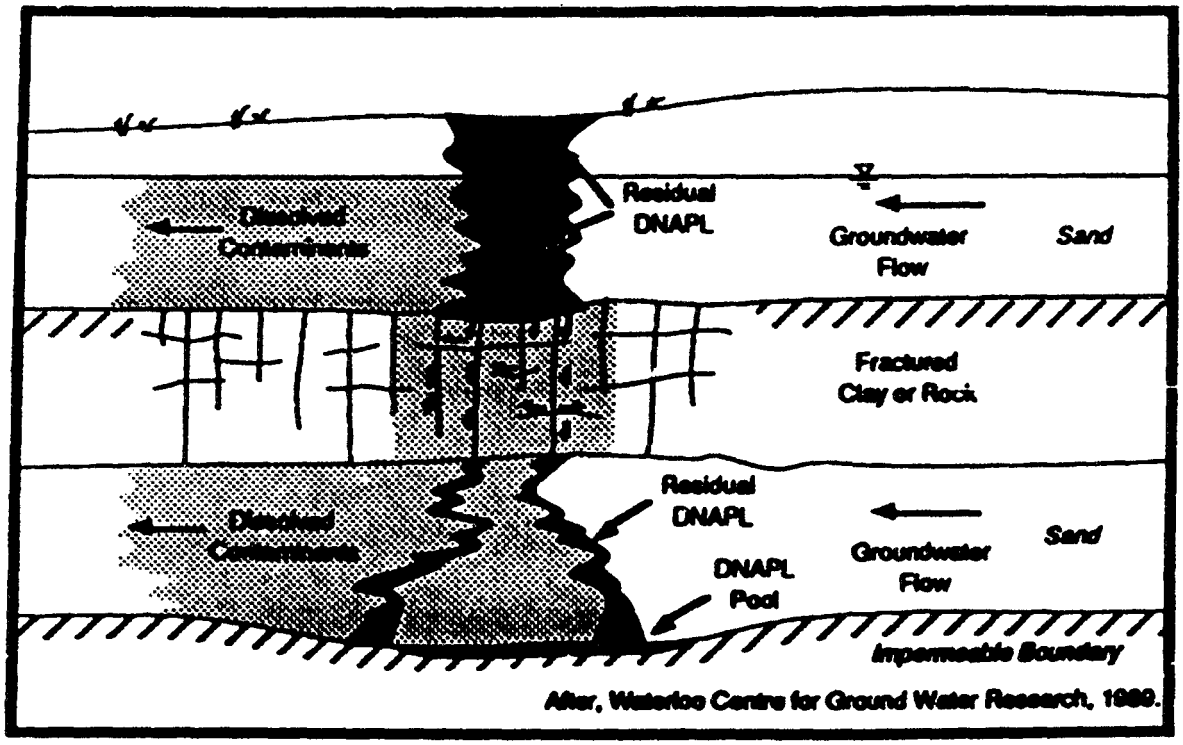
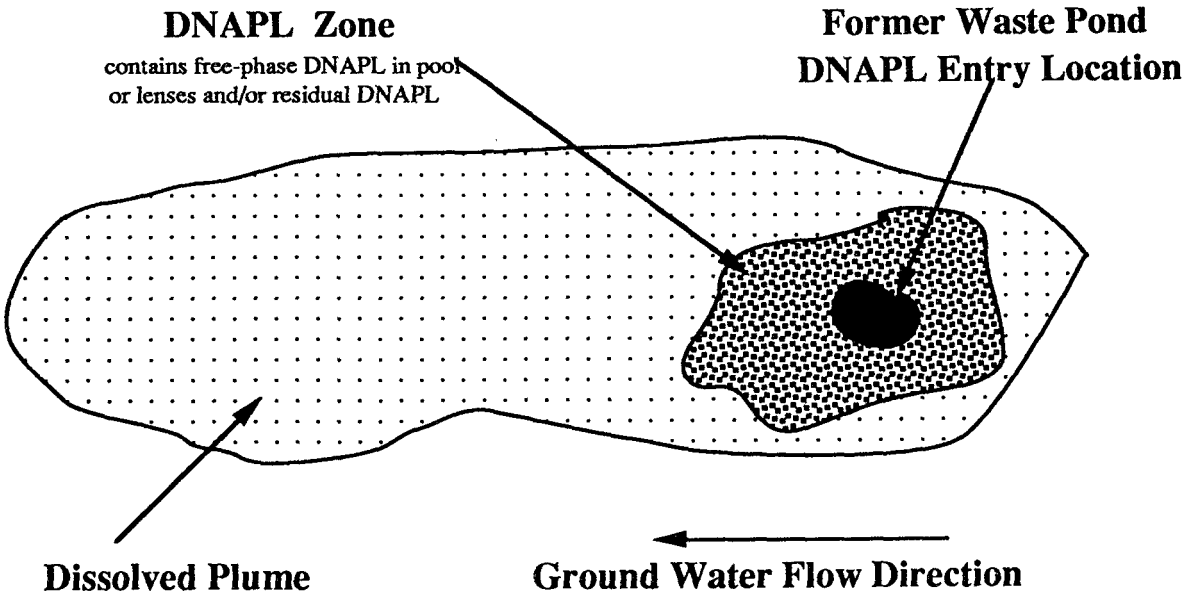


Figure 1-2. Schematic cross section of a site at which TCE has been discharged to a waste lagoon over a 20 year period as a separate organic liquid.





This study reviewed Superfund site data collected as if a site looks like Figure 1-1, and re-examined it to determine whether site data are actually more consistent with Figure 1-2. The relative likelihood of DNAPL occurrence is inferred by asking the following types of questions: Are site operators certain that no TCE was released in a nonaqueous form? Were high concentrations of dissolved TCE unexpectedly found in the lower zones? Were nonaqueous liquids observed in soil cores from the base of the lagoon? Has a pump and treat system removed a contaminant mass that is many orders of magnitude larger than that which is present in the dissolved plume? Together these types of information can help to indirectly assess whether DNAPL sources might be present below the water table. This study did not attempt to estimate the mass of DNAPL in the subsurface at any site, and does not describe the methods for doing so.

1.2 Potential Scope of the DNAPL Problem

Information from recent studies suggests there is a potential for DNAPL contamination at many Superfund sites. As previously noted, approximately 85% of the sites on the NPL reported ground water contamination during the Hazard Ranking System scoring process. Approximately 800 NPL sites, or 66% of the sites listed on the NPL, report solvents as waste materials (NPL Characterization Project, 1991). Forty-nine sites used creosote, and eight were coal gasification plants, which routinely disposed of coal tar. Of the twenty organic contaminants detected most frequently in ground water at Superfund sites (Table 1-2), thirteen are DNAPLs or DNAPL-related compounds. Of these thirteen, most are chlorinated solvents.

In the late 1980s, EPA conducted a study of the efficacy of pump and treat systems at 24 Superfund sites (Evaluation of Ground-Water Extraction Remedies, EPA Directive 9355.4-05). One of the conclusions of this study was that, a key factor preventing efficient site clean-up within a reasonable timeframe was the failure of remedial designs to account for the possibility of subsurface DNAPL. A more recent study of pump and treat remediation at 11 chlorinated solvent sites (Harman et al, 1993) found that the two major limits to aquifer restoration were inadequate site characterization and presence of unidentified reservoirs of subsurface DNAPL sources.

Despite the widespread use of DNAPL compounds, and the common detection of these contaminants dissolved in ground water, very few Superfund sites report direct observations of DNAPLs in the subsurface. An informal poll of the EPA Regions conducted as part of this study found 44 sites (less than 5% of the NPL sites) at which DNAPLs had been directly observed. Further, most of the encounters have been accidental. Therefore, in order to assess the pervasiveness of DNAPL at Superfund sites, this study used indirect indicators of DNAPL sources to assess the potential for DNAPL occurrence in the absence of direct observation.

Table 1-2. Organic contaminants detected most frequently in ground water at Superfund sites.

Ranking	Chemical
1	Acetone
2	Bis (2-ethylhexl) phthalate
3	Toluene
4*	**Trichloroethylene**
5*	**Chloroform**
6*	**Methylene Chloride**
7*	**Dichloroethylene, 1,2-**
8*	**Trichloroethylene, 1,1,1-**
9	Benzene
10*	**Tetrachloroethylene**
11	Xylenes
12*	**Dichloroethane, 1,1**
13	Ethylbenzene
14*	**Di-n-butyl phthalate**
15*	**Naphthalene**
16	Methyl Ethyl Ketone
17*	**Chloroebenzene**
18*	**Dichloroethylene, 1,1**
19*	**Phenol**
20*	**Carbon Disulfide**

SOURCE: Superfund Chemical Analysis Results (SCAR), downloaded from the CLP Analytical Results Database (CARD). The CARD database was published in 1988 and contains results from the Contract Laboratory Program (CLP) analyses of samples taken from Superfund sites.

* = DNAPLs or DNAPL-related compounds.

1.3 Overall Study Strategy

The approach used for this study was to screen a large sample of sites to identify good candidates for detailed analysis, evaluate a subset of sites in detail for indirect indications of DNAPL occurrence, and then extrapolate the findings to all NPL sites across the country. 712 sites were surveyed. The detailed analysis included 310 Superfund sites in five EPA Regions and was performed using a standardized data collection form. The form requested information pertaining to DNAPL indicators that were most uniformly available in site documents. The subgroup of sites studied constitutes one quarter (25%) of the sites listed on the NPL.

In selecting the subset of sites, only those were considered that were far enough along in the site investigation process that sufficient data could be obtained for an evaluation of DNAPL occurrence, and to obtain a range of hydrogeological settings and site use types.

At forty sites, DNAPL had been directly encountered in the subsurface. Although this subgroup is not entirely representative of DNAPL sites addressed by the Superfund program as a whole, it represents the only available standard for measuring the relative importance of indirect indicators of DNAPL occurrence. For the other 270 sites studied in detail, dissolved organic contaminants had been detected in ground water but there were no direct observations of DNAPL in the saturated zone. For this subset, a ranking system was developed that assigned a high, medium, or low potential for DNAPL occurrence. The system separately analyzed the site use history and ground water data, and then combined the information into a single estimate, using a modified version of that outlined in the Fact Sheet "Estimating the Potential for Occurrence of DNAPL at Superfund Sites (Appendix B).

Once the potential for DNAPL presence had been estimated for a site, it was grouped with similar sites to see if there were other factors that would influence DNAPL occurrence. Sites were grouped by hydrogeological setting, prior use, and ground water contaminant type. The final task was to extrapolate, from the results of this study to the remaining NPL sites. This provided an indication of the pervasiveness of DNAPLs at all NPL sites. These results would then allow the Superfund program to evaluate, and refine as appropriate, the policies associated with ground water remediation.

CHAPTER 2
DATA COLLECTION AND MANAGEMENT

In developing a data collection strategy for this study, two factors were balanced: the number of sites evaluated and the amount of information collected from each site. To incorporate a representative sample of site uses and hydrogeologic settings, as many sites as possible were evaluated given the time frame of the study. Specific goals of the data collection effort were to:

- collect site information in a consistent manner for comparative analysis;
- obtain enough detailed information on the sites known to have DNAPLs to test the assumptions regarding indirect indicators of DNAPL occurrence;
- obtain information from a broad spectrum of sites, those with both high and low DNAPL probability; and
- collect information encompassing a range of site uses and hydrogeological settings.

In all, detailed information on 310 Superfund sites in five EPA Regions, including 40 sites at which DNAPL had been directly observed in the saturated zone, were collected and evaluated.

2.1 Data Needs

Site information from Remedial Investigation (RI) and other site characterization reports, and other site documents provided the bulk of the information used to evaluate the potential presence of DNAPL. The tool used for recording this information was a site survey form (Appendix A). The site survey form was very detailed, and included information that would enable evaluation of the indirect DNAPL indicators listed in the DNAPL Fact Sheet (Appendix B). One form was completed for each site. A list of general categories of site information collected is provided in Table 2-1.

Table 2-1. Basic Information on Each Site Collected for the DNAPL Site Assessment Study.

Site History

- Site use and years of use
- Historical industrial and waste disposal practices
- Hazardous substances and chemicals on-site
- Information on known releases of hazardous substances and chemicals

Site Investigation

- Observation of LNAPLs and DNAPLs
- Maximum observed concentrations of organic chemicals in ground water
- Main contaminant sources
- Presence of DNAPL-related spatial and temporal patterns in ground water

Extent of Field Program

- Stage in the Superfund process
- Number of monitoring wells and ground-water samples analyzed for organics
- General understanding of hydrogeology, contaminant sources, and ground-water contamination

Hydrogeological Information

- Unconsolidated and bedrock materials
- Depth to bedrock and to ground water
- Dimensions of ground-water plume

Survey Response

- General comments on survey content
- Comments on DNAPL information and research needs

2.2 DNAPL Survey Response

The number of sites for which detailed information was obtained from each region is listed in Table 2-2.

Table 2-2. Number of sites evaluated in each region during the study period (November 91 - December 92).

EPA Region	Number of Superfund sites in Region*	Number of Superfund sites evaluated in detail	Percent of Superfund sites evaluated in detail
Region 1	84	79	94%
Region 3	162	92	57%
Region 5	267	74	28%
Region 6	74	23	31%
Region 9	125	42	33%
Total	712	310	44%

* This number represents the number of active sites on the NPL in the region at the time of the study (FY 92).

CHAPTER 3
ANALYSIS OF DNAPL OCCURRENCE

The methodology used for establishing the potential for DNAPL occurrence in ground water at Superfund sites is based on the approach outlined in the Fact Sheet, "Estimating the Potential for Occurrence of DNAPLs at Superfund Sites" (Appendix B). In keeping with the Fact Sheet, two broad categories of Superfund site data were considered:

(1) information from the **site use history**, and

(2) data obtained during the site investigation of **ground water contamination**.

These data were evaluated independently and then combined into a single estimate of the relative probability of the presence of subsurface DNAPL. In order to apply the method consistently across a wide variety of site types, specific means of answering the questions posed by the DNAPL Fact Sheet were defined. Based on experience evaluating a large number of sites, modifications and refinements were made to the Fact Sheet approach. This chapter outlines the method of ranking sites for DNAPL probability and discusses the findings regarding the potential for DNAPL occurrence at the 270 NPL sites. The ranking system was also applied to the 40 sites where DNAPLs were observed present, as a measure of the effectiveness of the methodology.

The ranking system uses a baseline of information that was easily obtainable for the majority of sites, and by its nature cannot consider all of the complexities of each site. DNAPL potential is not a parameter that is easily quantified, and the best estimates of DNAPL occurrence result from careful weighing of many lines of evidence. The site rankings may be suitable for long-term program planning, for targeting sites for further study, and for establishing broad trends. A site ranking should not be taken as the definitive word on the occurrence of DNAPL, or if present, it's mass at any given site. For individual sites, there is no viable substitute for careful and thorough evaluation of all site data by an experienced site interpreter.

3.1 Site History Ranking

Investigation of site uses over the active period of operation can yield important indirect evidence that DNAPLs have been released. This section describes the method of analyzing site history information and applies a site history ranking system to the 40 known DNAPL sites and to the 270 sites for which the potential for DNAPL occurrence was to be estimated.

Method for Evaluating Site History Information

Currently, the DNAPL Fact Sheet poses three questions regarding the site use

history:

(1) Does the **industry (site) type** suggest a high probability of historical DNAPL release?

(2) Does a **process or waste practice** employed at the site suggest a high probability of DNAPL release?

(3) Were there any **DNAPL-related compounds** used in appreciable quantities at the site?

Modifications to these questions were made in order to focus on actual knowledge of onsite use, disposal, and release of DNAPLs throughout the site history. The last question was expanded to include general types of substances (e.g., solvents, oils, pesticides, etc.) that may have been present at the site. The term, "appreciable quantities" was defined as at least 5 drums per year. Although much smaller quantities can easily migrate to ground water (Poulsen and Kueper, 1991) and cause substantial dissolved-phase contamination, quantities of fewer than five drums per year are unlikely to have been documented for most Superfund sites. Finally, information was gathered on known releases of DNAPL substances to the environment, specifically the form (non-aqueous vs. dissolved in water) of these releases.

Considering these modifications, five aspects of the site history must be answered in order to obtain a site history ranking using this system:

(1) Does the **site type** suggest a high probability of historical DNAPL release?

(2) Did **site operations** include industrial processes or waste management practices that suggest a high probability of DNAPL release?

(3) Were any **DNAPL-related compounds or substances** used in appreciable quantities (>5 drums/yr) at the site?

(4) If DNAPL-related substances were present on site, were there **known releases** of them?

(5) If there were known releases, were the materials released primarily in **nonaqueous form**, or as components of an aqueous solution?

The method of ranking site history information is based on "yes" answers to the above questions, or positive indicators of DNAPL presence (contained on the survey form,

Appendix A). This approach was taken because there is no site historical information that can be used to entirely rule out the possibility of DNAPL releases. Careful logs of daily site operations and chemical inventories were rarely kept at Superfund sites. DNAPL compounds, particularly the chlorinated solvents, are so widely used that their presence, at least in small quantities, is possible at virtually any site. Consequently, the direct knowledge of a DNAPL-related practice, substance, or release can be used in establishing DNAPL probability for a site, but a lack of such knowledge does not constitute evidence that DNAPLs were absent at the site.

In order to answer the five site history questions, lists of site types, hazardous substances, and site operations that are associated with DNAPL contamination were developed. These lists, presented as Table 3-1, expand upon those found in the DNAPL Fact Sheet and in unpublished work by Cherry and Feenstra (1991). Table 3-1 is used to determine whether or not the answers to the first three questions related to the site history ranking are "yes" or "no". A site receives a "yes" answer if it falls within the categories of site types listed in section A, has handled hazardous substances listed in section B, or has site operations listed in section C. If a site does not fit under one of these categories it receives a "no". The "yes" answers are then recorded in the first three columns of the Site History Ranking Assignment (Table 3-2).

Two questions remain to be answered in order to determine the final site history ranking from Table 3-2. They both refer to the form in which a release of DNAPL-related compound occurred. The DNAPL compound may have been released in a nonaqueous form, (e.g. pure solvent discharged to an unlined lagoon) or an aqueous form (e.g. solvent washed from a floor with water and discharged to a dry well). If either of these conditions occurred, then a "yes" answer is recorded in the appropriate column in Table 3-2. The final site history ranking is then read from the far right hand column. The history ranking can then be applied to the matrix table combining the site history ranking and the ground water contamination ranking (Table 3-10).

Table 3-2 is the "Site History Ranking Assignment" table. It shows the possible combinations of "yes" answers to the five site history questions, and the assignment of the history ranking based upon the answers. The site history ranking ranges from 1 (low DNAPL likelihood) to 6 (high DNAPL likelihood). For instance, the eighth line of Table 3-2 describes a site which reports a facility type and waste disposal practice that have a high probability of DNAPL release, but DNAPL-related substances were not present in appreciable quantities at the site. This combination of answers is assigned a rank of 2.

Table 3-1 also lists the number of sites that reported each of the DNAPL-related facilities, substances, or practices for the 40 known DNAPL sites and the 270 sites for which DNAPL probability was to be estimated. More than half of the facility types designated as "DNAPL-related" are reported for the known DNAPL sites. All of the listed DNAPL-related substances are reported at the known DNAPL sites except for asphalt. Nearly 90% of the DNAPL-related site operations are reported at the known DNAPL sites. These data

suggest that the site history features targeted by the study for their potential association with DNAPL contamination do in fact characterize sites with known DNAPL contamination.

Many of the DNAPL-associated site history characteristics are also reported at the 270 sites for which DNAPL probability must be estimated. Of the DNAPL-related site types, electronics and electrical equipment manufacturing and fabricated metal production were the most frequently reported manufacturing activities. Other site types frequently encountered included organic chemicals production, liquid hazardous waste disposal, storage and transport facilities, and solvent recycling.

Solvents were by far the most pervasive DNAPL substances, and they were reported at nearly three quarters (75%) of the sites. Metal cleaning and degreasing, solvent loading and unloading, storage of drummed solvents, and storage of solvents in underground tanks were commonly reported industrial practices. Two waste disposal practices, dumping of liquid wastes onto the ground and discharge of liquids to lagoons and surface impoundments were practiced at a majority of the sites. Spills and leaks were reported at nearly half of the sites. These findings indicate that use and disposal of DNAPLs, particularly solvents, occurred relatively routinely at the subgroup of Superfund sites included in this study.

It is clear from Table 3-2 that the controlling factor in the assignment of a higher ranking is the reported presence of DNAPL substances on-site. Site operations and practices are given lesser weight because they merely imply the use or disposal of DNAPL-related compounds, rather than absolutely confirming them. Known releases of DNAPL substances, particularly in a non-aqueous form, significantly increase the likelihood of subsurface DNAPL. All sites at which there was a known release of a DNAPL substance in nonaqueous form receive the highest ranking (6).

One potential source of bias in the estimate of DNAPL probability from site history information is a noted tendency for those who provided site data to infer historical practices from site characterization information. For example, it would be natural to infer a historical release of DNAPL substances for a site at which DNAPL had been directly observed in the subsurface, even if the release was not actually reported. Such an inference would bias the site history evaluation for the known DNAPL sites in favor of a higher site history ranking. The survey form specifically requests that no site history information be inferred from site investigations.

Results of Site History Evaluation

Table 3-3 shows the number of sites reporting at least one of the five DNAPL indicators from site history information. For the known DNAPL sites, 85% or more reported each of the indicators. For the remaining 270 sites, more than 61% of the sites had at least one DNAPL-related site type, while nearly three quarters of the sites reported DNAPL-related substances onsite, indicating there are site types other than those targeted at which DNAPL-related substances are present in appreciable quantities. More than 90%

reported site operations for which one would expect some use or disposal of DNAPL substances. This finding implies that the potential number of sites using DNAPL compounds is actually higher than the number reporting known chemical use. For example, at some sites, metal cleaning and degreasing may have been a routine practice, but the solvents used may not have been documented as part of site activities. Alternatively, the quantities may have been too small to report. Almost two thirds of the sites (56%) reported releases of DNAPL substances and chemicals, either dissolved in water, as a separate, nonaqueous phase, or in unknown form. At one third of the sites (33%), releases of DNAPLs in a nonaqueous form are known to have occurred.

Figure 3-1 presents the distribution of the historical ranking for the 310 sites of this study. The same ranking method was applied to the 40 known DNAPL sites and to the 270 sites at which DNAPL occurrence was to be estimated. The distributions are presented separately for comparative purposes. The distribution of site history ranking for the known DNAPL sites represents a standard against which the site evaluation techniques can be measured.

Ideally, the known DNAPL sites should all receive a site history ranking of 6, the highest DNAPL probability. As shown in Figure 3-1a, the site history ranking for 85% of the known DNAPL sites is in fact 6. This distribution indicates that, for 34 of the 40 known DNAPL sites, there was a documented release of a DNAPL to the environment. However, for six of the sites, no releases were reported over the history of site use. One example of such a site is a dry cleaning plant where no spills or leaks of dry cleaning fluids were ever documented, even anecdotally, yet subsequent site investigations revealed a loading area draining to a drywell that had clearly received DNAPL releases. Other releases that occur beneath the ground surface, such as leaks from pipelines, are also rarely discovered in advance of site investigations.

Of the remaining 270 sites there is a wider range in assigned rankings (Figure 3-1b), but the majority of sites are clustered in the higher probability range. Fully 80 percent of these sites receive rankings greater than or equal to three, signifying a medium to high likelihood of subsurface DNAPL. This finding confirms the initial expectation that the use and disposal of DNAPL compounds was common at Superfund sites, and that site practices permitted either deliberate or accidental release of these substances to the environment. Using site history information alone, there are very few sites at which the possibility of subsurface DNAPL can be ruled out.

