United States Air Force
Environmental Restoration Program

FINAL

Remediation of Chlorinated Solvent
Contamination on Industrial and Airfield Sites

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Prepared For

Air Force Center for Environmental Excellence
Brooks AFB, Texas

REMEDIATION OF CHLORINATED SOLVENT CONTAMINATION ON INDUSTRIAL AND AIRFIELD SITES

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TABLE OF CONTENTS

TABLE OF CONTENTS (CONTINUED)

TABLE OF CONTENTS (CONTINUED)

S:\ES\WP\PROJECTS\730486\75.doc

TABLE OF CONTENTS (Continued)

LIST OF TABLES

LIST OF FIGURES

SECTION 1

INTRODUCTION

1.1 DOCUMENT OBJECTIVE

The purpose of this document is to provide Air Force environmental managers with more effective methods for remediating and managing chlorinated solvent contaminated sites. To date, the Department of Defense has identified over 1500 sites where chlorinated solvents are the primary contaminants driving remediation requirements. The majority of these sites have already entered remedial design or remedial action, although very few sites have attained cleanup goals. Many pump-and-treat systems with less than 5 years of operation have already become inefficient at contaminant removal and expensive to operate. While some remediation systems are necessary to contain contamination and prevent degradation of public water supplies, most sites are located in industrial/airfield areas where there is little risk of human or ecological exposure. This document combines the "lessons learned" from two decades of remediation experience with the recent emphasis on risk-based and site-specific cleanup objectives. The intended result is a more realistic approach to chlorinated solvent remediation on industrial/flightline sites.

1.2 BACKGROUND

1.2.1 Scope of the Problem

Chlorinated solvents such as trichloroethylene (TCE) have been widely used as cleaning solutions by the Air Force and the electronics industry for over 50 years. Other solvents such as 1,1,1- trichloroethane (1,1,1-TCA), perchloroethene (PCE), and chorobenzenes have seen limited use on Air Force facilities. As a result of the widespread production, transportation, use, and disposal of solvents, chlorinated solvent contamination is present at numerous sites throughout North America and Europe. For example, chlorinated solvents account for ten of the top twenty organic contaminants detected most frequently at hazardous waste sites (Table 1.1). Prior to environmental regulations, these solvents were frequently disposed of in sanitary and storm sewers, disposal pits, and fire training areas at hundreds of Air Force facilities. The Department of Defense (DOD) has identified chlorinated solvents at nearly 50 percent of its 3,212 contaminated waste sites and TCE appears as a major groundwater contaminant at 35 percent of all DOD sites (USEPA, 1997a).

1-1

TABLE 1.1[a/]
FREQUENCY OF DETECTION OF MOST COMMON ORGANIC CONTAMINANTS AT HAZARDOUS WASTE SITES

Ranking Based on Number of Sites at Which Organic Contaminant was Detected in Any Medium (USEPA, 1991a)	Organic Contaminant	DNAPL Chemical	Percentage of 1,300 Sites at Which Contaminant was Detected in Any Medium (USEPA, 1991a)	Ranking on Number of Sites at Which Organic Contaminant was Detection in Groundwater (Plumb and Pitchford, 1985)	Percentage of 183 Sites at Which Contaminant was Detected in Groundwater (Plumb and Pitchford, 1985)
1	Toluene	No	60.5	2	31.15
2	Trichloroethene	Yes	57.3	1	34.43
3	Methylene Chloride	Yes	54.7	3	31.15
4	