Based on the large proportion of the known DNAPL sites that received the highest site history ranking, we are confident that the combination of DNAPL indicators targeted from site history information is in fact highly associated with subsurface DNAPL. However, it is also clear that a medium or low site history ranking cannot be used to discount the possibility of subsurface DNAPL. For some portion of sites, lower rankings may instead reflect a lack of knowledge of actual site activities.

Table 3-1. Site History Ranking Characteristics and the Number of Study Sites Fitting Each Category.

A. Facility Types	Sites with Observed DNAPLs (40)	Remaining sites (270)
General Manufacturing		
Aircraft maintenance and repair	0	3
Aircraft manufacturing	0	4
Automobile and motorcycle manufacturing	0	1
Capacitors and transformers manufacturing	2	1
Electronics and electrical equipment manufacturing	2	39
Engine manufacturing	0	3
Fabricated metal product manufacturing	1	30
Tool and die manufacturing	0	0
Weapons and explosives manufacturing	0	6
Waste Management		
Liquid hazardous waste disposal	6	37
Liquid hazardous waste incineration	0	8
Liquid hazardous waste storage and transport	1	14
Liquid hazardous waste treatment	3	2
Solvent recycling	3	13
Transformer reprocessing and/or recycling	0	1
Organic Chemical Production		
Coal gasification	3	0
Coking operations (steel industry, etc)	4	2
Organic chemical manufacturing	2	10
Organic chemical packaging, distribution, and storage	0	6
Pesticide distribution, packaging, and transport	0	1
Pesticide and herbicide production	1	8
Solvent manufacturing	1	3
Solvent packaging, distribution, transport and recycling	0	1
Transformer oil production	0	0
Miscellaneous		
Wood preservation	13	5
Dry cleaning plant	2	2
Fire-fighter training area	1	2

Table 3-1. Site History Ranking Characteristics and the Number of Study Sites Fitting Each Category. (continued)

		Sites with Observed DNAPLs (40)	Remaining sites (270)
B.	**Hazardous Substances**		
	Asphalt	0	3
	Capacitor and transformer debris	3	5
	Coal tar	8	5
	Creosote	14	5
	PCB-laden waste oils	3	12
	PCBs	3	12
	Pesticides	2	29
	Solvents, chlorinated	13	115
	Solvents, undifferentiated	9	89
	Transformer oil	3	1
C.	**Site Operations**		
	Industrial Practices		
	Electronic parts and electronics cleaning	2	34
	Metal cleaning and degreasing	1	59
	Metal machining	0	16
	Paint and lacquer stripping	0	5
	Solvent loading and unloading	5	60
	Storage of drummed solvents in uncontained areas	7	60
	Storage of solvents in underground tanks	4	47
	Storage of solvents in above-ground tanks	3	28
	Tool and die operations	1	3
	Transformer salvage or recycling	1	3
	Wood treatment	13	5
	Waste Management Practices		
	Drum disposal/burial	5	78
	Lagoon/liquid waste surface impoundment	22	91
	Leaks from above-ground tanks	5	38
	Leaks from underground tanks and pipelines	7	59
	Liquid wastes discharged to septic systems	2	21
	Liquid wastes dumped from tank trucks	1	24
	Liquid wastes dumped onto open ground	12	112
	Liquid wastes released to drains and sumps	5	33
	Releases during chemical loading and unloading	11	34
	Releases during fires or explosions	6	12
	Spills	17	55
	Underground injection wells	2	3

Table 3-2. Site History Ranking Assignments from Combinations of DNAPL Indicators.

DNAPL-Related			Known Release		
Facility Type	Site Operations	Hazardous Substances	Aqueous or Unknown Form	Non-aqueous Form	Hist Ranking
					1
			Y		1
	Y				1
				Y	1
	Y		Y		1
				Y	1
Y					2
Y	Y				2
Y			Y		2
Y	Y		Y		2
Y				Y	3
Y	Y			Y	3
		Y			3
Y		Y			3
	Y	Y			3
		Y	Y		3
Y		Y	Y		4
	Y	Y	Y		4
Y	Y	Y			5
Y	Y	Y	Y		5
Y		Y		Y	6
		Y		Y	6
	Y	Y		Y	6
Y	Y	Y		Y	6

Table 3-3. Number of Sites Reporting DNAPL Indications from Site History Information.

DNAPL Indications from Site History Information	Observed DNAPL Sites (40)	Remaining Sites (270)
At least one industrial facility associated with the use or disposal of DNAPLs	34 (85%)	164 (61%)
More than 5 drums per year of DNAPL-related compounds on site	36 (90%)	197 (73%)
At least one industrial or waste management practice with a likelihood of DNAPL release	39 (98%)	245 (91%)
Known release of DNAPL compounds (dissolved in water, as a separate phase, or in unknown form)	37 (93%)	152 (56%)
Known release of DNAPL compounds in nonaqueous form	34 (85%)	90 (33%)

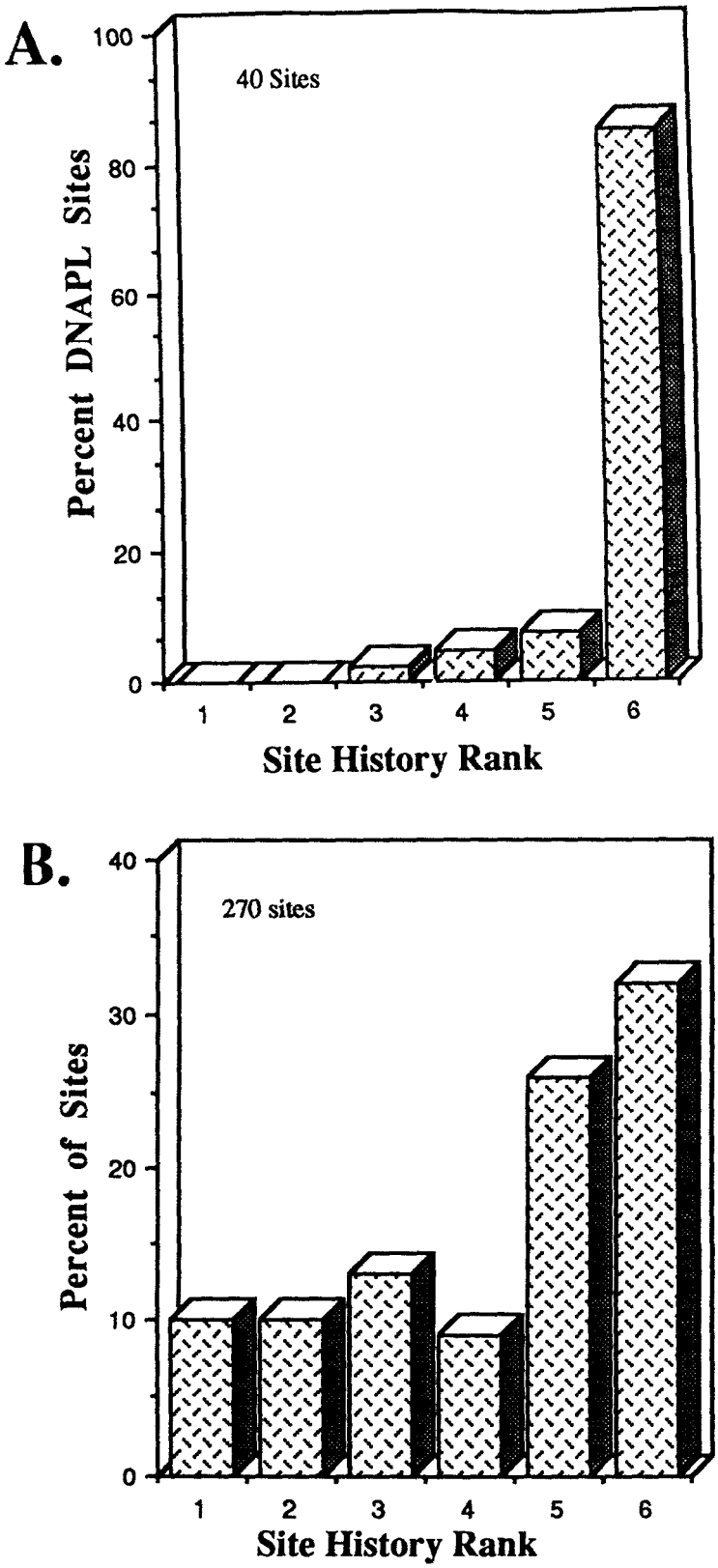


Figure 3-1. Distribution of site history rankings for the 40 known DNAPL sites and the 270 sites at which DNAPL probability must be estimated.

Certainty of Estimates from Site History Information

Since the site history ranking system relies on positive indicators of DNAPL presence, it may not accurately represent DNAPL probability for sites at which the history of site operations is not well known. In evaluating the certainty of the site history rankings, two factors were considered: (1) the general amount of site history knowledge; and (2) the relative availability of the specific indicators targeted.

To provide some measure of the amount of site history knowledge, the survey form asked the site manager or hydrogeologist to provide their opinions on the general degree of site history understanding. Table 3-4 shows the number of sites for which the site history is considered very well, well, generally, or poorly understood. At least a general knowledge of the site history was available for 94% of the sites. Managers of the known DNAPL sites generally reported a greater degree of site history understanding than the other sites studied. This greater site history knowledge may have contributed to the fact that DNAPL was encountered at these sites.

Table 3-4. Relationship of Degree of Site History Understanding to Site History Ranking.

How well understood is the site history?	DNAPL Sites (40)	Remaining Sites (270)	Percent of 270 Sites	Average Site History Ranking (270 sites)
Very Well	17	48	17%	5
Well	14	121	45%	4
Generally	9	86	32%	4
Poorly	0	15	6%	1-3

For the remaining 270 sites, Table 3-4 also shows the average site history ranking for the various categories. Sites that are very well understood have a significantly higher ranking, on average, than those that are poorly understood, so there is some potential for an underestimation of DNAPL potential for sites where historical practices are not well documented. The implication of these results is that careful documentation and research of historical site practices will increase both the certainty of DNAPL site diagnosis and the likelihood that DNAPL-related substances or practices will be discovered.

The specific knowledge of the individual indicators evaluated has bearing on the

certainty of the site history evaluation as well. Some amount of research and inference was often required to answer relatively obvious and straight-forward site history questions posed by the data collection form. The information that was easiest to extract from site investigation reports was the facility type and a description of the general site operations, two features that carry less weight in the ranking system. The names of specific chemicals used or disposed of onsite were less commonly known than general categories of substances. Liquid organics were commonly reported at the sites studied, but the form of these liquids (aqueous solutions or pure-phase compounds) was not clearly identified in site documents. The mechanisms of release of organic liquids were usually documented, but their form upon release was not often reported, even when known. For example, of the sites with known releases of DNAPL chemicals, 30% had no information on the form of the release. As site investigators become more knowledgeable about techniques of investigating potential DNAPL sites, documentation of the form will improve. Since the form of the compound upon release is a key factor in the site history ranking, any improvements in the reporting of this particular aspect of the site history will also increase the reliability of DNAPL site diagnosis. For this study, the majority of sites evaluated included sufficient site history knowledge and documentation.

3.2 Ground Water Contamination Ranking

Data from site investigations provide information on the possible routes of transport of DNAPL to the subsurface, and can assist in evaluating the likelihood that DNAPL has reached the saturated zone. The DNAPL Fact Sheet poses three questions concerning data collected during site investigations:

(1) Has **DNAPL** been found in monitoring wells, observed in soil cores, or physically observed in the aquifer?

(2) Do **chemical analyses** of ground water or soil indicate the possible presence of DNAPL at the site?

(3) Is it likely that the existing **field program** could miss DNAPL at the site?

This study separated the Fact Sheet's methodology into two parts. First, the potential for subsurface DNAPL was established based on direct observations of DNAPLs and chemical analysis of ground water (questions 1 & 2) and each site has assigned a **ground water contamination ranking.** The extent of the field program (question 3) is then evaluated to provide an indication of the certainty of the ground water contamination ranking.

Method of Evaluating Ground Water Contamination Data

In this study the analysis focused on parameters that were available at a broad spectrum of site types and were of comparable quality from site to site. Unfortunately some data that are very useful for establishing DNAPL probability for individual sites could not be applied to the full range of site types encountered. For example, this study's method of evaluating site contamination differs from that of the Fact Sheet in that it did not consider chemical analyses of soils. For individual sites, properly collected soil data can be crucial in establishing DNAPL likelihood. Most soils data were from the unsaturated zone, and the companion data necessary for evaluating the significance of the concentrations, such as the soil moisture content and fraction of organic carbon, were rarely provided. The method of collecting soil samples was not uniform, and site-to-site comparisons would not necessarily have been valid. Thus, soils data was not used as a factor in the ground water contamination ranking.

One indicator that does not appear in the Fact Sheet was added; the presence of temporal trends in concentrations of DNAPL compounds that suggest the possibility of a subsurface, nonaqueous, source. As site data were reviewed, it was determined that many sites had removed major near-surface sources of contamination, yet plume generation continued, and the zones of maximum dissolved-phase contamination did not appear to move with time. At these sites, the potential for a subsurface DNAPL source is higher than at sites showing a rapid decline in concentrations in near-source wells.

In order to address questions 1 and 2 of the Fact Sheet, this study evaluated site contamination information to answer these four questions:

(1) Have there been **direct DNAPL observations** in ground water samples, monitoring wells, soil cores, or test pits?

(2) Do **maximum concentrations** of DNAPL-related compounds in ground water (as a percentage of their pure-phase solubilities) indicate the possible presence of DNAPL in ground water?

(3) Do **spatial patterns** of dissolved-phase contamination include concentrations of DNAPL compounds that are inexplicably high at depth beneath source areas?

(4) Do **temporal trends** in concentrations of DNAPL compounds in ground water indicate the possible presence of a subsurface, nonaqueous source?

As previously noted, there are 40 sites at which DNAPL presence is certain. These sites were used to test the assumptions regarding the data that indirectly indicate DNAPL occurrence, by ignoring the DNAPL find and evaluating ground water information in a

manner comparable to the evaluation of the 270 sites for which DNAPL probability must be estimated.

In analyzing ground water data, each site is classified according to the magnitude of the concentrations of DNAPL in ground water expressed as a percentage of their pure-phase solubilities. The maximum concentrations of compounds detected in ground water was used rather than examining the entire body of chemical data for each site. Based on the theoretical understanding of the distributions of dissolved-phase contamination emanating from a site, these maximum concentrations are most indicative of the presence of a nonaqueous source below the water table.

For the 40 known DNAPL sites, the maximum concentrations that would have been detected if the DNAPL had not been directly encountered were evaluated by reviewing the information on the maximum concentrations from wells other than those in which the DNAPLs were found. This approach ensured that ground water data from these sites would be comparable to ground water data from the 270 sites at which DNAPL was to be estimated.

For a single-component DNAPL, the concentration of the compound in ground water that is in equilibrium with the DNAPL should theoretically equal the pure-phase solubility of the compound. For example, the concentration of dissolved TCE in ground water contacting a TCE DNAPL should be 1,000 mg/L, or 100% of TCE's solubility. As the dissolved contaminant is carried away from the DNAPL source, concentrations will reduce to lesser and lesser percentages of the compound's pure-phase solubility. Factors that produce dissolved-phase concentrations that are significantly lower than the pure-phase solubility, even in samples obtained quite near a single-component DNAPL source, are summarized in Table 3-5. It is clear from this table that the concentrations observed will depend greatly on individual site conditions and investigation techniques.

As noted by Cherry and Feenstra (1991), site conditions are so variable that it is not possible to accurately prescribe the dissolved chemical concentration that reflects the presence of subsurface DNAPL. However, computer modelling has shown that, in a hypothetical aquifer of horizontally layered sands with a tetrachloroethylene (PCE) DNAPL source, ground water samples taken from wells 50 m down gradient from the source will yield dissolved concentrations of only 0.1% to 5% of PCE's solubility (Anderson et al., 1991). Case studies of known DNAPL sites also point to the remarkably low concentrations that can be observed in routine monitoring prior to a DNAPL encounter (Kueper and McWhorter, 1991). The concentrations that are now generally accepted by the research community as indicating subsurface DNAPL across a wide range of site types are on the order of 1% or more of a compound's solubility (Cherry and Feenstra 1991, EPA Fact Sheet, Cohen and Mercer, 1993).

As a reference point for understanding the magnitude of concentrations represented by various percentage solubilities, Table 3-6 lists these two parameters for four DNAPLs:

Table 3-5. Summary of factors that contribute to less-than-saturation concentrations of DNAPL compounds in ground water at sites with a **single-component DNAPL source.**

Factor	Explanation
Borehole Dilution	DNAPL will be heterogeneously distributed over vertical intervals tapped by monitoring wells. The 10-50 foot well screens typical of the Superfund program are likely to draw water from both DNAPL-contaminated and relatively uncontaminated strata or fracture systems. The sample obtained from such a well would be diluted relative to that of a well screened over a shorter interval tapping a DNAPL zone.
Well Placement	Regardless of the screened interval, wells equidistant from a DNAPL source in the downgradient flow direction can have widely varying dissolved concentrations depending on whether they are tapping the transport route of dissolved contaminants emanating from DNAPL pools or residual. The DNAPL zones can also be very small relative to the spacing of wells. These conditions especially hold true in fractured rock systems and in very heterogeneous overburden.
Ground Water Sample Collection Method	Excessive purging can dilute water samples. Some known DNAPL sites have reported that higher dissolved concentrations are obtained when kemmerer bottles or bottom-loading bailers are used to extract water from the base of wells than when standard sampling techniques are used.
Dispersion	Dissolved contaminants emanating from a DNAPL source will be subject to dispersion, particularly in the direction of ground water flow. Their concentrations will reduce with time and with distance from the DNAPL source.
DNAPL Dissolution kinetics	Dissolution of contaminants from the DNAPL may occur too slowly in relation to diffusion or advection of the dissolved phase away from the DNAPL-water interface to attain the theoretical dissolved concentration expected under equilibrium conditions. This factor would especially hold true in settings with naturally high ground water velocities or near pumping wells.

TCE, TCA, PCE, and methylene chloride. For example, 1% of the pure-phase solubility is a much lower concentration for the least soluble compound, PCE, than for the other three. Table 3-6 also shows the number of sites in the study reporting each of the contamination levels.

For a **multi-component DNAPL,** the solubilities of each of the constituents in ground water will generally be depressed in proportion to the mole fraction of the compound in the DNAPL. These depressed solubilities are called **effective solubilities.** For example, in a DNAPL composed of half TCE and half PCE, the effective solubility of TCE will be 500 mg/L (half of TCE's pure-phase solubility of 1,000 mg/L) and the effective solubility of PCE will be 75 mg/L (half of PCE's pure-phase solubility of 150 mg/L). Ground water directly in contact with a multi-component DNAPL, then, could contain dissolved concentrations that are 100% of the effective solubilities of its constituents, but lesser percentages of the pure-phase solubilities.

Table 3-6. Concentrations of Tetrachloroethylene, Trichloroethane, Trichloroethylene, and Methylene Chloride expressed as percentages of their pure-phase solubilities, and the number of Superfund sites in this study (out of 310) reporting each level of contamination.

Percent of Pure - Phase Solubility	Tetrachloroethylene (PCE)		1,1,1 Trichloroethane (TCA)		Trichloroethylene (TCE)		Methylene Chloride (Dichloromethane)	
	ug/L	# sites*	ug/L	# sites*	ug/L	# sites*	ug/L	# sites*
100%	**150,000**	**---**	**950,000**	**---**	**1,000,000**	**---**	**13,200,000**	**---**
50%	75,000	9	475,000	2	500,000	9	6,600,000	0
10%	15,000	23	95,000	13	100,000	29	1,320,000	1
3%	4,500	41	28,500	25	30,000	49	396,000	3
1%	1,500	52	9,500	39	10,000	78	132,000	11
0.1%	150	89	950	78	1,000	131	13,200	28
0.01%	15	120	95	101	100	165	1,320	47

* Number of sites reporting this concentration or higher.

All of the factors that contribute to lowering these saturation concentrations in actual ground water samples for a single-component DNAPL (Table 3-5) also apply to multi-component DNAPLs. Additional factors that affect ground water concentrations for multi-component DNAPLs are listed in Table 3-7. For individual sites with several DNAPL compounds present at high concentrations in ground water, the most suitable method for evaluating site data is to calculate effective solubilities and then express contaminant concentrations as a percentage of these solubilities. The contaminant concentrations that are generally accepted to be indicative of multi-source DNAPLs are 1% or more of the compound's effective solubility. In some cases approximations of the effective solubilities of compounds can be back-calculated from ground water concentration data obtained from a single sample with high hits of DNAPL chemicals (Feenstra, 1990).

Table 3-7. Summary of factors that contribute to less-than-saturation concentrations of dissolved-phase chemicals emanating from a **multi-component DNAPL** source, in addition to those listed in Table 3-5.

Factor	Explanation
Initial DNAPL Composition	The aqueous solubility of each DNAPL constituent will be depressed in proportion to its mole fraction in the DNAPL.
DNAPL Weathering	Over time, a greater mass of the more soluble constituents of the DNAPL will dissolve into the ground water, leaving behind a DNAPL composed of a lesser and lesser proportion of the most soluble constituent. These changes in DNAPL composition will lower the solubilities of the soluble DNAPL constituents, and the ground water concentrations will reflect these changes.

In this study, a broader representation of site conditions was sought, and therefore the maximum concentrations of contaminants site-wide and over the entire period of investigation rather than concentrating on a single sample from a single well was collected. The site analytical data therefore often (although not exclusively) come from many locations, and many different sample events. By taking this approach, we have accounted for the likelihood of heterogeneously distributed sources and sample locations at individual sites (to the extent possible given the constraints of this study). This approach renders the data unsuitable for the back-calculation of effective solubilities. Instead, all concentration data

are expressed as a percentage of the pure-phase solubilities of the compounds.

Multi-component DNAPL sources were accommodated by considering the three DNAPL compounds found at the highest concentrations in ground water, rather than considering only the highest contaminant concentration. Three compounds were chosen to keep the method simple and applicable to the greatest number of sites.

The system for assigning ground water rankings is outlined in Table 3-8. Note that a site with only one DNAPL compound at 1% of its pure phase solubility is classified with a lower probability of subsurface DNAPL than a site with three DNAPL compounds at 1% of their solubilities. This is because one would expect lower contaminant concentrations at sites with DNAPL sources containing three compounds than at sites with DNAPL sources containing one compound.

Applying the methodology used in this study for developing a ground water contaminant ranking is straight forward. Effective solubilities are not calculated for this method, one simply calculates the maximum per cent solubilities for the three DNAPL compounds present at the highest concentration in the dissolved phase and then applies that information to the Contaminant Ranking Assignment (Table 3-8). The numerical ranking is then read from the far left-hand column. The contaminant ranking can then be applied to the matrix table combining the site history ranking and the ground water contaminant ranking (Table 3-10) for obtaining the overall likelihood of DNAPL presence at a site.

Table 3-8. Contaminant Ranking Assignment, ranking of sites based on maximum percentage solubilities of DNAPL Compounds.

Ranking by Magnitude of Ground Water Contamination	Maximum Percentage Solubilities for DNAPL-related Compounds in Ground Water	Likelihood of Subsurface DNAPL
1	No DNAPL compounds or One DNAPL compound at < 0.1% or Two at < 0.03% or Three at < 0.01%	Low
2	One DNAPL compound at 0.1% to 1% or Two at 0.03% to 0.1% Three at 0.01% to 0.03%	Low
3	One DNAPL compound at 1% to 3% or Two at 0.3% to 1% or Three 0.01% to 0.3%	Medium
4	One DNAPL compound at 3% to 10% or Two at 1% to 3% solubility or Three at 0.3 to 1% solubility	High
5	One DNAPL compound at 10% to 50% or Two at 3% to 15% solubility or Three at 1% to 5% solubility	High
6	One DNAPL Compound at > 50% or Two at > 25% or Three at > 15%	Very High

To establish the final ground water contamination ranking, direct DNAPL observations in the unsaturated zone were noted and DNAPL-related spatial patterns and temporal trends in ground water contamination were examined. It was assumed that sites with DNAPL observations in the unsaturated zone have a higher likelihood of subsurface DNAPL than sites without direct observations, so these sites are raised by one point in the classification system.

In the ranking system, spatial patterns and temporal trends in ground-water contamination are considered significant only if DNAPL-related compounds are among the major contaminants at the site. A site is considered to have major DNAPL-related compounds contamination if the ground water ranking (Table 3-8) is two or greater. At such sites, half a point is added to the site's ground-water contamination ranking if high concentrations of DNAPL compounds found at depth beneath source areas cannot be adequately explained by dissolved-phase transport.

"Significant" temporal trends are defined as sharp decreases in concentrations for 3 or more years, slight increases for 5 or more years, sharp increases for 3 or more years, and steady concentrations for 5 or more years. If any of the last three conditions hold true, half a point is added to the ranking. The observation of sharp decreases in concentrations over time leads to a half point decrease in the ranking.

In total, these adjustments do not change the ranking of a site by more than one point, and they are most important for sites with a ground water contaminant ranking of two and three, where the concentrations are not high enough to place a site definitively in a "high" category. The lesser reliance on spatial patterns and temporal trends to establish site ranking in part reflects the difficulty in interpreting data from site investigations that were not specifically designed to characterize these aspects of site contamination.

Results of Ground Water Contamination Evaluation

As with the site history information, this section separately examines the various indicators that factor into the ground water contamination ranking and then presents the composite ranking in barchart form. To give a general feeling for the major DNAPL-related contaminants observed in ground water at significant concentrations, Figure 3-2 shows the distribution of the DNAPL-related compounds found most frequently at the maximum concentrations in ground water. The three most prevalent contaminants, TCE, PCE, and 1,1,1 TCA, are all chlorinated hydrocarbons that are used ubiquitously as industrial solvents. At the subgroup of Superfund sites evaluated in this study, use of chlorinated solvents and site operations associated with their use were commonly reported. In terms of the compounds found in ground water, then, the data match the expectations from site history information.

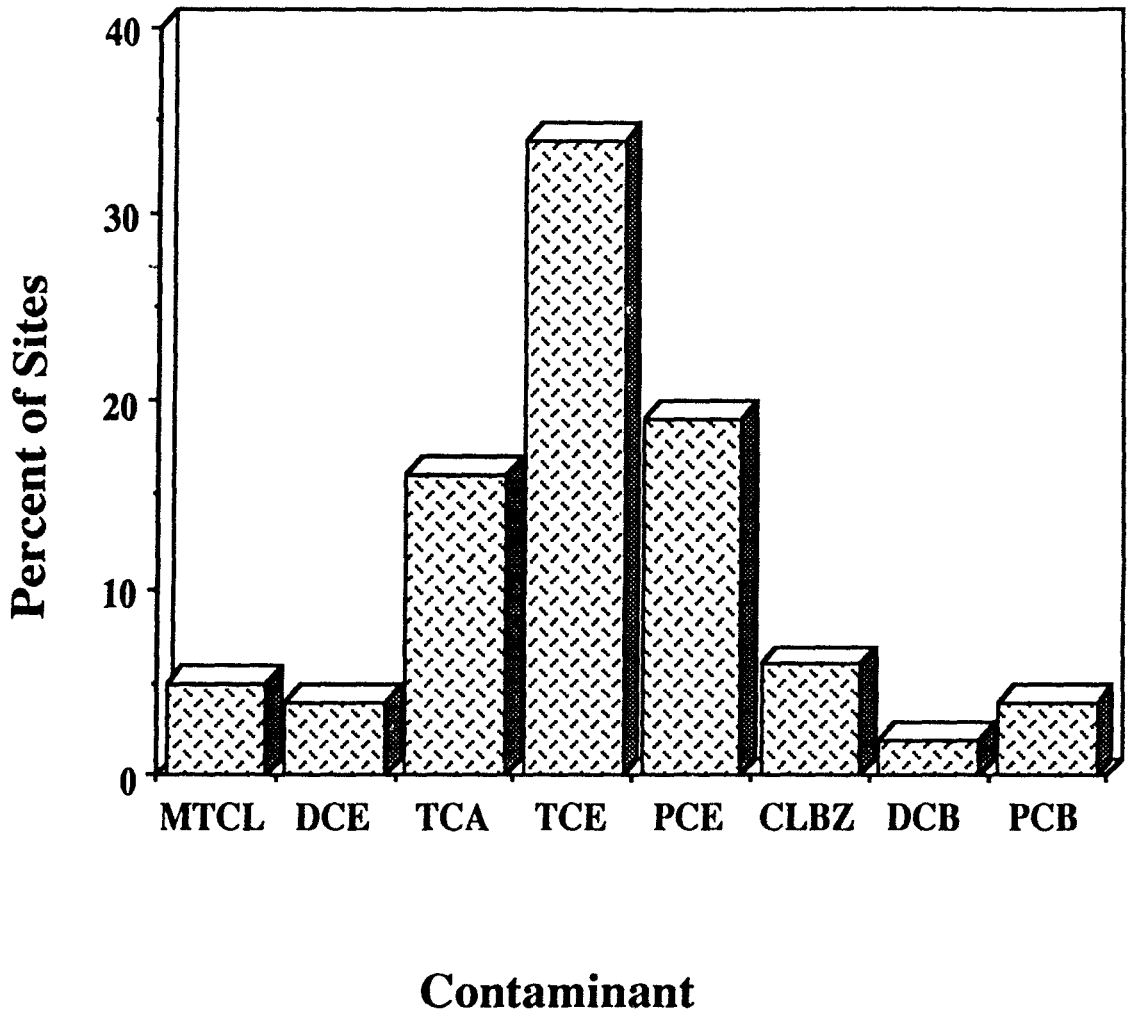
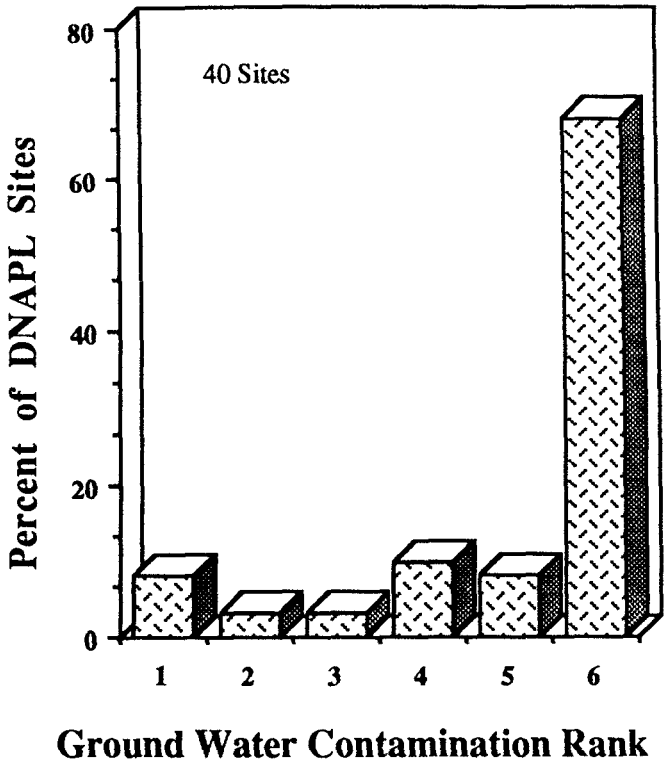


Figure 3-2. Distribution of the contaminants found most frequently at the highest concentrations (as a percentage of their pure-phase solubility) in ground water.

The key ground water contamination indicators used to establish DNAPL probability were the three maximum concentrations of DNAPL compounds as a percentage of their pure phase solubilities. Figure 3-3 shows the results of applying the ranking system outlined in Table 3-8 to the 40 known DNAPL sites and to the 270 sites at which DNAPL probability must be estimated.

Most of the known DNAPL sites received the three highest ground water contamination ranking. For these sites, the system would have predicted a high likelihood of subsurface DNAPL prior to the actual identification of DNAPL at the site. However, some of the known DNAPL sites receive lower rankings. At this latter group of sites, site monitoring outside of the DNAPL find did not detect the expected high concentrations of DNAPL compounds in ground water. This result emphasizes the fact that the ability to establish DNAPL likelihood based on ground water data is limited by the scope of field investigations. One group of DNAPL sites, the four that received a ranking of 1, are somewhat atypical in that they are all creosote/coal tar sites at which DNAPL was found so early in the investigation that all efforts were aimed at locating and characterizing the free phase and very few ground water samples were taken.

Of the 270 sites at which DNAPL has not been directly observed, 60% received a ranking of three or greater, signifying a medium to very high likelihood of subsurface DNAPL. Sites in this group with rankings of 5 or 6 can be considered very likely candidates for subsurface DNAPL. The status of sites with rankings of 2, 3, and 4 is less clear, and for these sites, the other indicators such as spatial and temporal patterns of dissolved-phase contamination, can help to estimate DNAPL presence.



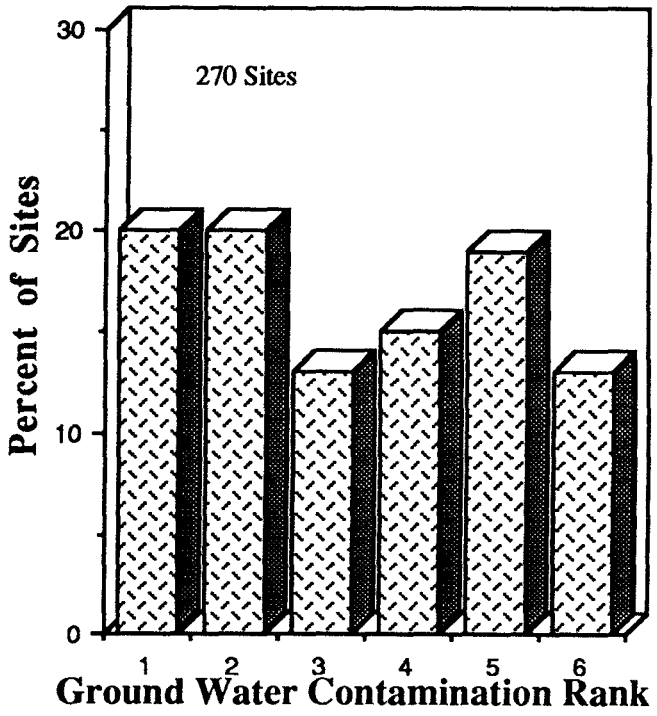


Figure 3-3. Distribution of ground water contamination rankings for the 40 known DNAPL sites and for the 270 sites at which DNAPL probability must be estimated (see Table 3-8 for key to classes).

3.3 Composite Site Ranking

Once the site history ranking and ground water contamination ranking was established, these two rankings were combined into a single estimate of DNAPL probability. For purposes of this study, there are four categories, defined in Table 3-9. This section outlines the method of combining the rankings and discusses the results of the composite site ranking.

Table 3-9. Definitions of the Four Composite Rankings.

DEFINITE	DNAPL directly encountered below the water table in soil cores and/or ground water samples.
HIGH	DNAPL strongly suspected based on ground water data and site history information. Proceed with site investigation and remediation plans assuming subsurface DNAPL source is present.
MEDIUM	Information from site history and ground water investigation indicate moderate potential for subsurface DNAPL. Important to gather additional site information regarding possible DNAPL presence. Best to proceed as if site is a DNAPL site until further investigations indicate otherwise.
LOW	Based on available site history and ground water information, DNAPL sources are unlikely. DNAPL potential at some sites in this category may be underestimated due to lack of information. Modify expectations if further investigation show evidence of DNAPL sources.

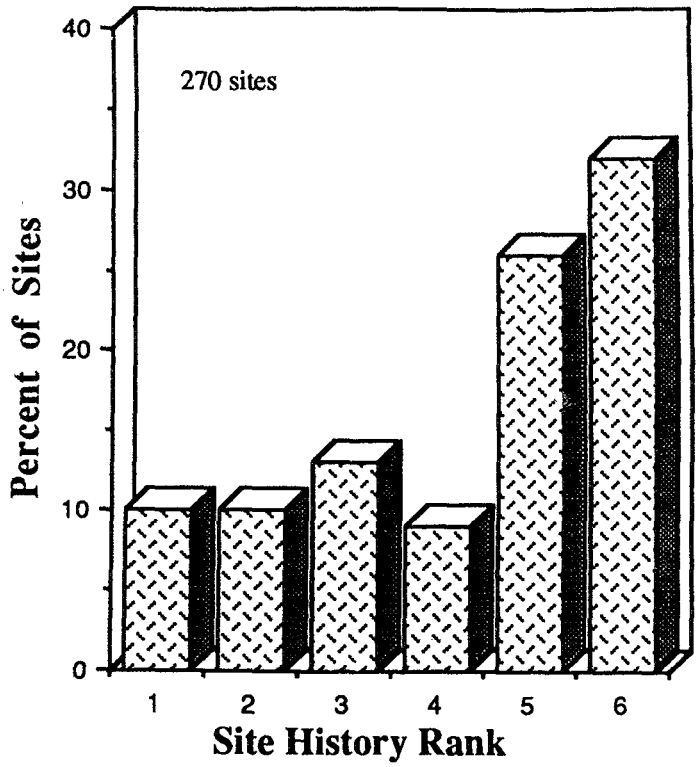
Combining the Site History and Ground Water Rankings

The 40 known DNAPL sites receive a composite ranking of DEFINITE. For the 270 sites at which DNAPL probability must be estimated, a matrix was developed (Table 3-10) for assigning a high, medium, or low potential for subsurface DNAPL based on the independent rankings each site received from the Site History Ranking and the Ground Water Contamination Ranking. Figure 3-4 shows the distribution of the site history and

ground water contamination rankings for the 270 sites. Based on site history information alone, most sites have a medium to high potential for DNAPL occurrence. The history ranking system has a tendency to rank sites at the high end of the scale. Based on ground water data, there is a wider range in the potential for subsurface DNAPL. The ground water contamination ranking system has a tendency to rank sites at the lower end of the scale. This could, in part, be due to the limited amount of ground water characterization data available for a site.

In combining the two ranking factors, the greatest emphasis was placed on information carrying the greatest certainty. Both ranking systems were based on positive indicators of DNAPL occurrence, so the higher rankings carry greater certainty than the lower rankings. For sites receiving a high ranking based on ground water data but a low ranking based on site history information, the ground water data prevails because it more accurately reflects the status of contamination in ground water. For the opposite case, a high site history ranking and a low ground water contamination ranking, the site history information carries more weight, particularly when the extent of site characterization is low. For sites with a low ranking on both counts, there is some potential that a lack of site knowledge is contributing to the low rankings, but a low match in the rankings can add to the reliability of site information for well characterized sites.

In order to apply the combined ranking system to a site one must first determine the site history ranking from Table 3-2 and the ground water contaminant ranking from Table 3-8. Using Table 3-10, locate the intersection point of the site history ranking and the ground water contamination ranking. Refer to Table 3-9 for the explanation of the combined ranking.



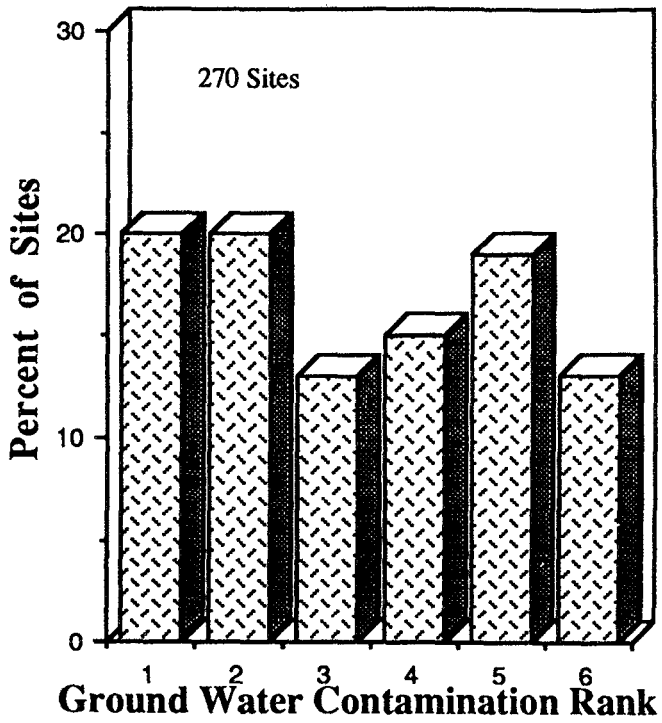


Figure 3-4. Comparison of Site History Ranking and Ground Water Contamination Ranking for the 270 sites at which the potential for DNAPL occurrence must be inferred.

Site Hist Rank	Ground Water Contam. Rank					
	6	5	4	3	2	1
6	Hi	Hi	Hi	Med	Med	Med
5	Hi	Hi	Hi	Med	Med	Lo
4	Hi	Hi	Med	Med	Lo	Lo
3	Hi	Hi	Med	Med	Lo	Lo
2	Hi	Hi	Med	Med	Lo	Lo
1	Hi	Hi	Med	Med	Lo	Lo

Table 3-10. Matrix for combining the site history ranking and ground water contamination rankings at sites for which the potential for DNAPL occurrence must be estimated.

Results of Composite Ranking

Figure 3-5 shows the results of applying the combined ranking system to the 270 sites for which we are estimating the potential for DNAPL occurrence. Sixty five (65%) percent received a medium to high ranking, while 35% have a low potential for DNAPL occurrence. Table 3-9 provides an explanation of the implications of these rankings.

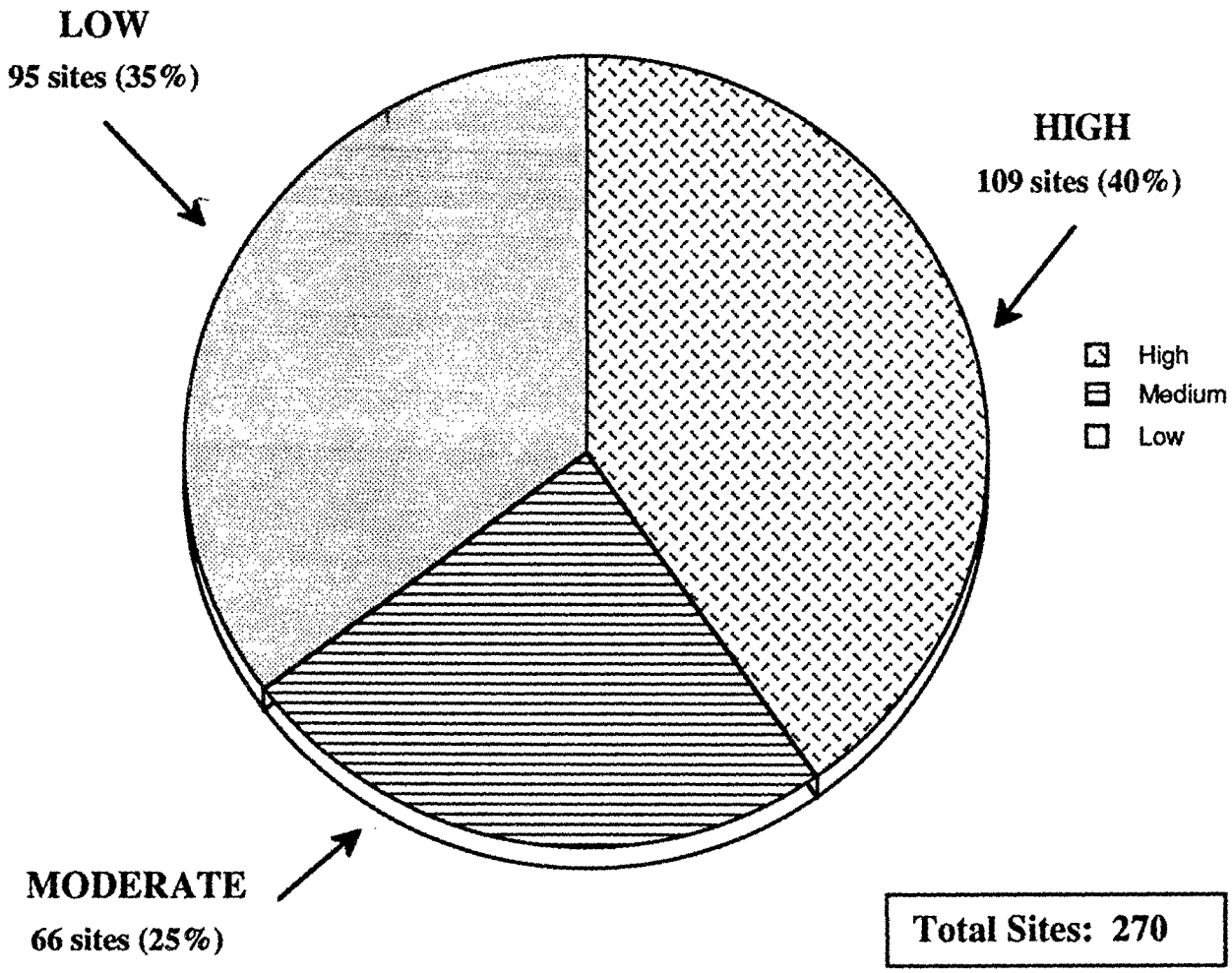


Figure 3-5. Potential for DNAPL occurrence at 270 sites evaluated. Rankings defined in Table 3-9.

3.4 Effect of Hydrogeological Setting on DNAPL Occurrence

Transport of DNAPL in the subsurface has been shown to be very sensitive to the geological media through which it passes (Poulsen and Kueper, 1992). Site geology has the potential to affect many aspects of DNAPL contamination, including the likelihood that DNAPL will reach the saturated zone, the ultimate depth of DNAPL transport, the extent of lateral spreading of the DNAPL zone, the likelihood that DNAPL pools will form, and the spatial distribution of the dissolved-phase plume emanating from a DNAPL source. These factors in turn affect the ease of site characterization for DNAPLs and the overall potential for site remediation.

Hydrogeological Categories

Geological information was collected as part of this study so that the relationship of the hydrogeological setting of sites to the likelihood of subsurface DNAPL could be assessed. For example, a thick unsaturated zone could offer some protection against migration of the nonaqueous phase to the water table. As a starting point in the analysis, each site was assigned a hydrogeological setting category according to those defined by Heath (1984). Table 3-11 names and describes the twelve broadly defined hydrogeological regions in the United States.

The majority of Superfund sites are located in six settings: the Northeast and Superior Uplands, the Glaciated Central Region, the Non-Glaciated Central Region, the Piedmont-Blue Ridge Region, the Atlantic and Gulf Coastal Plain, and the Western Alluvial Basins. All of these settings share the common characteristic of a flat to gently rolling topography. In addition, most U.S. population centers are located in these six hydrogeological regions. The Non-glaciated Central and Piedmont regions have poor ground water yields, while the remaining four have relatively abundant ground water resources. Regions such as the Western Mountain Ranges and Columbia and Colorado Plateaus are more rugged and less populated, and contain far fewer industries and hazardous waste sites, and were not considered in this study.

Each of the 310 sites evaluated was assigned a hydrogeological setting category based on detailed geological information. In collecting data on the hydrogeology, concentration was focused on the geological character of deposits directly beneath source areas, so the category would reflect the nature of the material through which a DNAPL might have passed. Figure 3-6 shows the distribution of the sites studied according to hydrogeological setting.

Figure 3-7 shows the results of the site history ranking and ground water contamination ranking as they relate to sites located in the various hydrogeologic regions. These results indicate that no single hydrogeologic setting has a significantly greater likelihood of subsurface DNAPL than another.

Table 3-11. Descriptions of the Hydrogeological Settings for sites studied, Heath (1984).

Hydrogeological Setting for Sites Studied	Description
Western Alluvial Basins	Thick alluvial (locally glacial) deposits in basins and valleys bordered by mountains
Non-glaciated Central Region	Thin regolith over fractured sedimentary rocks
Glaciated Central Region	Thick glacial deposits over fractured sedimentary rocks
Piedmont and Blue Ridge Region	Thick regolith over fractured crystalline and metamorphosed sedimentary rocks
Northeast and Superior Uplands	Thick glacial deposits over fractured crystalline rocks
Atlantic and Gulf Coastal Plain	Complex interbedded sands, silts, and clays

Notes: Superfund sites are generally concentrated in the six highlighted regions Health's cutoff for "thick" vs "thin" deposits is 5 meters

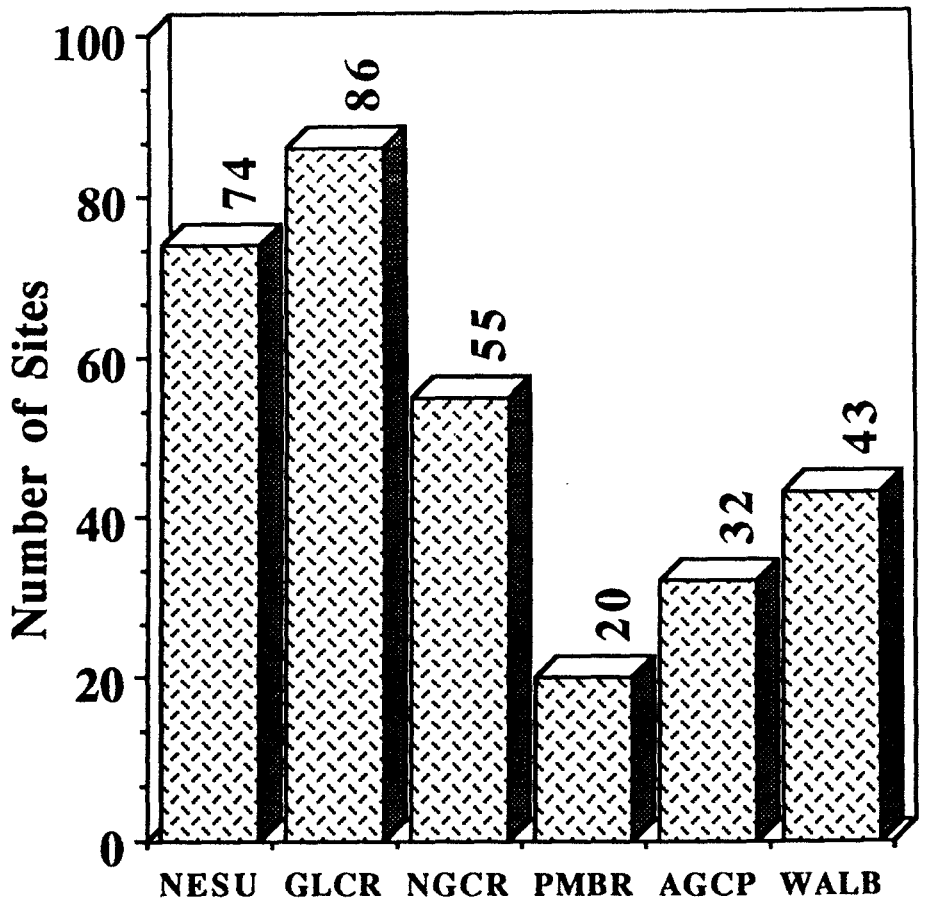


Figure 3-6. **Distribution of the 310 sites of this study according to Hydrogeological Setting. Refer to Table 3-11 for explanation of settings.**

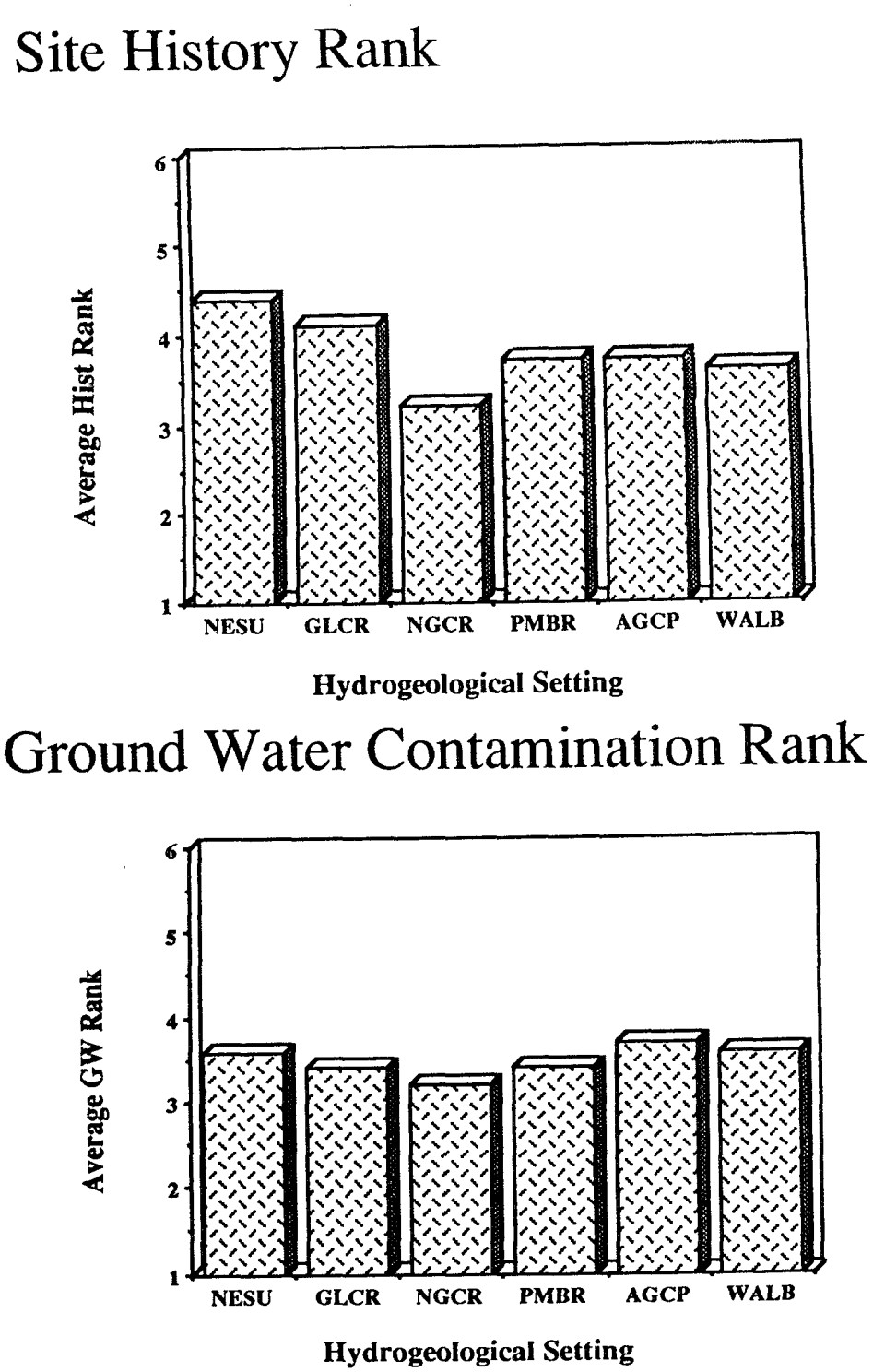


Figure 3-7. **Results of the Site History and Ground Water Contamination Ranks as Related to Hydrogeologoic Setting**

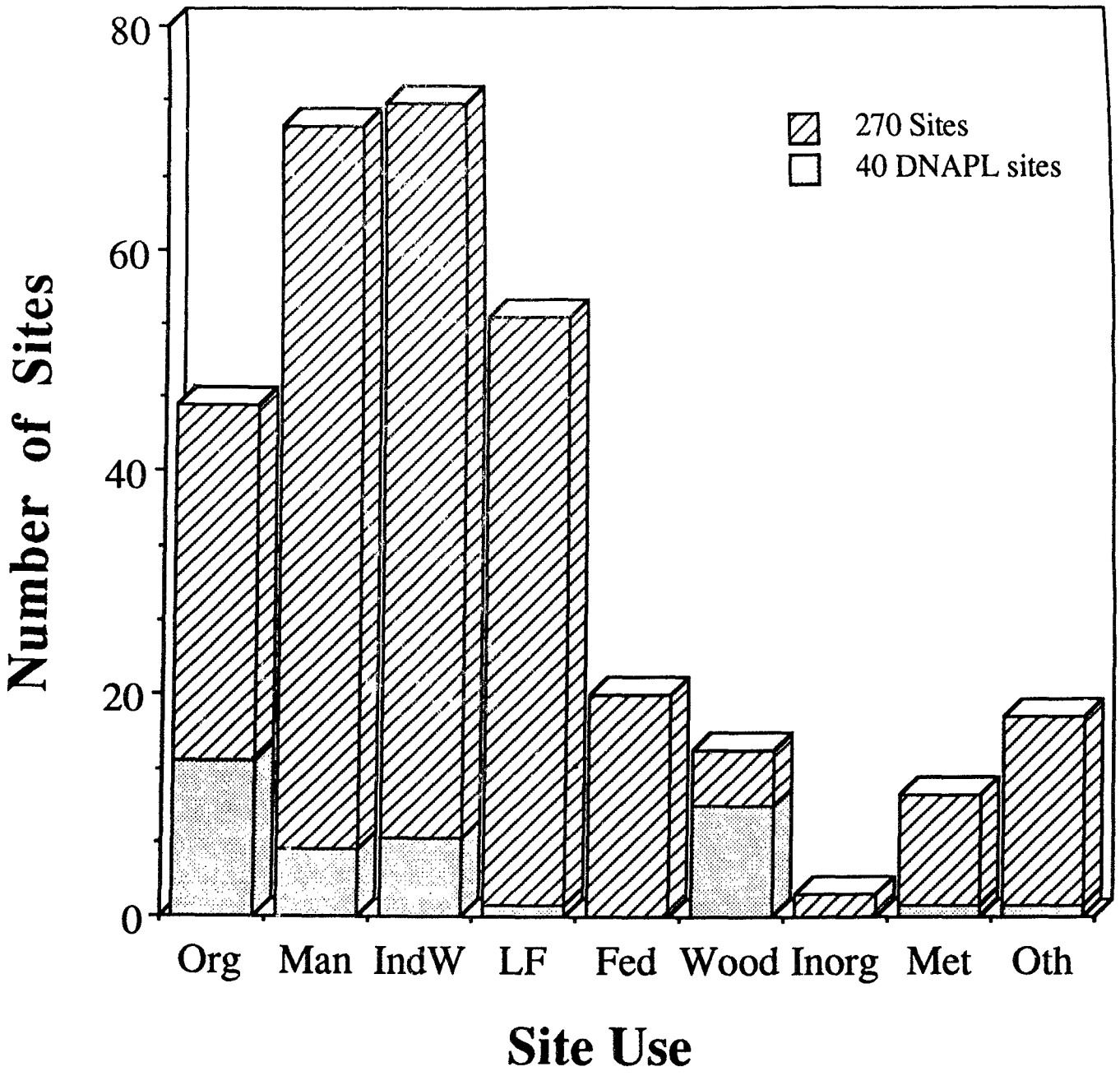
3.5 Relationship of Site Use to DNAPL Occurrence

The former use of a Superfund site has bearing on the ability to predict DNAPL contamination as well as on the likelihood of DNAPL occurrence. Site use also affects the nature of the site contamination, the remedial options, and the degree of difficulty of site remediation. To explore the association between site use and DNAPL occurrence, site uses were divided into nine major categories:

- Organic Chemical Production
- General Manufacturing
- Industrial Waste Management
- Combination Landfill
- Federal Facility
- Wood Treatment
- Inorganic Chemical Production
- Metal Industry/Mining
- Miscellaneous

Figure 3-8 shows the site use distribution for the 310 sites evaluated, and the specific site uses associated with these categories are listed in Table 3-12. The proportion of sites with direct observations of DNAPL below the water table are shown in a darker shade. The site uses where DNAPL observations were most commonly reported are wood treaters, organic chemical producers, and industrial waste managers.

Figure 3-9 shows the average site history rankings and ground water contamination rankings for each site use. Wood treatment operations received high marks for both rankings, partly due to the large percentage of known DNAPL sites in this group of sites. After wood treatment, organic chemical producers, industrial waste sites, and general manufacturing sites have the highest observed percentage solubilities and number of known DNAPL sites, and thus the highest ground-water rankings. In summary, the site findings indicate that some site uses will have a greater likelihood of subsurface DNAPL that others. Those with the highest probability are: wood treatment sites, organic chemical production sites, general manufacturing sites, and industrial waste disposal sites.



KEY:

ORG - organic chemical production: MAN - general manufacturing: INDW - industrial waste management: LF - combination landfill: FED - federal facility: INORG - inorganic chemical production: MET - metals industry/mining: OTH - miscellaneous

Figure 3-8. Site use distribution for the 310 sites.

Table 3-12. Major Categories of Site Uses.

Organic Chemical Production

Asphalt production or distribution plant
Coal gasification facility
Coal mining
Coking operations (steel industry)
Oil and gas mining
Oil storage (fuel oil, etc)
Organic chemical manufacturing
Organic chemical packaging, distribution and storage
Paint and dye production
Pesticide distribution, packaging, and transport
Pesticides and herbicide production
Petroleum refining and related industries
Pharmaceutical manufacturing
Resin and glue manufacturing
Solvent manufacturing
Solvent packaging distribution, transport and recycling
Synthetic fiber production
Transformer oil production

General Manufacturing

Agricultural equipment manufacturing
Air craft manufacturing
Air craft maintenance and repair
Automobile and motorcycle manufacturing
Automobile body repair or paint shop
Battery manufacturing
Capacitors and transformers manufacturing
Ceramics manufacturing
Construction company
Electronics and electrical equipment manufacturing
Engine manufacturing
Engine repair
Fabricated metal product manufacturing
Food manufacturing, packaging, and distribution
Lumber and wood products manufacturing
Other manufacturing
Paper and allied products manufacturing

Table 3-12. Major Categories of Site Uses (continued)

General Manufacturing (continued)
Plastics manufacturing
Printing or publishing facility
Rubber products manufacturing
Tannery
Textile mill
Textile printing and processing
Tool and die manufacturing
Weapons and explosives manufacturing
Weapons maintenance and repair

Industrial Waste Management
Drum reconditioning facility
Industrial landfill
Liquid industrial/hazardous waste disposal
Liquid industrial hazardous waste incinerator
Liquid industrial hazardous waste storage and transport
Liquid industrial hazardous waste treatment
Midnight dumping
Petroleum-related waste disposal
Solvent recycling
Transformer reprocessing and/or recycling
Waste oil processing, storage, transport

Landfill
Combination municipal and industrial landfill

Other Waste Facilities
Municipal landfill
Publicly owned sewage treatment works
Recyclers of solid waste
Septic services
Solid waste incineration facility
Tire disposal facility
Waste storage and transfer facility
Waste transportation

Table 3-12. Major Categories of Site Uses (continued)

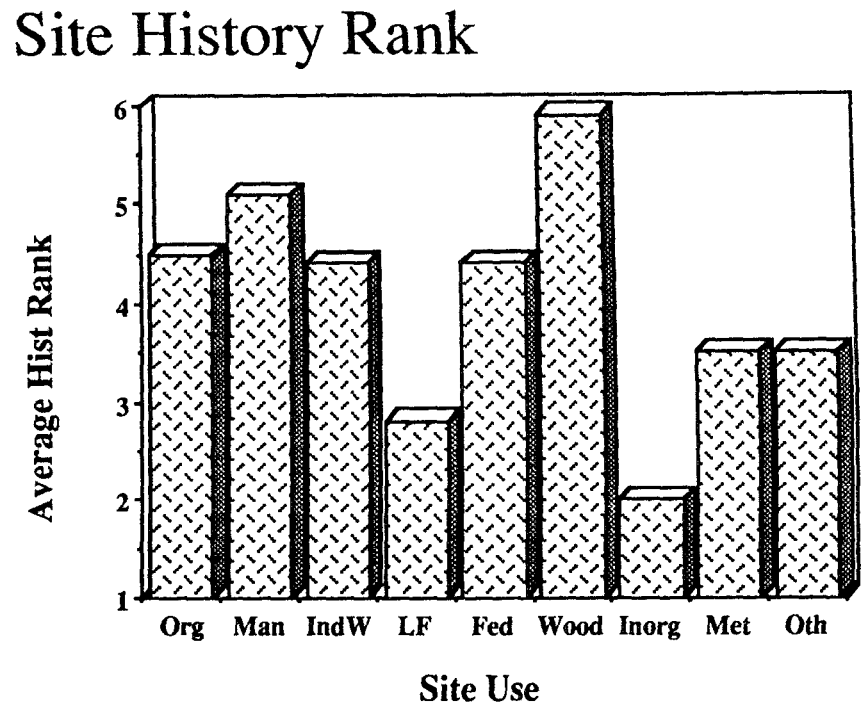
Federal Facilities
Department of Energy facility
Military Base

Wood Treatment
Wood preservation plant

Inorganic Chemical Production
Asbestos manufacturing
Chemical manufacturing (unspecified)
Chemical mixing and batching (unspecified)
Fertilizer manufacturing
Inorganic chemical manufacturing
Inorganic chemical packaging, distribution, and storage
Inorganic waste processing
Non-metallic mineral mining

Metal Industry/ Mining
Battery recycling
Electroplating facility
Metals mining
Metal recycling
Ore mill
Primary metals industry
Salvage/scrap yard

Miscellaneous
Airport
Dry cleaning plant
Fire-fighter training area
Nuclear power plant, radiation lab, etc
Power plants (non-nuclear) and associated facilities
Railroad yard and rail car maintenance facility
Research laboratory, agricultural station, or similar facility
Unknown



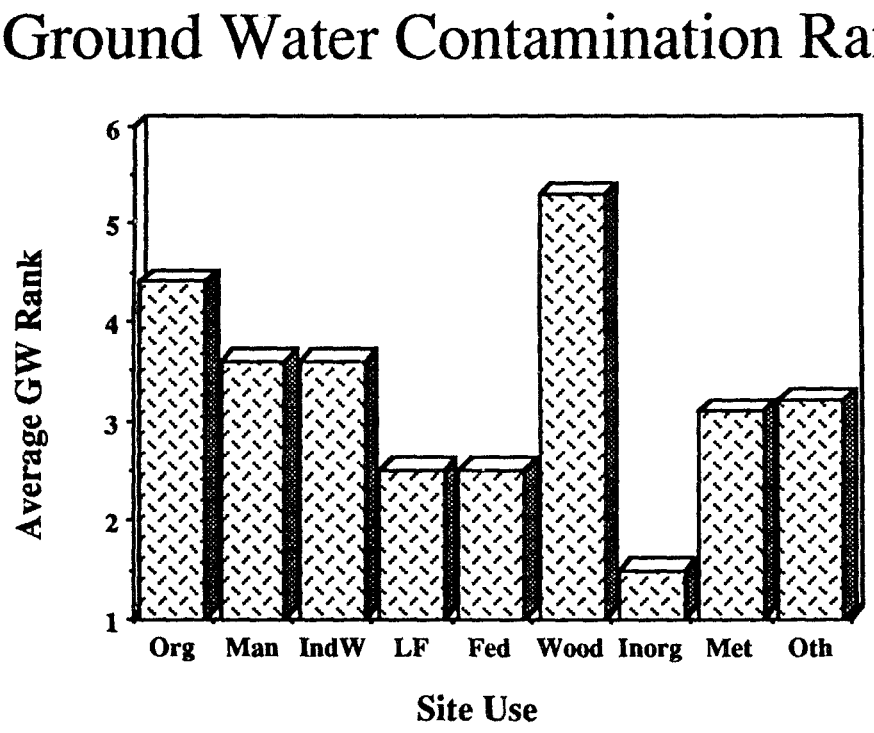


Figure 3.9. Site History Rank and Ground Water Contamination Rank by Site Use Type.

3.6 Site Contaminant Type and DNAPL Occurrence

The hazardous substances that have been used, stored, or disposed of at Superfund sites vary widely in their compositions and physical and chemical properties. In evaluating the potential for subsurface contamination by DNAPLs, it is useful to group sites with similar contaminants. Based on the site types encountered during this study, and on DNAPL site groupings suggested by Cherry and Feenstra (1991), eight categories of contaminant types were established for which one would expect distinctive types of subsurface contamination.

- inorganic chemicals
- light petroleum products
- chlorinated solvents
- mixed industrial solvents
- creosote
- coal tar
- PCB oil/solvent
- other organic compounds (including pesticides)

Site history information (type of chemicals used or stored at the site over its history of operation) and site characterization information (key ground water contaminants) were used to assign contaminant type categories. The first two categories have a relatively low DNAPL likelihood. The remaining six site types all have a significant potential for subsurface contamination by DNAPL chemicals. Figure 3-10 shows the distribution of site contaminant types for the 310 sites of this study.

Inorganic Chemical Sites

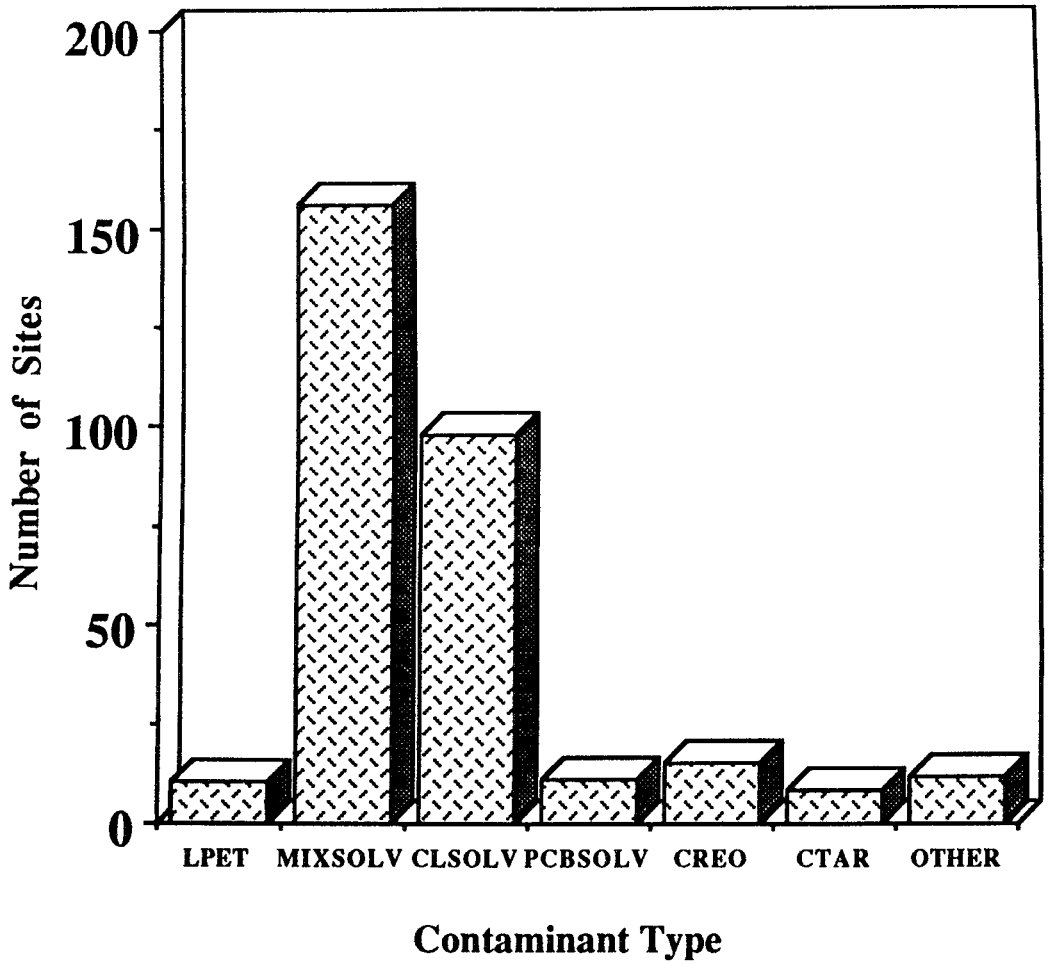
Inorganic element sites are those at which no organic contamination of ground water has been found and for which the key site uses are thought to have generated only inorganic chemicals. This study included two sites that indicated minor organic contamination in soils, but in general these were excluded.

Light Petroleum Product Sites

Light petroleum product sites are those at which the only hazardous substances used on site were lighter than water, and for which little or no DNAPL-related compounds have been found in ground water. One example of a Superfund site use in this category was a rubber manufacturing plant, which had other DNAPL compounds present.

Chlorinated Solvent Sites

These are sites at which the main contaminants are chlorinated solvents. Product

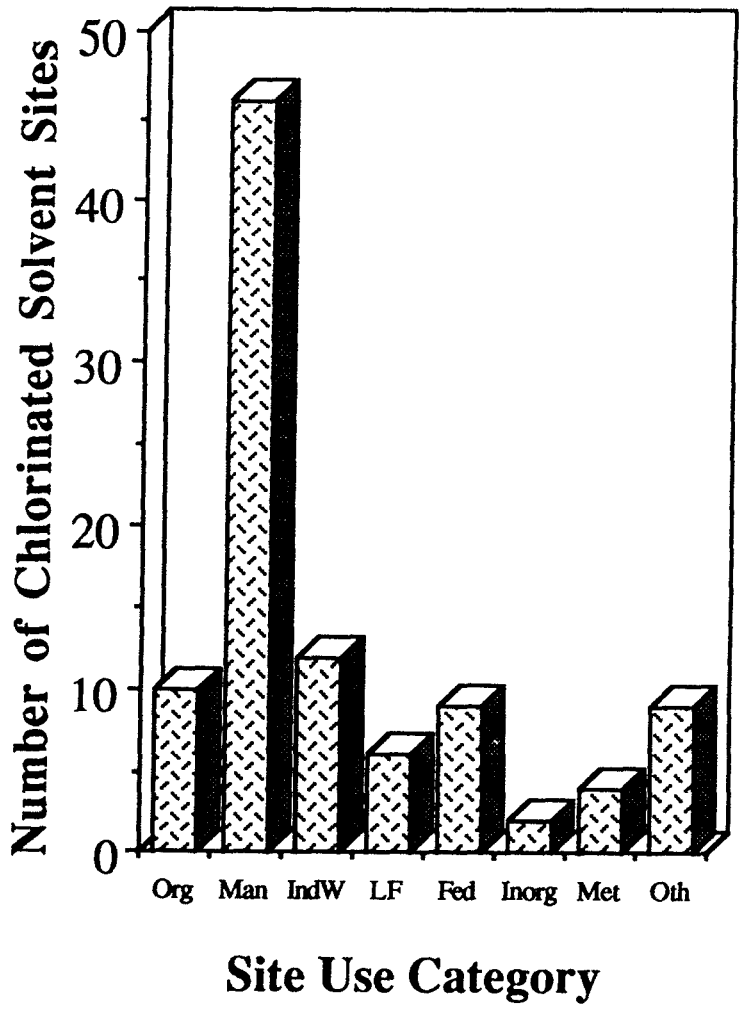


Key:
LPET - Light petroleum products
CLSOLV - Chlorinated solvents
MIXSOLV - Mixed industrial solvents
PCBSOLV - PCB oil/ solvents
CREO - Creosote
CTAR - Coal tar
OTH - Other organic compounds

Figure 3-10. Distribution of the 310 sites evaluated according to site contaminant type.

or waste streams, or ground water contamination composed entirely of one or more of these compounds place a site in the chlorinated solvents category. Ninety-eight sites, or nearly a third of the sites received this designation.

Since solvent use is common among a wide range of industries, there are numerous site uses associated with this site contaminant category. Figure 3-11 shows the site use distribution of the 98 chlorinated solvent sites evaluated. Table 3-13 lists the frequency of detection of chlorinated solvents at greater than 0.01% of solubility at these sites.



ORG - organic chemical production: MAN - general manufacturing: INDW - industrial waste management: LF - combination landfill: FED - federal facility: INORG - inorganic chemical production: MET - metals industry/mining: OTH - miscellaneous

Figure 3-11. Site Use Distribution for the 98 Chlorinated Solvent Sites.

Table 3-13. Compounds reported at > =0.01% solubility in ground water at the ninety-eight chlorinated solvent sites.

Compound	Form and color of Pure Product	No. of Sites	% Sites
Carbon Tetrachloride	Colorless liquid	2	2
Chlorobenzene	Colorless liquid	4	4
Chloroform	Clear liquid	1	1
Dichlorobenzene, 1,2-	Colorless liquid	5	5
Dichloroethane, 1,1-	Colorless oily liquid	14	14
Dichloroethane, 1,2-	Colorless oily liquid	5	5
Dichloroethylene, 1,1-	Colorless liquid	30	31
Dichloroethylene, cis 1,2-	Colorless liquid	9	9
Dichloroethylene, trans 1,2-	Colorless liquid	31	31
Methylene Chloride	Colorless liquid	11	11
Tetrachloroethylene	Colorless liquid	42	43
Trichloroethane, 1,1,1-	Colorless liquid	40	41
Trichloroethane, 1,1,2-	Colorless liquid	5	5
Trichlorethylene	Clear or blue liquid	76	78
Trichlorofluoromethane, 1,1,2	Colorless liquid	1	1

Mixed Industrial Solvent Sites

These are sites at which a great range of DNAPL compounds have been used, stored, or disposed of, but site contaminants are generally dominated by a few chlorinated solvents. They may also contain BTEX compounds, pesticides, and poly-nuclear aromatics, and phenols. One hundred fifty-five sites in this study received this designation. Figure 3-12 shows the distribution of site uses associated with mixed solvent sites. In general, industrial waste management sites and landfills receive the widest range in waste materials and account for the greatest number of these sites.

Table 3-14 shows the main chemicals observed at the 155 mixed industrial solvent sites and their frequency of detection at >0.01% of solubility. The compounds seen most frequently were the monoaromatic hydrocarbons and chlorinated solvents.

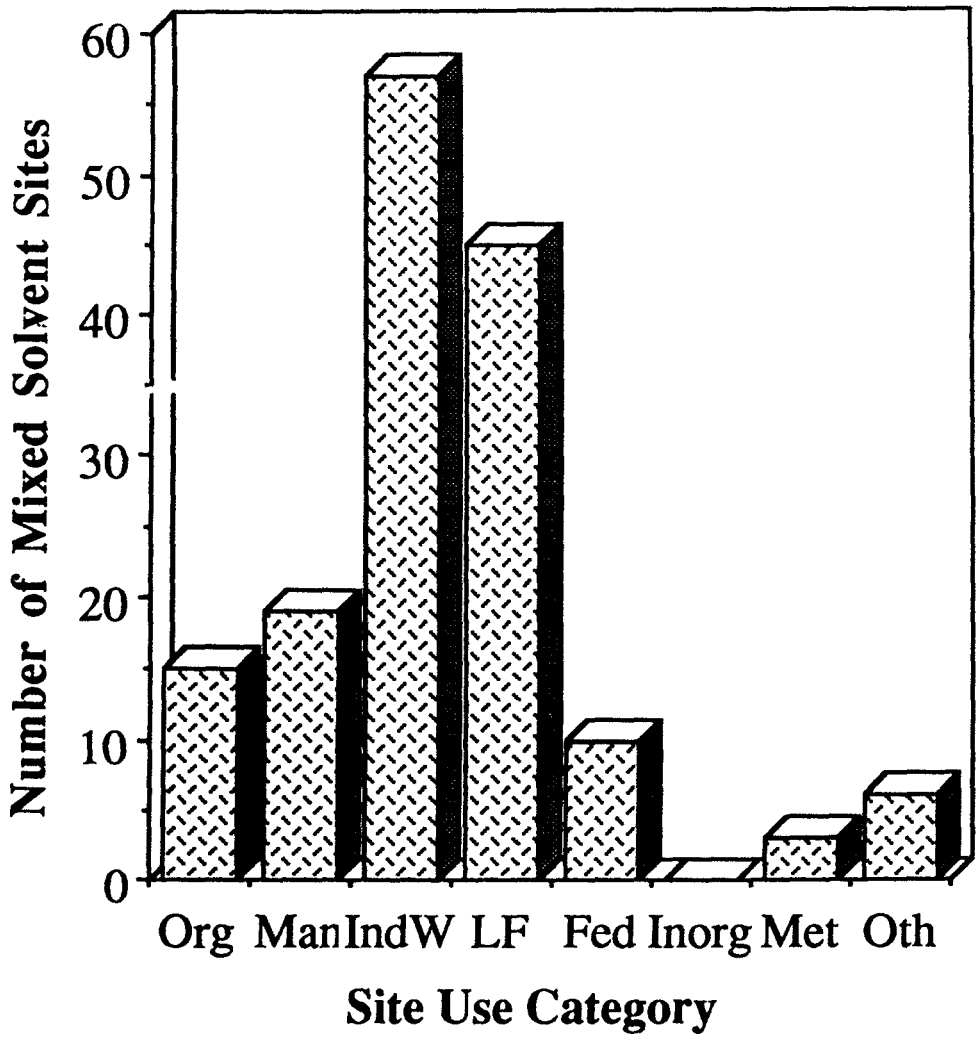


Figure 3-12. Site use distribution for the 155 sites in the mixed industrial solvents category. Refer to Figure 3-11 for key.

Table 3-14. Main Compounds reported at >0.01% Solubility in Ground Water at Mixed Industrial Solvent Sites.

Compound	# sites	% sites
Light Petroleum Products:		
Benzene	60	39
Ethylbenzene	80	52
Styrene	7	5
Toluene	105	68
Xylenes	78	51
Chlorinated Solvents:		
Carbon Tetrachloride	7	5
Chlorobenzene	31	20
Chloroethane	12	8
Chloroform	13	8
1,2 Dichlorobenzene	18	12
1,4 Dichlorobenzene	18	12
1,1 Dichloroethane	40	26
1,2 Dichloroethane	21	14
1,1 Dichloroethylene	33	21
cis-1,2 Dichloroethylene	10	6
trans-1,2 Dichloroethylene	61	39
Methylene Chloride	34	22
1,1,2,2 Tetrachloroethane	6	4
Tetrachloroethylene	73	47
1,1,1 Trichloroethane	59	38
1,1,2 Trichloroethane	8	5
Trichloroethylene	82	53
Trichlorofluoromethane	4	3
Vinyl Chloride	52	34
Pesticides:		
1,2 Dichloropropane	8	5
Ethylene Dibromide	3	2

Table 3-14. Main Compounds reported at >0.01% Solubility in Ground Water at Mixed Industrial Solvent Sites (continued).

Compound	# sites	% sites
Poly Nuclear Aromatics and Phenols:		
Acenapthene	6	4
Benzo(a)anthracene	5	3
Chrysene	5	3
Dimethylphenol, 2,4-	6	4
Fluoranthene	5	3
Fluorene	6	4
Methyl naphthalene, 2-	11	7
Naphthalene	28	18
Pentachlorophenol	4	3
Phenanthrene	6	4
Phenol	3	2
Pyrene	8	5
Other:		
Acetone	3	2
Benzoic acid	4	3
Dibenzofuran	1	1
Isophorne	4	3
Methyl Ethyl Ketone	20	13
Methyl Isobutyl Ketone	17	11
Tetrahydrofuran	2	1

Creosote/Coal Tar Sites

Creosote sites are a relatively small and distinctive group in the Superfund program. They are related to only two site uses: wood preservation, and creosote production. Of the 15 sites in this category, 10 have had direct observations of creosote DNAPL in the saturated zone, and six reported LNAPLs floating on the water table. Contaminants typically found in ground water at creosote sites are listed in table 3-15.

Coal tar sites are generally associated with coal gasification or coal tar production operations. Contaminants typically found in ground water at coal tar sites are listed in table 3-16. Creosote and coal tar sites should be considered as definite DNAPL sites.

Table 3-15. Compounds Found at > 0.01% Solubility in Ground Water at Creosote Sites

Compound	# sites	% sites
Benzene	3	20
Ethylebenzene	5	33
Toluene	5	33
Xylenes	6	40
Acenapthene	12	80
Anthracene	6	40
Benzo(a)anthracene	1	7
Benzo(a)pyrene	1	7
Benzo(b)fluoranthene	3	20
Chrysene	7	47
o-cresol	1	7
p-cresol	2	13
Dibenzo(a,h)anthracene	1	53
Dibenzofuran	3	20
Dimethylphenol, 2,4-	2	13
Fluoranthene	8	53
Fluorene	11	73
2-Methyl Napthalene	9	60
Napthalene	12	80
Pentachlorophenol	9	60
Phenanthrene	12	80
Phenol	1	7
Pyrene	9	60

Table 3-16. Compounds Found at > 0.01% Solubility in Ground Water at Coal Tar Sites

Compound	# sites	% sites
Benzene	6	75
Ethylbenzene	5	63
Styrene	3	38
Toluene	5	63
Xylenes	5	63
Acenapthene	5	63
Anthracene	3	38
Chrysene	3	38
Dimethylphenol, 2,4-	3	38
Fluoranthene	4	50
Fluorene	4	50
2-Methyl Napthalene	5	63
Napthalene	5	63
Phenanthrene	3	38

PCB/Solvent Sites

PCB contamination usually encompasses a class of chlorinated compounds that includes up to 209 variations or congeners with different physical and chemical characteristics. They were commonly used as mixtures called Aroclors. The most common are Aroclor-1254, Aroclor-1260, and Aroclor 1242. PCBs alone are not usually mobile. However, they are often found with oils, which may carry the PCBs as a separate phase. PCBs are most commonly associated with electrical transformer manufacturing, salvage, and recycling site uses. Table 3-17 shows the DNAPL compounds found at PCB sites in this study.

Relationship Between Contaminant Type to the Likelihood of Subsurface DNAPL

Figure 3-13 shows the relationship of contaminant type to the likelihood of DNAPL presence for the site history ranking and ground water contamination ranking. The results of this study indicate that certain contaminant types can be directly associated with a medium to high probability of subsurface DNAPLs. Those that continuously received a high ranking include creosote, coal tar, and PCBs. However, these sites tend to represent a

small proportion of Superfund sites, are easily linked to specific site uses and tend to have a relatively small impact in terms of volume of subsurface contamination (when compared to the solvent sites).

In addition, the chlorinated solvent and mixed solvent sites that represent the majority of Superfund sites, are associated with a wide range of site uses, and cover the entire range of likelihood of subsurface DNAPL. However, current research indicates that they have a relatively large impact in terms of volume of subsurface contamination.

Conclusions

Figure 3-14 shows the extrapolation of the results of this study to current universe of sites on the NPL. Approximately 60% of NPL sites either have, or could be expected to have a medium to high potential of having DNAPLs present, providing a source of ground water contamination in the subsurface. The remainder of sites could be expected to fall within the category of "low to unlikely." This means that the potential for subsurface DNAPL should be considered at the majority of Superfund sites. Site characterization efforts should focus on determining the potential of DNAPL presence early in the site investigation process.

In order to extrapolate the results to the entire universe of NPL sites, four categories of site conditions were established (listed below). Ground water contamination information for each NPL site was evaluated and each site was assigned to one of the four categories. The sources of ground water contaminant information included the NPL Site Characterization Database, the NPL Summary Booklets, RPMs, remedial investigation reports, and other site documents. For the five regions that were visited for this study, all site contaminant information was verified. The sites in the remaining five regions were assigned to a category based on the information obtained from the sources just mentioned. The results were as follows:

- observation of DNAPLs below the water table (5%)
- organic contaminants in ground water, but no DNAPL observation (80%)
- only inorganic contaminants in ground water (10%)
- no contaminants in ground water (5%)

At the top of the spectrum are 5% of sites for which DNAPL contamination has been established with certainty. At the bottom of the spectrum, the 10% of sites with inorganics only and the 5% with no ground water contamination, are those at which DNAPLs can be ruled out. The remaining 80% are those at which no DNAPL has been observed, but organic contaminants are present in the dissolved phase and thus, have some potential for DNAPL contamination.

The 270 sites which were ranked via the methods discussed in this study were drawn from the pool of NPL sites with organics in the ground water. They make up a little over 25% of that group. This subset of 270 sites was representative of the distribution of site use types of the overall 80% of the sites exhibiting organic contamination. Therefore, since the distributions were the same, a high degree of confidence is placed on the direct extrapolation of the proportions from the subset of 270 sites to the sites with organics present in ground water. The final percentages of sites falling within the high, medium, and low probabilities were calculated by adding those sites with DNAPLs observed, only inorganics present, and no ground water contamination back into the set of all sites. Therefore, the percentage of sites in the high, medium, or low categories are lower for the set of all NPL sites that for the subset of sites. The results of this study suggest that it is important for any future refinements of policies for investigating and addressing contaminated ground water at Superfund sites to consider carefully the likely presence of DNAPLs.

The site historical information ranking system correlated well with the information from the sites known to have DNAPLs present. The historical information focused on site use, past disposal practices and release of DNAPL compounds throughout the period of site operation. This type of information can yield important direct and indirect evidence that DNAPL have been released. However, the lack of such information does not constitute evidence that DNAPL were absent at a site.

The ground water contaminant ranking system (expressed as a per cent of maximum solubility) also correlated well with information from the sites known to have DNAPLs present. The presence of a DNAPL compound in ground water is one of the best indirect indicators of the likelihood of DNAPL presence. The presence of dissolved-phase DNAPL in ground water does not confirm the presence of a pure-phase DNAPL source in the subsurface. However, the concentrations that are now generally accepted by the research community as indicating a high likelihood of a subsurface source of DNAPL, across a wide range of site types, are on the order of 1% or more of a compound's solubility.

The analysis of hydrogeologic setting on DNAPL occurrence indicated that there was no identifiable hydrogeologic setting that had a greater likelihood of exhibiting subsurface DNAPL than another. In addition, dissolved-phase DNAPL contamination was just as likely to be present in aquifers with a deep vadose zone as those with a shallow water table.

The relationship of site use to DNAPL occurrence was evaluated in order to determine if certain site uses (site types) exhibited a greater likelihood for subsurface DNAPL than others. The results indicated that indeed, certain site types continuously ranked as having a high likelihood of DNAPLs present. Those with the highest likelihood of having DNAPLs include: wood-treating sites, general manufacturing sites, organic chemical productions sites, and industrial waste landfills.

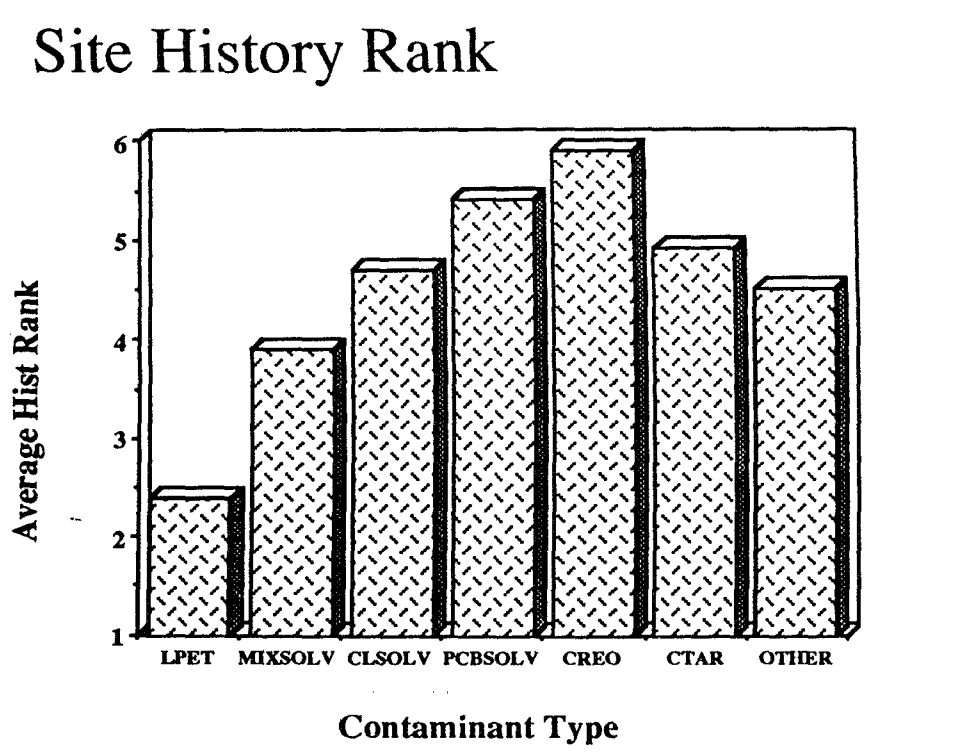
The relationship between site contaminants and DNAPL occurrence was evaluated

in order to determine if there were certain suites of compounds present at concentration levels above their theoretical maximum solubilities that would exhibit a higher likelihood of subsurface DNAPLs than at sites where that situation does not exist. The results correlate well with the types of DNAPL compounds associated with specific site types. The contaminants most directly associated with DNAPL presence included: creosote compounds, coal tar compounds, Polychlorinated Biphenyls (PCBs), chlorinated solvents, and mixed solvents. However, even though creosote, coal tar, and PCB sites were easily linked with specific site uses, and have a relatively high likelihood of subsurface DNAPL, they represent only a very small proportion of the universe of NPL sites. The majority of NPL sites exhibit chlorinated and mixed solvent contaminants present in ground water. These sites are more difficult to assess because they are associated with a wide range of uses.

The results of this study also suggest that the emphasis of future research efforts for ground water remediation, emphasis should be placed on chlorinated solvents and mixed solvents sites, as these represent the majority of sites having DNAPL-related compounds present as a separate phase and as a source of dissolved-phase ground water contamination.

Table 3-17. Compound found in ground water at PCB/Solvent sites

Compound	Color and Form of Pure Product at Room Temperature	Number of Sites	Percent of Sites
Benzene		2	18
Ethylbenzene		3	27
Toluene		4	36
Xylenes		3	27
Dichlorobenzene, 1,2-	Colorless liquid	2	18
Dichlorobenzene, 1,3-	Colorless liquid	3	27
Dichlorobenzene, 1,4-	White volatile crystals	3	27
Trichlorobenzene, 1,2,3-	Platelets	3	27
Trichlorobenzene, 1,2,4-	Colorless liquid	5	45
Trichlorobenzene, 1,3,5-	Crystals	1	9
PCB 1242	Clear, colorless oil	2	18
PCB 1248	Colorless oil	1	9
PCB 1254	Light yellow viscous liquid	5	45
PCB 1260	Yellow soft sticky resin	6	55
PCBs (total)	Yellowish oily liquid	3	27
Tetrachloroethylene		3	27
Trichloroethylene		5	45



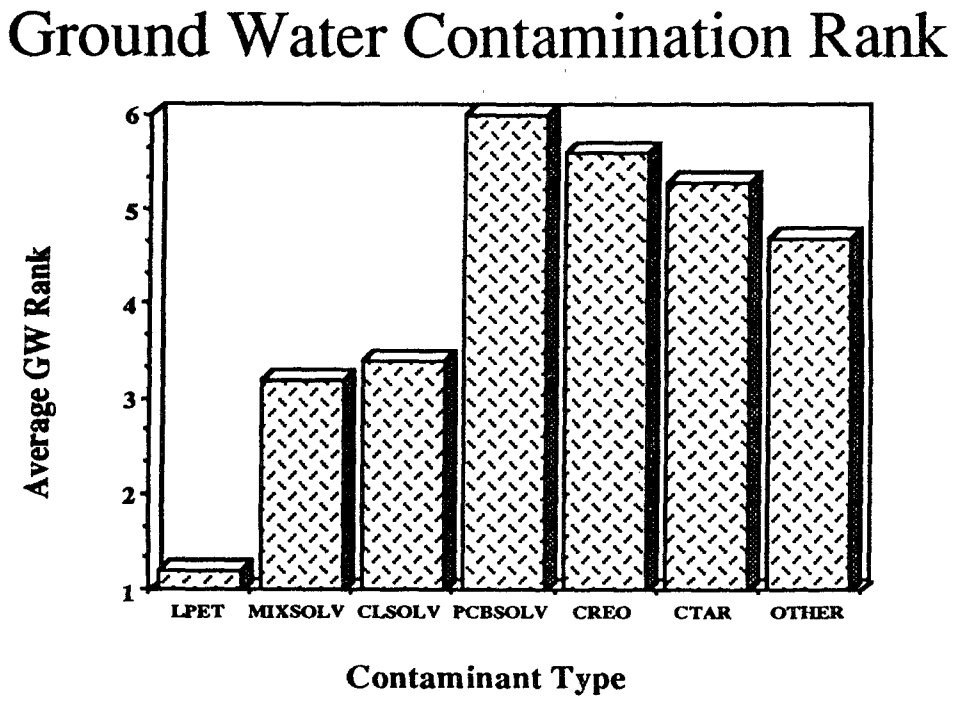


Figure 3-13. Relationship of Contaminant Type to Likelihood of Subsurface DNAPL.

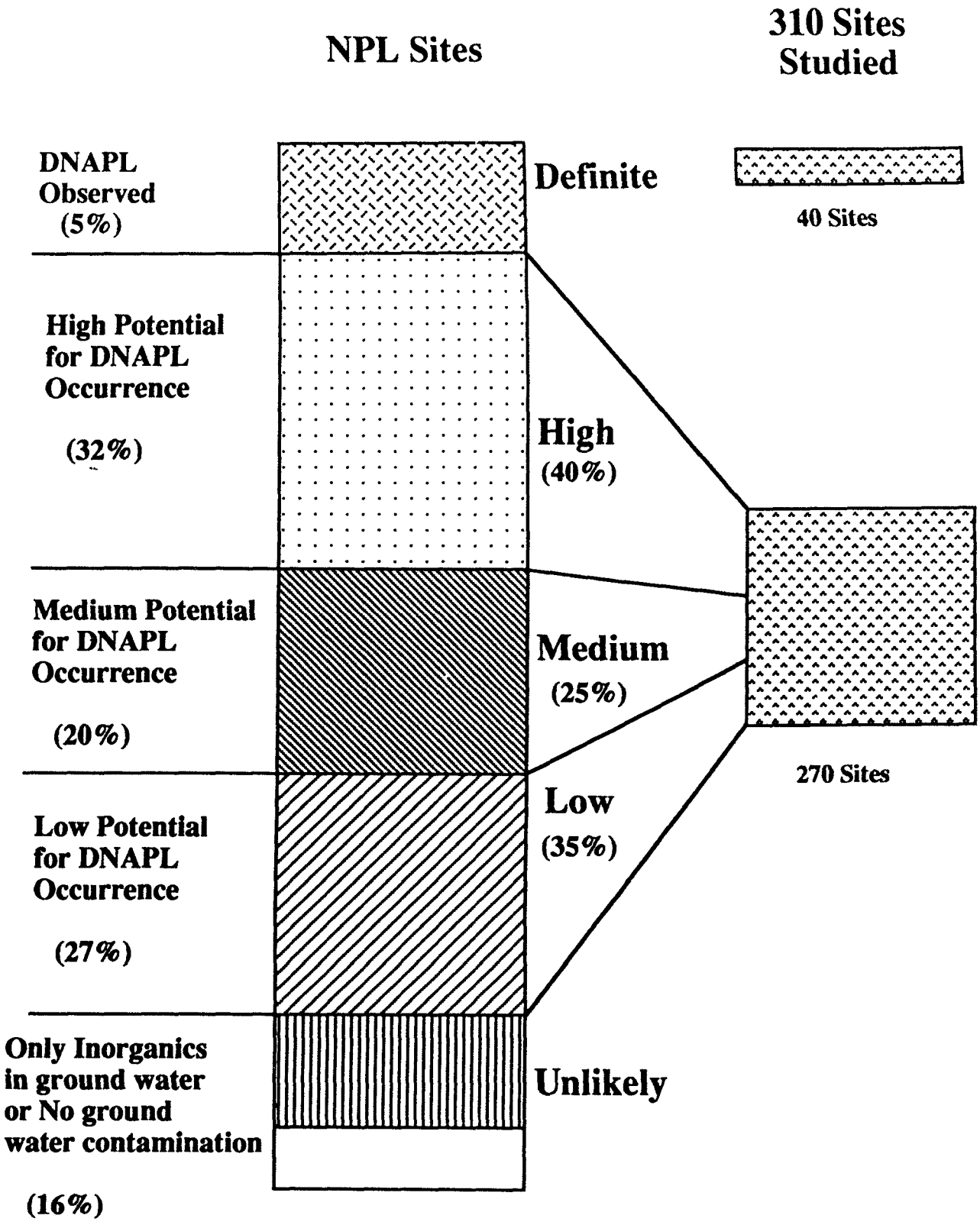


Figure 3-14. Extrapolation of the Study Results to the Universe of NPL Sites.

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APPENDIX A

DNAPL SITE ASSESSMENT STUDY

********** Please use blue or red ink when filling out this form -- thank you! **********

Site name: _____

EPA ID: _____ State: _____

Site RPM: _____

RPM telephone number: _____

Your name, position, and
telephone number
(if not RPM) _____

For how many years have you been
involved with this site? _____

At what state in the Superfund process is this site
(RI in progress, RD, RA, etc.), especially with respect
to ground water contamination? _____

Does this site have organic chemical contamination?

Yes Maybe No Unknown

<u>Sites without organic chemical contamination:</u>

Does the site have groundwater contamination
with inorganic chemicals? Yes Maybe No Unknown

Please fill out only section 1.A.
of this form (pg. 1).

<u>Sites with known or possible organic chemical contamination:</u>

Specifically, is ground water at the site
contaminated with organic chemicals? Yes Maybe No Unknown

Please fill out the rest of this form.

DNAPL SITE ASSESSMENT STUDY
REGION 9

Organization of the Data Collection Form

1. Site History Section

1.A. Site Use

If the activity associated with the contamination at this site is completely unknown, please check here and proceed to Section 2 (Site Investigation Section, p. 7). _____

What were the major uses of this site? Please record the key site activity(ies) (e.g. combination municipal and industrial landfill, computer chip manufacturing, wood preservation, solvent recycling) and the period during which the activity occurred (i.e.1952 - 1975), to the best of your knowledge.

	Activity Period (years)	
	Start	Stop
_____	_____	_____
_____	_____	_____
_____	_____	_____

Is this site a multi-source site (that is, does it have a number of distinct source facilities, such as an industrial park, or is it a very large facility with multiple source areas, such as a military base)? Yes No Unknown

If yes, you may choose to answer the questions on this form with respect to only one or a few source areas that are most likely to have DNAPL on (for instance, areas with chlorinated solvent disposal). See the project hydrogeologist for more explanation.

Please add any comments you would like to make on historical site uses.

_____

_____

_____

_____ **HISTCMT1**

1.B. Hazardous Substances and Chemicals

Please circle the abbreviations for those substances which are known to have been used, produced, stored, or disposed of at the site in significant quantities (> 5 drums/year). The substances and chemicals listed below are related to NAPLs to varying degrees (those marked with a "*" are strongly related to DNAPLs).

AUFL		Automotive fluids (transmission, brake, etc.)
BTRY		Batteries and/or associated wastes
CPTF	*	Capacitor and/or transformer debris (PCB-related)
CTAR	*	Coal tar
CREO	*	Creosote
CUTO		Cutting oils
FOIL		Fuel oils
GASO		Gasoline
ISEW		Industrial sewage
KERO		Kerosene
LABC		Laboratory chemicals and/or wastes
OCHM		Organic chemicals (besides PCBs and solvents)
OCWS	*	Organic chemical waste drums and/or containers
PNTS		Paints, lacquers and/or pigments
PCBO	*	PCB-laden oils
TPCB	*	PCBs
PCP	*	Pentachlorophenol
PEST	*	Pesticides and/or herbicides
PRPL		Propellants, jet fuel
		Solvents:
SOLC	*	Chlorinated
SOLN		Non-chlorinated
SOLV	*	Undifferentiated
STBM		Still and/or tank bottoms
TRNF	*	Transformer oil
UMOL		Used motor oil
WOIL		Waste oils

Please list any other hazardous substances or chemicals that are known to have been used, produced, stored, or disposed of in significant quantities at the site. If you list chemicals, please indicate only those chemicals for which records or other knowledge of historical site use exist, not chemicals whose historical presence is inferred from their current presence as site contaminants:

_____

_____

OTHERSUBST

_____

1.C. Releases of Hazardous Substances and Chemicals

This section documents the potential mechanisms for release of hazardous chemicals and substances at the site.

1.C.1 Industrial Practices

Please circle the abbreviations for any industrial practices which have occurred at this site. These practices typically use DNAPL chemicals and have a moderate to high probability of historical DNAPL release.

ELCL	Electrical parts and electronics cleaning
FFTA	Fire fighter training
MTCL	Metal cleaning and degreasing
MTMC	Metal machining
PTST	Paint and lacquer stripping (of furniture, etc.)
SAST	Storage of solvents in aboveground tanks
SUST	Storage of solvents in underground storage tanks
SDRM	Storage of drummed solvents in uncontained areas
SLUL	Solvent loading and unloading
TLDI	Tool-and-die operations
TRNF	Transformer breaking or recycling
WDPR	Wood treatment

Please list below any other industrial practices which may have used DNAPLs (chlorinated solvents, coal tar, creosote, PCB-laden oils) and possibly caused their release at this site:

_____

_____

_____

_____ **OTHERINDP**

1.C.2. Waste Disposal Practices and Unintentional Releases

Please circle the abbreviations for those waste disposal practices and unintentional releases which occurred at this site. The practices which indicate a high probability of DNAPL release (assuming DNAPL substances were present on-site) are marked with a "*".

Waste Disposal Practices

DRUM	*	Drum disposal/burial
LAGO	*	Lagoon/liquid waste surface impoundment
LWIN		Liquid waste incineration
LWSW		Liquid wastes discharged to surface water bodies
LWSS		Liquid (non-sanitary) wastes discharged to septic system or dry well
LWOG	*	Liquid wastes dumped onto open ground or into unlined trenches
LWTT	*	Liquid wastes dumped from tank trucks
LWDS	*	Liquid wastes released from drains and sumps
SLDG		Non-sewage sludge disposal
SWIN		Solid waste incineration
SWLF		Solid waste landfill
SWSW		Solid waste discharged to surface water bodies
UGIW	*	Underground injection well

Unintentional Releases

LAST		Leaks from aboveground tanks
LDRM		Leaks from drum storage areas
LUTP	*	Leaks from underground tanks and pipelines
CLUL		Releases during chemical loading and unloading
EXFR		Releases during explosions or fires
SPIL	*	Spills

Please list below any other means by which hazardous substances and chemicals were released to the environment at the site:

_____

_____

_____

_____ **OTHERWASTP**

1.C.3. Known Releases of DNAPL Related Substances

Specifically, were there known releases to the environment, such as spills, leaks, or disposal, of the DNAPL-related substances or chemicals present at the site? Yes Maybe No

No DNAPL substances present

If DNAPL-related substances or chemicals were released, were they released primarily as a separate non-aqueous phase or dissolved in water? Sep. phase Dissolved Both Unknown

No known releases

_____

_____

_____

_____ **RELCMT**

Considering the substances and chemicals present, please estimate the total volume of **organic chemicals** released to the environment at this site, to the best of your knowledge. (Record a range, if necessary).

_____ Units: gallons drums

Roughly, what is the uncertainty associated with this answer?

Low Medium High Very High

Check here if the volume released cannot be estimated: _____

1.D. Additional comments

In your opinion, how well understood is the site history of this site, especially concerning the activities and substances that caused contamination?	Very Well Well Generally Poorly

Please discuss below any additional information about site history that may be relevant to the probability of DNAPL occurrence:

_____

_____

_____

_____

_____

_____ **HISTCMT2**

2. Site Investigation Section

2.A. Observation of Subsurface Non-aqueous Phase Liquids (NAPLs)

In this section, we are specifically interested in observations of separate organic liquids in the subsurface. Subsequent sections will address the dissolved phase.

Was the possible presence of subsurface NAPLs investigated directly during any site investigations? Yes No Unknown

Specifically, was the possible presence of DNAPLs investigated? Yes No Unknown

If yes, what techniques were used to look for DNAPLS?

LOOKCMT

Were any non-aqueous phase liquids (NAPLs) observed in the subsurface at this site? Yes Maybe No
(if you are uncertain, check boring logs for observations of oily liquids)

If yes, what was their nature?
Lighter than water (LNAPL)
Denser than water (DNAPL)
Unknown

If a NAPL was observed, had it reached the water table? Yes Maybe No

If NAPLs have been or may have been observed, please describe how they were encountered (in a test pit, soil boring, ground water sample, etc.). Also note whether the NAPLs were found within contained waste zones (for example, within a lined lagoon or landfill, or outside the boundaries of waste areas. Please be as specific as possible.

NAPLENC

If NAPLs have not been observed or only LNAPLs have been observed, please proceed to Section 2.B. (Contamination of ground water, p. 9). If known or suspected DNAPLs were observed at this site, please fill out the questions on this page:

Where were DNAPLs observed with respect to the water table? Above Below Both Unclear

In which material was DNAPL observed? (Circle all that apply)
Unconsolidated material
Bedrock
Ground Water
Surface Water

What is the maximum depth below ground surface at which DNAPLs have been observed? (feet) _____

If the DNAPL was analyzed, please describe its composition below or attach a copy of the analytical results. (We are interested in a sample of the free-phase DNAPL itself, not an associated ground-water sample).

Chemical	% in DNAPL

If measured, what was the density of the DNAPL mixture? (g/cm^3) _____

How much, if any, DNAPL has been removed from the subsurface? (Please include units.) _____

If you have any additional comments on the DNAPL observation (e.g. what was its color and texture?), please record them below:

_____

_____

_____ **DNAPLCMT**

2.B. Contamination of Ground Water

This section records indirect indicators of DNAPL presence using levels and patterns of dissolved-phase ground-water contamination.

2.B.1 Sources of Ground Water Contamination

Please circle the abbreviations for the main sources for ground water contamination at the site. Those sources most associated with DNAPL contamination (assuming that DNAPL substances were present on-site) are marked with an "*".

AGST		Aboveground tanks
LWOG	*	Area(s) of liquid waste dumping
BDRM	*	Buried drums
DRSP		Drains and/or sumps
DRMS		Drum storage areas
IPRA		Industrial processing areas
FFTA	*	Fire fighter training area
LAGO	*	Lagoons/trenches for liquid waste disposal
LWIN		Liquid waste incinerator
LULA		Loading and unloading areas
SSYS		Septic systems
SWLF		Solid waste landfill
SOLU	*	Solvent use area
SPIL	*	Spill area
UGIW	*	Underground injection well
UGST	*	Underground tanks and pipelines

Other major sources of ground water contamination:

_____

_____ **OTHSOURC**

Please estimate the horizontal area of the source(s) at the site. (Record a range, if necessary. Record the original source area if the source has since been removed.):

_____ _____ Units (circle one): acres ft^2

Check here if the source area cannot be estimated: _____

What is the typical depth to ground water at the site (feet)? Min.: _____ Max.: _____

2.B.2 Major Ground Water Contaminants

Please list the compounds that you consider to be the major ground water contaminants at the site. Include inorganic chemicals if these are driving the site investigation.

_____	_____
_____	_____
_____	_____

Are organic chemicals present in bedrock at concentrations greater than MCLs? Yes Maybe No Unknown

2.B.3. Maximum Contaminant Concentrations

Please use the following table (Table 1: Maximum Contaminant Concentrations) to record the maximum concentrations of organic chemicals found in ground water at this site. The table includes the organic contaminants most commonly found at Superfund sites and gives their densities and water solubilities, as listed in the Subsurface Remediation Guidance Table 3 (EPA/540/2-90/011b).

- We want to define the maximum ground-water concentrations observed over the entire site history, not just in the latest sampling rounds, so please try to provide those to the best of your knowledge.
- Unless the site has significant semi-volatile contamination in the ground water (as at creosote or coal tar sites), you may confine your answers to the volatile organic compounds.
- If there are major organic site contaminants which are not listed on the table, please include them on the lines at the bottom of the table.

Theoretically, ground water in direct contact with DNAPL should exhibit concentrations of the DNAPL chemicals that equal the chemicals' effective solubilities (i.e., if the DNAPL contains 50% TCE, the ground-water concentration should be 500 mg/l which is 50% of TCE's solubility limit). However, due to sampling procedures and heterogenous DNAPL distribution in the subsurface, the maximum observed concentrations of DNAPL-forming chemicals even at sites at which DNAPLs have been directly observed are often much lower than the chemicals' effective solubilities. Depending on site conditions, concentrations as low as a few percent of a chemical's solubility can represent an indication of subsurface DNAPL.

Table 1: Maximum Concentration Table

See Section 2.B.3. for instructions in filling out this table. Chemicals marked with a "*" have densities greater than water and will behave as DNAPLs in the subsurface if present as a nonaqueous liquid.

	Chemical	Density (g/cm^3)	Water Sol. (ppb)	Max. GW (ppb)	
	Volatiles				
	Benzene	0.877	1,780,000		BENZ
	2-Butanone (Methyl ethyl ketone)	0.805	268,000,000		MEK
*	Carbon Tetrachloride (Tetrachloromethane)	1.595	800,000		CTET
*	Chlorobenzene	1.106	490,000		CLBZ
	Chloroethane (Ethyl Chloride)	0.941	5,700,000		CLEA
*	Chloroform (Trichloromethane)	1.485	8,220,000		CLFM
*	1,1-Dichloroethane	1.175	5,500,000		1DCA
*	1,2-Dichloroethane	1.253	8,690,000		2DCA
*	1,1-Dichloroethylene	1.214	400,000		1DCE
*	Cis-1,2-Dichloroethylene	1.284	3,500,000		C2DC
*	Trans-1,2-Dichloroethylene	1.257	6,300,000		T2DC
*	Total-1,2-Dichloroethylene[1]	1.27	9,800,000		2DCE
*	1,2-Dichloropropane	1.158	2,700,000		2DCP
	Ethyl Benzene	0.867	152,000		EBNZ
*	Ethylene Dibromide (1,1-Dibromoethylene)	2.172	3,400,000		EDB
	4-Methyl-2-Pentanone (Methyl isobutyl ketone)	0.802	19,000,000		MIBK
*	Methylene Chloride (Dichloromethane)	1.325	13,200,000		MTCL
	Styrene (Vinyl Benzene)	0.906	300,000		STYR

Key:

Density: Density, g/cm^3, generally at 20E C.
Water sol.: Solubility in water, generally at 20E C.
Max. GW: Maximum concentration of chemical observed in ground water at site, reported in ug/l or ppb.
[1] The densities and solubilities for these totals vary depending upon the exact mix of constituents.
Note: To calculate the percentage of aqueous solubility for a compound, divide the maximum concentration (Max. GW) by chemical's solubility in water (Water sol.) and multiply by 100.

Table 1: Maximum Concentration Table (cont.)

	Chemical	Density (g/cm^3)	Water Sol. (ppb)	Max. GW (ppb)	
	Volatiles (cont.)				
*	1,1,2,2-Tetrachloroethane	1.600	2,900,000		PCA
*	Tetrachloroethylene	1.625	150,000		PCE
	Tetrahydrofuran	0.889	300,000,000		THF
	Toluene	0.867	515,000		TOLU
*	1,1,1-Trichloroethane	1.325	950,000		1TCA
*	1,1,2-Trichloroethane	1.444	4,500,000		2TCA
*	Trichloroethylene	1.462	1,000,000		TCE
	Vinyl Chloride (Chloroethylene)	0.912	1,100,000		VNCL
	Xylenes (total)[1]	0.87	568,000		TXYL
	Semi-Volatiles				
	Aroclor 1242	1.385	450		PC42
	Aroclor 1254	1.538	12		PC54
	Aroclor 1260	1.440	3		PC60
	Acenaphthene	1.225	3,900		ACNP
	Anthracene	1.250	75		ATHR
	Benzo(a)anthracene	1.174	14		BATR
	Bis-(2-ethylhexyl)phthalate	0.981	400		BEHP
	Chrysene	1.274	6		CRYS
	o-Cresol (2-Methylphenol)	1.027	31,000,000		OCRS
	p-Cresol (4-Methylphenol)	1.035	24,000,000		PCRS
	m-Cresol (3-Methylphenol)	1.038	23,500,000		MCRS
	Total cresols (Methylphenols)[1]	1.03	78,500,000		TCRS

[1] The densities and solubilities for these totals vary depending upon the exact mix of constituents.

Table 1: Maximum Concentration Table (cont.)

Chemical	Density (g/cm^3)	Water Sol. (ppb)	Max. GW (ppb)	
Semi-Volatiles (cont.)				
1,2-Dichlorobenzene	1.306	100,000		2DCB
1-4,Dichlorobenzene	1.248	80,000		4DCB
2,4-Dimethylphenol	1.036	6,200,000		4DMP
2,4-Dinitrophenol	1.680	6,000,000		4DNP
Fluoranthene	1.252	265		FLRA
Fluorene	1.203	1,900		FLRE
2-Methyl Naphthalene	1.006	25,400		2MNP
Naphthalene	1.162	31,000		NAPH
Pentachlorophenol	1.980	14,000		PCP
Phenol	1.058	84,000,000		PHNL
Phenanthrene	0.980	1,180		PHNT
Pyrene	1.271	148		PYRN
1,2,4 Trichlorobenzene	1.574	30,000		124T

Other site contaminants:

_____ _____

_____ _____

Please add any comments you would like to make on the information in this table.

_____

_____ **MAXCONTTBL**

In what geologic unit were the maximum concentrations found?

Unconsolidated material

Bedrock

Unclear

2.B.4. Patterns of Ground Water Contamination

Because the movement of DNAPLs is driven primarily by gravity and capillary forces, DNAPLs may migrate into unexpected areas in the subsurface, such as the deeper portions of aquifers, below aquitards, or areas which are hydrologically upgradient or across-gradient. This behavior gives rise to patterns of ground-water contamination which differ from those generated by completely dissolved-phase contamination. Subsurface DNAPL will also act as a long-term source of dissolved contamination, so concentrations of DNAPL chemicals in the most contaminated monitoring wells are likely to remain steady or increase over long time periods. Erratic concentration data, both spatial and temporal, are also expected at DNAPL sites.

Spatial patterns:

Are ground-water concentrations of DNAPL-related organic contaminants expectionally high at depth below any source areas?	Yes	Maybe	No	Unknown
If yes or maybe, can these high concentrations be explained by ground-water flow patterns in these locations, such as downward vertical gradients?		Yes	Partially	No

Temporal patterns:

In general, how have the concentrations of DNAPL-related ground water contaminants in the most contaminated wells changed over time at the site?

Increased sharply (>1 order of magnitude)
Increased slightly (<1 order of magnitude)
Remained steady (no consistent increase or decrease)
Decreased slight (<1 order of magnitude)
Decreased sharply (>1 order of magnitude)

Insufficient data to observe pattern

On how long a period of years is this observation based? _____

In how many of these years were samples analyzed? _____

If you would like to explain any of your answers further or mention other interesting contamination patterns at the site, please do so below. We are particularly interested in any ground water contaminant patterns that are not easily explained by dissolved-phase transport. In addition, note any soils data that may be indicative of subsurface DNAPL. Please see the DNAPL project hydrogeologist if you would like assistance in interpreting soil or ground water contamination patterns at your site.

_____

_____

_____

_____

_____

_____ **CONTCMT**

2.C. Extent of Field Investigation

2.C.1. Sampling activities

Approximately how many ground-water monitoring points (wells, well-points, etc.) are associated with the site? _____

(Please count each sampling point separately. For example, nested monitoring wells whose screens are located at three discrete depths count as 3 points. Please do not include nearby residential wells.)

Approximatley how many pairs, nests or clusters of wells installed at multiple depths exist at the site? _____

Please estimate the number of ground-water samples that were analyzed for the major site contaminants over all stages of site investigation and circle the appropriate range. (Please do not include samples from residential wells)

None 161-10 11-25 26-50 51-75 76-100 101-150 151-200 >200

Is there a pump-and-treat system for ground-water clean-up operating at the site? Yes No

If yes, how long has the system been in operation? _____

2.C.3. Site Investigation Summary

In your opinion, how well understood are the following aspects of the site?
(please use the key as a general guide to answer this question)

Key:

Very Well	No further information necessary for RD/RA.
Well	A good general understanding, but questions remain in specific areas
Generally	Some understanding, but substantial characterization effort still needed
Poorly	Only preliminary information available

Contaminant Sources:	Very Well	Well	Generally	Poorly
Site Hydrogeology:	Very Well	Well	Generally	Poorly
Ground Water Contamination:	Very Well	Well	Generally	Poorly

2.D. Additional comments

Please describe any additional information from site investigations that may be relevant to the probability of DNAPL occurrence (for example, do pump and treat results match expectations?):

_____

_____

_____

_____

_____ **CHARCMT**

3. Background Site Information

This section is designed to help us understand the site and how DNAPLS might behave in the site setting. The project hydrogeologists will be extracting information from documentation that you supply. Please copy the following information from site investigation reports and attach to your completed survey form:

Check here if you have attached this information, or write NA if the information is not available for your site:

1. Site Map _____
2. Geological Cross Section of Site _____
3. Description of Site Geology (such as from RI) _____
4. Plume Map and Cross Section (if available) _____

********* TO BE FILLED OUT BY DNAPL PROJECT HYDROGEOLOGISTS *************

3.A. Geologic and Hydrogeologic Setting

We would like a general understanding of the geologic and hydrogeologic setting of the site. The movement of DNAPLs in the subsurface is very sensitive to geologic heterogeneity and will tend to flow along areas of increased permeability and downward through fractures. In addition, the question of whether DNAPLs will reach ground water is influenced by both the thickness and composition of the unsaturated zone.

Typical depth to bedrock at the site (feet): Min.: _____ Max.: _____

Geologic description

Unconsolidated sediments:
Were some or all of the unconsolidated sediments or soils deposited by glaciers or glacial-related water bodies? All Some None Unknown

Please describe the composition and texture (such as silt, sand with clay layers, etc.) of the unconsolidated materials. If roughly horizontal layers exist, please describe them from top to bottom. Include an estimate of the thickness of each layer, if possible.

UNCONSOL

Bedrock:
Please indicate the bedrock types which comprise the upper 150 feet of bedrock below the site (check all that apply). If necessary, explain your choices or add any additional information on the lines below.

S	Sedimentary	M	Metamorphic	I	Igneous
CONG	Conglomerate	NICE	Gneiss	GRNT	Granite
LIME	Limestone-dolomite	QTZT	Quartzite	BSLT	Basalt
		SHST	Schist		
SAND	Sandstone	SLAT	Slate		
SILT	Siltstone	MRBL	Marble		
SHAL	Shale				

Other: _____

BEDROCK

Does water move in the bedrock primarily through pore spaces, through fractures, or through solution channels?

Pore Spaces Fractures Solution channels Unknown

Is the site located in karst terrain? Yes No Possible, but unknown

3.B. Plume information

Has a ground-water plume been mapped at the site? Yes No

If yes, please describe the dimensions of the plume below.

Estimated length of plume (ft): _____

Estimated average width of plume (ft): _____

Estimated average thickness of plume (ft): _____

Boundary used to define plume:

Chemical (or TVOC): _____

Concentration (ppb): _____

Please indicate the approximate date of this information _____

If the volume or mass of contaminants in plume has been calculated, please record that amount here (including units). _____

Comments on information in sections A. and B.:

_____

_____

_____

_____

_____ **BKGDCMT**

*** * * END OF SECTION TO BE FILLED OUT BY PROJECT HYDROGEOLOGISTS * * ***

4. References and Final Comments

4.A. Reference Documents

Which documents do you recommend that we consult if we want to find more information concerning site history and ground-water contamination at this site? (Which do you refer to most often?) If you use the standard Superfund documents listed below, please check those that you use and indicate their dates and authors (typically consulting firms). If you use other documents, please describe them on the blank lines below:

_____ HRS Scoring Package Date: _____

_____ Remedial Investigation/Feasibility Study:

Title: _____

Date: _____ Author: _____

_____ Additional or Supplemental Remedial Investigation:

Title: _____

Date: _____ Author: _____

_____ Record(s) of Decision Date(s): _____

_____

_____

_____

_____

_____

_____ **DOCUMENTS**

4.B. Respondent opinion on possibility of DNAPLs

Based on the information that you have provided here as well as your broader knowledge of site conditions, what is your estimate of the probability of DNAPLs at this site?

Definite
High
Medium
Low

Please explain your estimate briefly:

_____

_____

_____

_____

_____

_____ **OPNEXPL**

While the exact measures to be taken in the case of possible DNAPL contamination vary from site to site, we recommend that at the least, the impact of potentially present DNAPLs be considered when planning further site investigations and remedial actions. The Quick Reference Fact Sheet on DNAPLs contains a list of the implications for site investigations if there is a moderate to high probability of DNAPLs.

4.C. Comments on Survey

For our information, how many hours did you spend filling out this form? _____

This survey will also be conducted in other regions. We would appreciate any suggested improvements or comments that you would like to make about this form:

_____

_____

_____

_____

_____ **SURVCMT**

Please note below any particular information concerning DNAPLs that would be helpful to you in your job or particular topics concerning DNAPLs that you think deserve more research:

_____

_____

_____

_____

_____ **DNAPLINFO**

APPENDIX B

United States Environmental Protection Agency | R.S. Kerr Environmental Research Laboratory | Office of Solid Waste and Emergency Response | Publication: 9355.4-07FS December 1991

Estimating Potential for Occurrence of DNAPL at Superfund Sites

Office of Emergency and Remedial Response
Hazardous Site Control Division (OS-220W)

Quick Reference Fact Sheet

GOALS

The presence of Dense Non-Aqueous Phase Liquids (DNAPL) in soils and aquifers can control the ultimate success or failure of remediation at a hazardous waste site. Because of the complex nature of DNAPL transport and fate, however, DNAPL may often be undetected by direct methods, leading to incomplete site assessments and inadequate remedial designs. Sites affected by DNAPL may require a different "paradigm," or conceptual framework, to develop effective characterization and remedial actions (2).

To help site personnel determine if DNAPL-based characterization strategies should be employed at a particular site, a guide for estimating the potential for DNAPL occurrence was developed. The approach, described in this fact sheet, requires application of two types of existing site information:

- **Historical Site Use Information**
- **Site Characterization Data**

By using available data, site decision makers can enter a system of two flowcharts and a classification matrix for estimating the potential for DNAPL occurrence at a site. If the potential for DNAPL occurrence is low, then conventional site assessment and remedial actions may be sufficient. If the potential for DNAPL is moderate or high, however, a different conceptual approach may be required to account for problems associated with DNAPL in the subsurface.

BACKGROUND

DNAPLs are separate-phase hydrocarbon liquids that are denser than water, such as chlorinated solvents (either as a single component or as mixtures of solvents), wood preservative wastes, coal tar wastes, and pesticides. Until recently, standard operating practice in a variety of industries resulted in the release of large quantities of DNAPL to the subsurface. Most DNAPLs undergo only limited degradation in the subsurface, and persist for long periods while slowly releasing soluble organic constituents to groundwater through dissolution. Even with a moderate DNAPL release, dissolution may continue for hundreds of years or longer under natural conditions before all the DNAPL is dissipated and concentrations of soluble organics in groundwater return to background levels.

DNAPL exists in the soil/aquifer matrix as free-phase DNAPL and residual DNAPL. When released at the surface, free-phase DNAPL moves downward through the soil matrix under the force of gravity or laterally along the surface of sloping fine-grained stratigraphic units. As the free-phase DNAPL moves, blobs or ganglia are trapped in pores and/or fractures by capillary forces (7). The amount of the trapped DNAPL, known as residual saturation, is a function of the physical properties of the DNAPL and the hydrogeologic characteristics of the soil/aquifer medium and typically ranges from 5% to 50% of total pore volume. At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Once in the subsurface, it is difficult or impossible to recover all of the trapped residual DNAPL. The conventional aquifer remediation approach, groundwater pump-and-treat, usually removes only a small fraction of trapped residual DNAPL (21, 26). Although many DNAPL removal technologies are currently being tested, to date there have been no field demonstrations where sufficient DNAPL has been successfully recovered from the subsurface to return the aquifer to drinking water quality. The DNAPL that remains trapped in the soil/aquifer matrix acts as a continuing source of dissolved contaminants to groundwater, preventing the restoration of DNAPL-affected aquifers for many years.

DNAPL TRANSPORT AND FATE - CONCEPTUAL MODELS

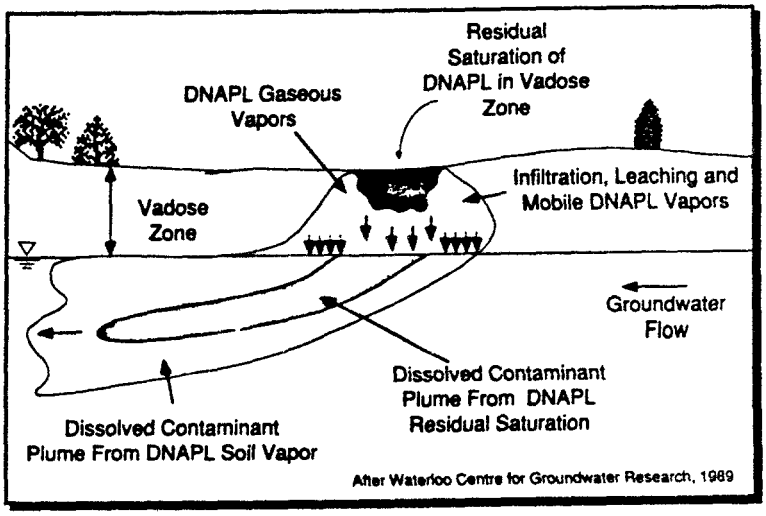
The major factors controlling DNAPL migration in the subsurface include the following (5):

- the volume of DNAPL released;
- the area of infiltration at the DNAPL entry point to the subsurface;
- the duration of the release;
- properties of the DNAPL, such as density, viscosity, and interfacial tension;
- properties of the soil/aquifer media, such as pore size and permeability;
- general stratigraphy, such as the location and topography of low-permeability units;
- micro-stratigraphic features, such as root holes, small fractures, and slickensides found in silt and/or clay layers.

To describe the general transport and fate properties of DNAPL in the subsurface, a series of conceptual models (24) are presented in the following figures.

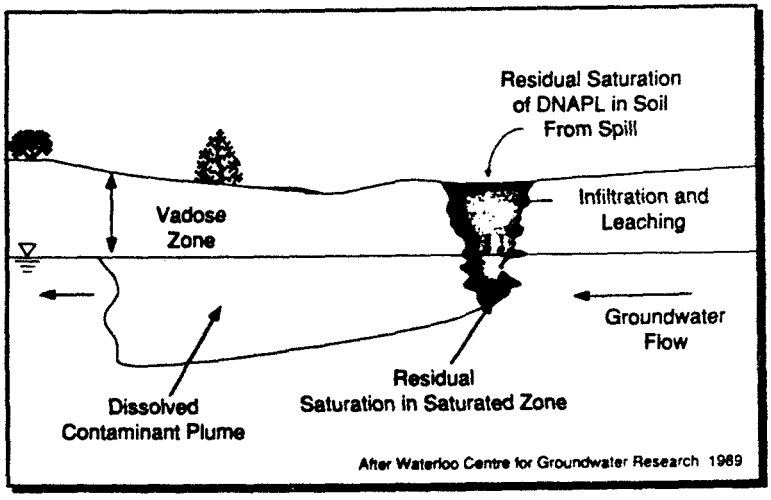
Case 1: DNAPL Release to Vadose Zone Only

After release on the surface, DNAPL moves vertically downward under the force of gravity and soil capillarity. Because only a small amount of DNAPL was released, all of the mobile DNAPL is eventually trapped in pores and fractures in the unsaturated zone. Infiltration through the DNAPL zone dissolves some of the soluble organic constituents in the DNAPL, carrying organics to the water table and forming a dissolved organic plume in the aquifer. Migration of gaseous vapors can also act as a source of dissolved organics to groundwater (16).



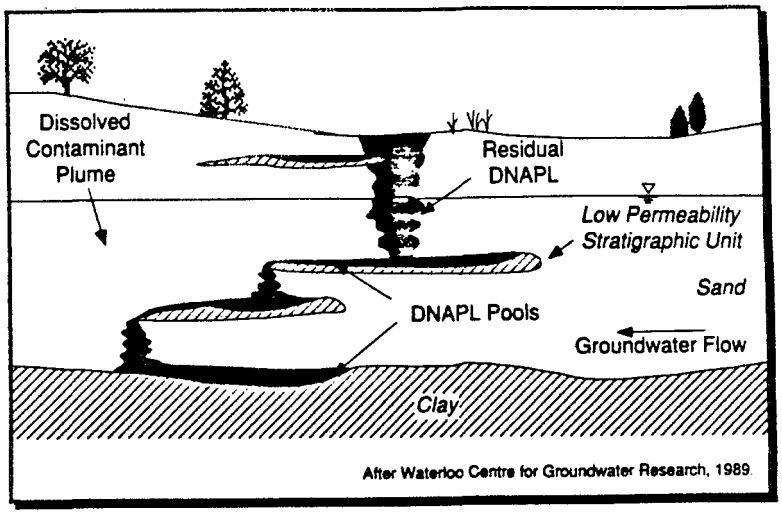
Case 2: DNAPL Release to Unsaturated and Saturated Zones

If enough DNAPL is released at the surface, it can migrate all the way through the unsaturated zone and reach a water-bearing unit. Because the specific gravity of DNAPL is greater than water, it continues downward until the mobile DNAPL is exhausted and is trapped as a residual hydrocarbon in the porous media. Groundwater flowing past the trapped residual DNAPL dissolves soluble components of the DNAPL, forming a dissolved plume downgradient of the DNAPL zone. As with Case 1, water infiltrating down from the source zone also carries dissolved constituents to the aquifer and contributes further to the dissolved plume.



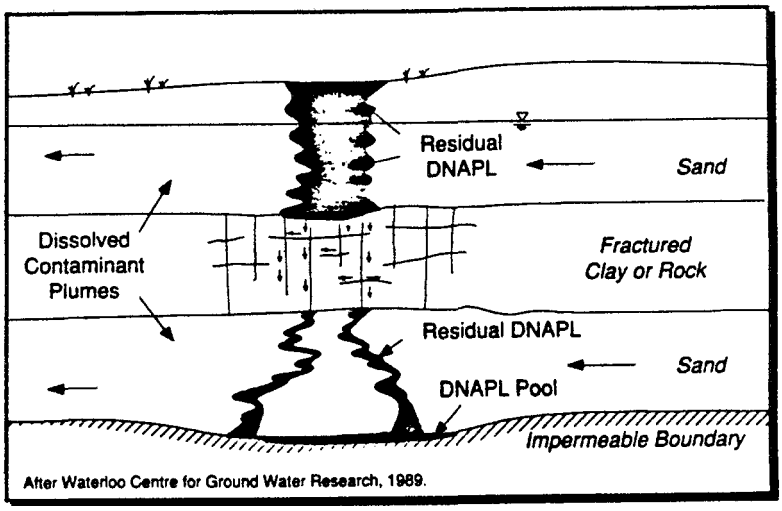
Case 3: DNAPL Pools and Effect of Low-Permeability Units

Mobile DNAPL will continue vertical migration until it is trapped as a residual hydrocarbon (Case 1 and Case 2) or until low-permeability stratigraphic units are encountered which create DNAPL "pools" in the soil/aquifer matrix. In this figure, a perched DNAPL pool fills up and then spills over the lip of the low-permeability stratigraphic unit. The spill-over point (or points) can be some distance away from the original source, greatly complicating the process of tracking DNAPL migration.



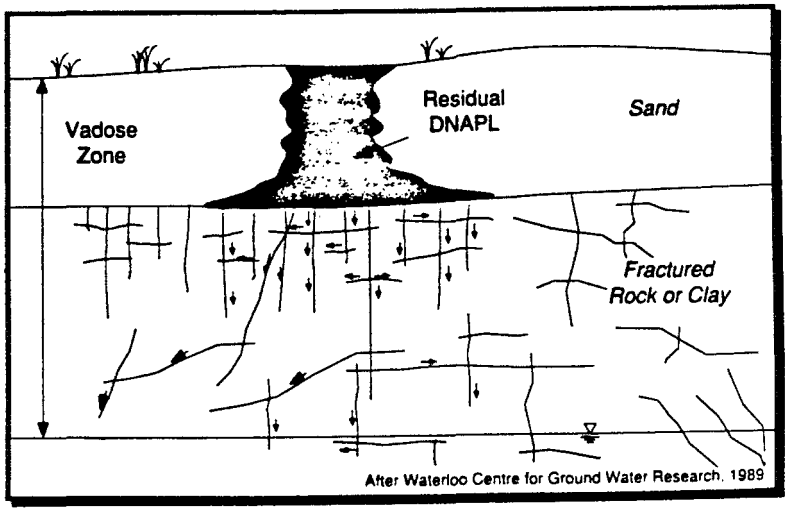
Case 4: Composite Site

In this case, mobile DNAPL migrates vertically downward through the unsaturated zone and the first saturated zone, producing a dissolved constituent plume in the upper aquifer. Although a DNAPL pool is formed on the fractured clay or rock unit, the fractures are large enough to permit vertical migration downward to the deeper aquifer (see Case 5, below). DNAPL pools in a topographic low in the underlying impermeable unit and a second dissolved constituent plume is formed.



Case 5: Fractured Rock or Fractured Clay System

DNAPL introduced into a fractured rock or fractured clay system follows a complex pathway based on the distribution of fractures in the original matrix. The number, density, size, and direction of the fractures usually cannot be determined due the extreme heterogeneity of a fractured system and the lack of economical aquifer characterization technologies. Relatively small volumes of DNAPL can penetrate deeply into fractured systems due to the low retention capacity of the fractures and the ability of some DNAPLs to migrate through very small (<20 microns) fractures. Many clay units, once considered to be relatively impermeable to DNAPL migration, often act as a fractured media with preferential pathways for vertical and horizontal DNAPL migration.



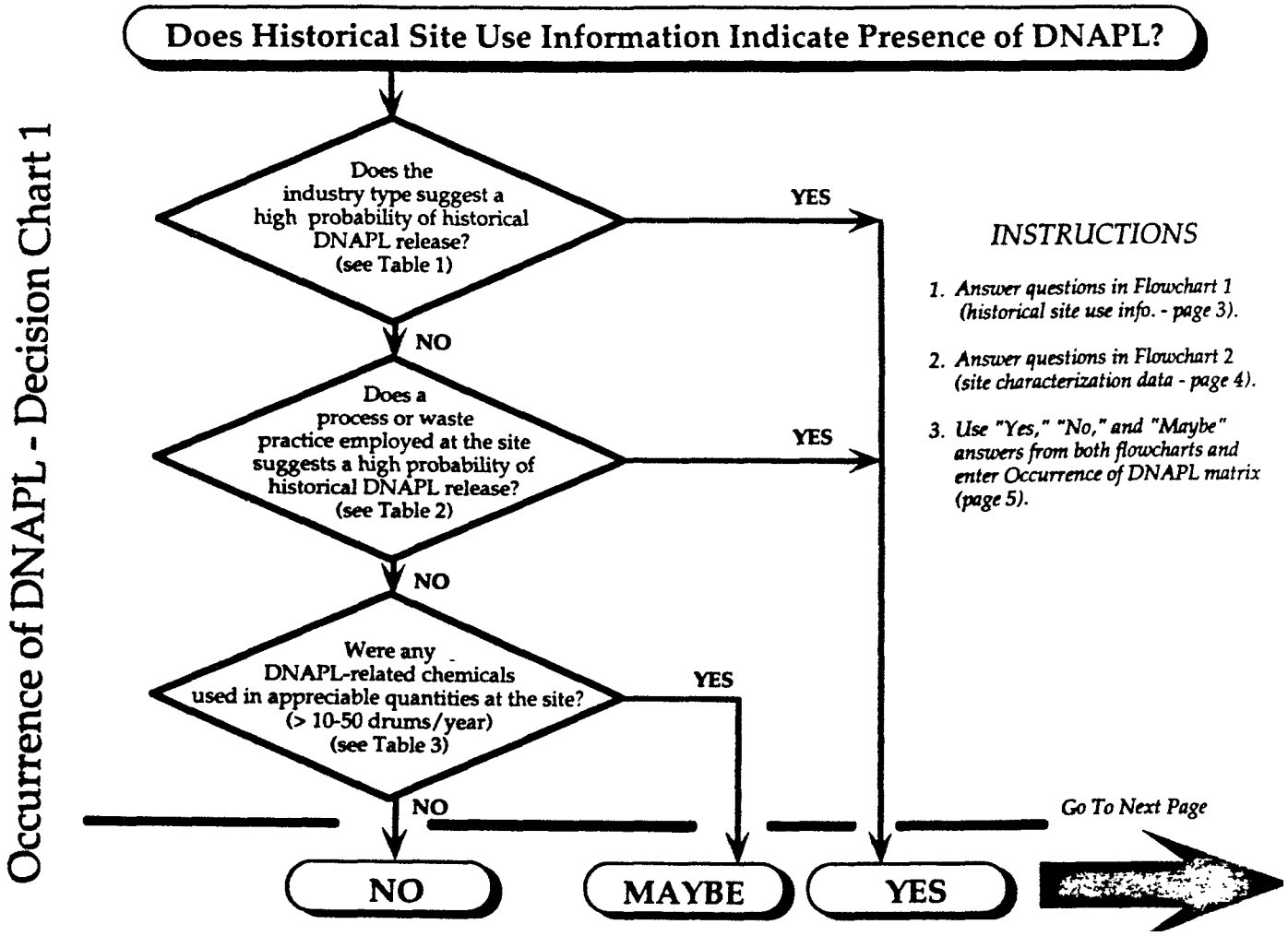


TABLE 1

Industries with high probability of historical DNAPL release:

- Wood preservation (creosote)
- Old coal gas plants (mid-1800s to mid-1900s)
- Electronics manufacturing
- Solvent production
- Pesticide manufacturing
- Herbicide manufacturing
- Airplane maintenance
- Commercial dry cleaning
- Instrument manufacturing
- Transformer oil production
- Transformer reprocessing
- Steel industry coking operations (coal tar)
- Pipeline compressor stations

TABLE 2

Industrial processes or waste disposal practices with high probability of historical DNAPL release:

- Metal cleaning/degreasing
- Metal machining
- Tool-and-die operations
- Paint removing/stripping
- Storage of solvents in underground storage tanks
- Storage of drummed solvents in uncontained storage areas
- Solvent loading and unloading
- Disposal of mixed chemical wastes in landfills
- Treatment of mixed chemical wastes in lagoons or ponds

Note:
The potential for DNAPL release increases with the size and active period of operation for a facility, industrial process, or waste disposal practice.

TABLE 3 DNAPL-Related Chemicals (20):

Halogenated Volatiles
Chlorobenzene
1,2-Dichloropropane
1,1-Dichloroethane
1,1-Dichloroethylene
1,2-Dichloroethane
Trans-1,2-Dichloroethylene
Cis-1,2-Dichloroethylene
1,1,1-Trichloroethane
Methylene Chloride
1,1,2-Trichloroethane
Trichloroethylene
Chloroform
Carbon Tetrachloride
1,1,2,2-Tetrachloroethane
Tetrachloroethylene
Ethylene Dibromide

Halogenated Semi-Volatiles
1,4-Dichlorobenzene
1,2-Dichlorobenzene
Aroclor 1242, 1254, 1260
Chlordane
Dieldrin
2,3,4,6-Tetrachlorophenol
Pentachlorophenol

Non-Halogenated Semi-Volatiles
2-Methyl Napthalene
o-Cresol
p-Cresol
2,4-Dimethylphenol
m-Cresol
Phenol
Naphthalene
Benzo(a)Anthracene
Flourene
Acenaphthene
Anthracene
Dibenzo(a,h)Anthracene
Flouranthene
Pyrene
Chrysene
2,4-Dinitrophenol

Miscellaneous
Coal Tar
Creosote

Note: Many of these chemicals are found mixed with other chemicals or carrier oils

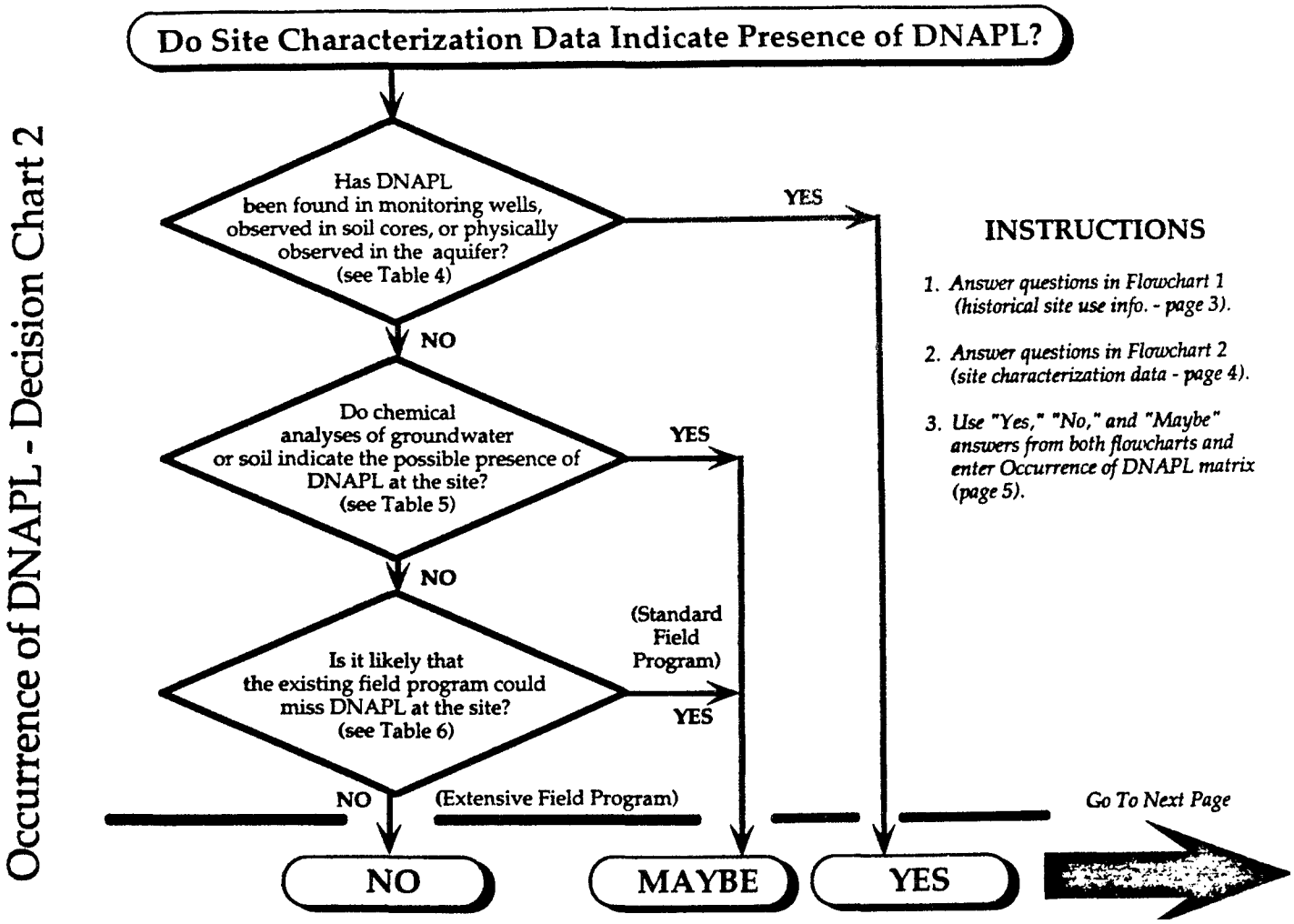


TABLE 4

Methods to confirm DNAPL in wells:

- NAPL/water interface probes that signal a change in conductivity of the borehole fluid
- Weighted cotton string lowered down well
- Pumping and inspecting recovered fluid
- Transparent bottom-loading bailers
- Mechanical discrete-depth samplers.

In general, the depth of DNAPL accumulation does not provide quantitative information regarding the amount of DNAPL present (24).

Methods to confirm DNAPL in soil samples:

Visual examination of cores or cutting may not be effective for confirming the presence of DNAPL except in cases of gross DNAPL contamination. Methods for enhancing visual inspectionof soil samples for DNAPL include:

- Shaking soil samples in a jar with water to separate the DNAPL from the soil (14).
- Performing a paint filter test, in which soil is placed in a filter funnel, water is added, and the filter is examined for separate phases (20).

TABLE 5

Conditions that indicate potential for DNAPL at site based on laboratory data:

Condition 1:
Concentrations of DNAPL-related chemicals (see page. 3) in groundwater **are > 1%** of pure phase solubility **or** effective solubility, (defined in Worksheet 1, pg. 6) (25).

Condition 2:
Concentrations of DNAPL-related chemicals on soils **are** > 10,000 mg/kg (equal to 1% of soil mass) (8).

Condition 3:
Concentrations of DNAPL-related chemicals in groundwater calculated from water/soil partitioning relationships and soil samples **are**> pure phase solubility(see Worksheet 2, pg. 6).

Condition 4:
Concentrations of DNAPL-related chemicals in groundwater **increase** with depth or appear in **anomalous** upgradien/across gradient locations (25).

TABLE 6

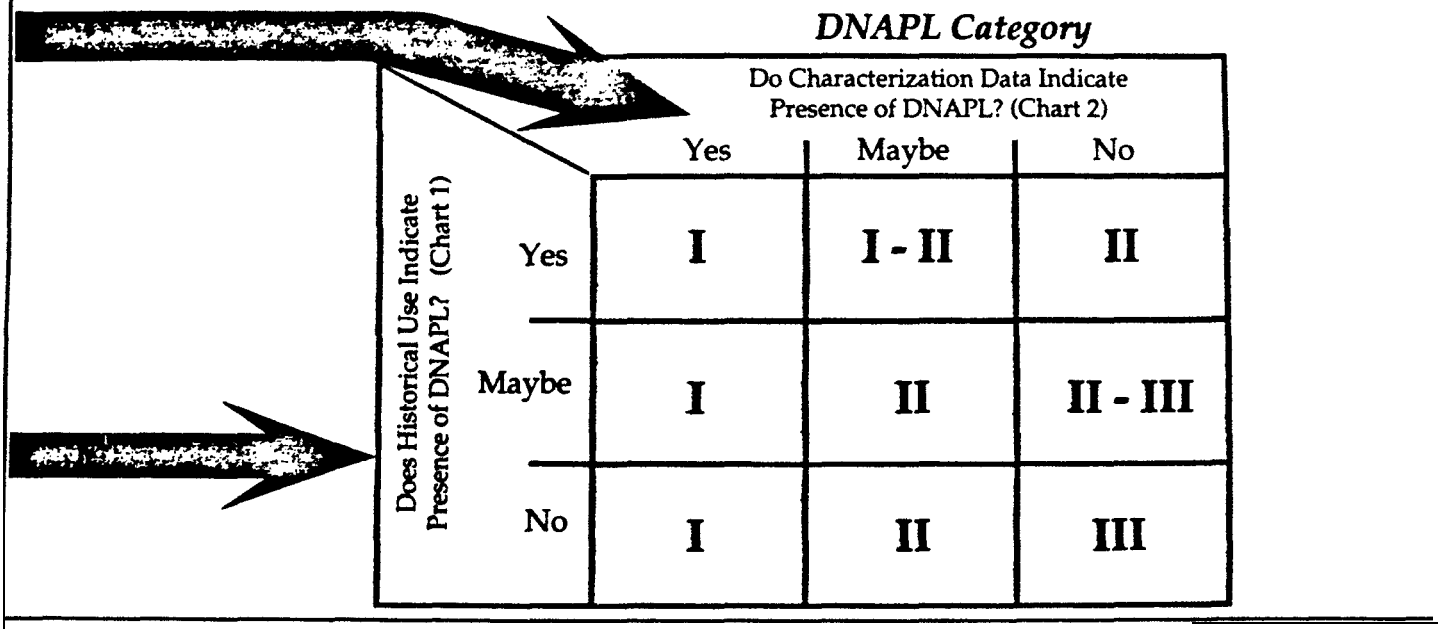
Characteristics of extensive field programs that can help indicate the presence or absence of DNAPL (if several are present, select "NO"):

- Numerous monitoring wells, with wells screened in topographic lows on the surface of fine-grained, relatively impermeable units.
- Multi-level sampling capability.
- Numerous organic chemical analuses N of soil samples at different depths using GC or GC/MS methods.
- Well-defined site stratigraphy, using numerous soil borings, a cone penetrometer survey, or geophysics.
- Data from pilot tests or "early action"projectsthat indicate if the site either:

1) responds as predicted by solute transport relationships (Suggest no DNAPL)
or
2) responds as if additional sources of dissolved contaminants are present in the aquifer (Suggests DNAPL is present) (11).

Note: This procedure is designed primarily for hydrogeologic settings comprised of gravel, sand, silt, or clay and may not be applicable to karst or fractured rock settings.

Potential for Occurrence of DNAPL at Superfund Sites



Category	Implications for Site Assessment
I Confirmed or high potential for DNAPL at site.	• The risk of spreading contaminants increases with the proximity to a potential DNAPL zone. Special precautions should be taken to ensure that drilling does not create pathways for continued vertical migration of free-phase DNAPLs. In DNAPL zones, drilling should be suspended when a low-permeability unit or DNAPL is first encountered. Wells should be installed with short screens ($\leq$ 5 feet). If required, deeper drilling through known DNAPL zones should be conducted only by using double or triple-cased wells to prevent downward migration of DNAPL. As some DNAPLs can penetrate fractures as narrow as 10 microns, special care must be taken during all grouting, cementing, and well sealing activities conducted in DNAPL zones. • In some hydrogeologic settings, such as fractured crystalline rock, it is impossible to drill through DNAPL with existing technology without causing vertical migration of the DNAPL down the borehole, even when double or triple casing is employed (4). • The subsurface DNAPL distribution is difficult to delineate accurately at some sites. DNAPL migrates preferentially through selected pathways (fractures, sand layers, etc.) And is affected by small-scale changes in the stratigraphy of an aquifer. Therefore, the ultimate path taken by DNAPL can be very difficult to characterize and predict. • In most cases, fine-grained aquitards (such as clay or silt units) should be assumed to permit downward migration of DNAPL through fractures unless proven otherwise in the field. At some sites it can be exceptionally difficult to prove otherwise even with intensive site investigations (4). • Drilling in areas known to be DNAPL-free should be performed before drilling in DNAPL zones in order to form a reliable conceptual model of site hydrogeology, stratigraphy, and potential DNAPL pathways. In areas where it is difficult to form a reliable conceptual model, an "outside-in" strategy may be appropriate: drilling in DNAPL zones is avoided or minimized in favor of delineating the outside dissolved-phase plume (4). Many fractured rock settings may require this approach to avoid opening further pathways for DNAPL migration during site assessment.
II Moderate potential for DNAPL at site.	• Due to the potential risk for exacerbating groundwater contamination problems during drilling through DNAPL zones, the precautions described for Category I should be considered during site assessment. Further work should focus on determining if the site is a "DNAPL site."
III Low potential for DNAPL at site.	• DNAPL is not likely to be problem during site characterization, and special DNAPL precautions are probably not needed. Floating free-phase organics organics (LNAPLs), sorption, and other factors can complicate site assessment and remediation activities, however.

Worksheet 1: Calculation of Effective Solubility (from Shiu, 1988; Feenstra, Mackay, & Cherry, 1991)

For a single-component DNAPL, the pure-phase solubility of the organic constituent can be used to estimate the theoretical upper-level concentration of organics in aquifers or for performing dissolution calculations. For DNAPLs comprised of a mixture of chemicals, however, the **effective solubility** concept should be employed:

S_i^e = the effective solubility (the theoretical upper-level dissolved-phase concentration of a constituent in groundwater in equilibrium with a mixed DNAPL; in mg/l)

$$S_i^e = Xi\ S_i$$

Where S_i = the mole fraction component i in the DNAPL mixture (obtained from a lab analysis of a DNAPL sample or estimated from waste characterization data)

X_i = the pure-phase solubility of compound i in mg/l (usually obtained from literature sources)

For example, if a laboratory analysis indicates that the mole fraction of trichloroethylene (TCE) in DNAPL is 0.10, then the effective solubility would be 110 mg/l [pure phase solubility of TCE tomes mole fraction TVE: (1100 mgl) * (0.10) = 110 mg/l]. Effective solubilities can be calculated for all components in a DNAPL mixture. Insoluble organics in the mixture (such as long-chained alkanes) will reduce the mole fraction and effective solubility of more soluble organics but will not comtribute dissolved-phase organics to groundwater. *Please note that this relationship is approximate and does not account for non-ideal behavior of mixtures, such as co-solvency, etc.*

Worksheet 2: Method for Assessing Residual NAPL Based on Organic Chemical Concentrations in Soil Samples (from Feenstra, MacKay, and Cherry, 1991)

To estimate if NAPLs are present, a partitioning calculation based on chemical and physical analyses of **soil samples from the saturated zone** (from cores, excavations, etc.) Can be applied. This method tests the assumption that all of the organics in the subsurface are either dissolved in groundwater or adsorbed to soil (assuming dissolved-phase sorption, not the presence of NAPL). By using the concentration of organics on the soil and the partitioning calculation, a theoretical pore-water concentration of organics in groundwater is determined. If the theoretical pore-water concentration is greater than the estimated solubility of the organic constituent of interest, then NAPL may be present at the site. See Feenstra, MacKay, and Cherry (1991) for a description of the complete methodology.

Step 1: Calculate S_i^e, the effective solubility of organic constituent of interest. See Worksheet 1, above.

Step 2: Determine **Koc**, the organic carbon-water partition coefficient from one of the following:
A) Literature sources (such as 22) or
B) From empirical relationships based on **Kow**, the octanol-water partition coefficient, which is also found in the literature (22). For example, **Koc** can be estimated from **Kow** using the following expression developed for polyaromatic hydrocarbons (8):

$$\text{Log Koc} = 1.0 * \text{Log Kow} - 0.21$$

Other empirical relationships between Koc and Kow are presented in refs. 4 and 15.

Step 3: Determine **foc**, the fraction of organic carbon on the soil, from a laboratory analysis of clean soils from the site. Values for **foc** typically range from 0.03 to 0.00017 mg/mg (4). Convert values reported in percent to mg/mg.

Step 4: Determine or estimate **ρb**, the dry bulk density of the soil, from a soils analysis. Typical values range from 1.8 to 2.1 gms/cc (kg/l). Determine or estimate **φw**, the water-filled porosity.

Step 5: Determine **Kd**, the partition (or distribution) coefficient between the pore water (groundwater) and the soil solids:

$$Kd = Koc * foc$$

Step 6: Using **Ct**, the measured conc. of the organic compound in saturated soil in mg/kg, calculate the theoretical pore water conc. assuming no DNAPL (e.g., Cw in mg/l):

$$Cw = \frac{(Ct * \rho b)}{(Kd * \rho b + \varphi w)}$$

Step 7: Compare **Cw** and S_i^e (from Step 1):

$Cw > S_i^e$ suggests possible **presence** of DNAPL

$Cw < S_i^e$ suggests possible **absence** of DNAPL

GLOSSARY (adapted from Cherry, 1991):

DNAPL: A Dense Non-Aqueous Phase Liquid. A DNAPL can be either a single-component DNAPL (comprised of only one chemical) or a mixed DNAPL (comprised of several chemicals). DNAPL exists in the subsurface as free-phase DNAPL or as residual DNAPL (see following definitions). DNAPL does **not** refer to chemicals that are dissolved in groundwater.

DNAPL ENTRY LOCATION: The area where DNAPL has entered the subsurface, such as a spill location or waste pond.

DNAPL SITE: A site where DNAPL has been released and is now present in the subsurface as an immiscible phase.

DNAPL ZONE: The portion of a site affected by free-phase or residual DNAPL in the subsurface (either the unsaturated zone or saturated zone). The DNAPL zone has organics in the vapor phase (unsaturated zone), dissolved phase (both unsaturated and saturated zone), and DNAPL phase (both unsaturated and saturated zone).

DISSOLUTION: The process by which soluble organic components from DNAPL dissolve in groundwater or dissolve in infiltration water and form a groundwater contaminant plume. The duration of remediation measures (either clean-up or long-term containment) is determined by 1) the rate of dissolution that can be achieved in the field, and 2) the mass of soluble components in the residual DNAPL trapped in the aquifer.

EFFECTIVE SOLUBILITY: The theoretical aqueous solubility of an organic constituent in groundwater that is in chemical equilibrium with a mixed DNAPL (a DNAPL containing several organic chemicals). The effective solubility of a particular organic chemical can be estimated by multiplying its mole fraction in the DNAPL mixture by its pure phase solubility (see Worksheet 1, page 6).

FREE-PHASE DNAPL: Immiscible liquid existing in the subsurface with a positive pressure such that it can flow into a well. If not trapped in a pool, free-phase DNAPL will flow vertically through an aquifer or laterally down sloping fine-grained stratigraphic units. Also called mobile DNAPL or continuous-phase DNAPL.

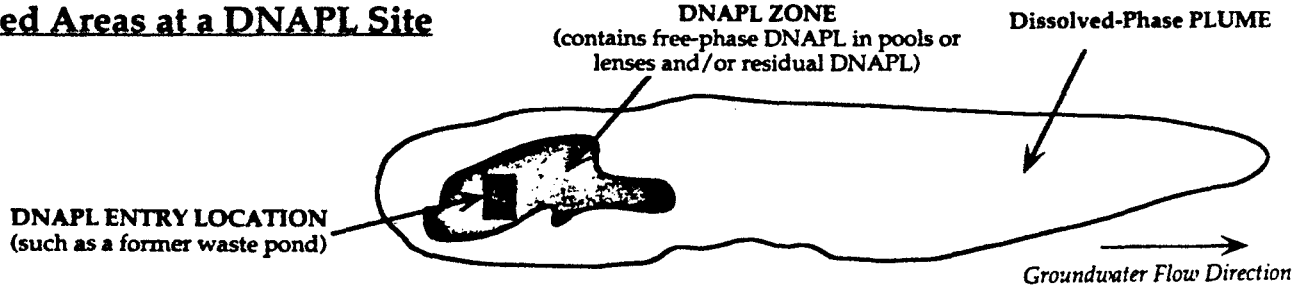
PLUME: The zone of contamination containing organics in the dissolved phase. The plume usually will originate from the DNAPL zone and extend downgradient for some distance depending on site hydrogeologic and chemical conditions. To avoid confusion, the term "DNAPL plume" should not be used to describe a DNAPL pool; "plume" should be used only to refer to dissolved-phase organics.

POOL and LENS: A pool is a zone of free-phase DNAPL at the bottom of an aquifer. A lens is a pool that rests on a fine-grained stratigraphic unit of limited areal extent. DNAPL can be recovered from a pool or lens if a well is placed in the right location.

RESIDUAL DNAPL: DNAPL held in soil pore spaces or fractures by capillary forces (negative pressure on DNAPL). Residual will remain trapped within the pores of the porous media unless the viscous forces (caused by the dynamic force of water against the DNAPL) are greater than the capillary forces holding the DNAPL in the pore. At most sites the hydraulic gradient required to mobilize all of the residual trapped in an aquifer is usually many times greater than the gradient that can be produced by wells or trenches (27).

RESIDUAL SATURATION: The saturation (the fraction of total pore space containing DNAPL) at which DNAPL becomes discontinuous and is immobilized by capillary forces (14). In unsaturated soils, residual saturation typically ranges from 5% to 20% of total pore volume, while in the saturated zone the residual saturation is higher, with typical values ranging from 15% to 50% of total pore volume (14,17). At many sites, however, DNAPL migrates preferentially through small-scale fractures and heterogeneities in the soil, permitting the DNAPL to penetrate much deeper than would be predicted from application of typical residual saturation values (16).

Defined Areas at a DNAPL Site



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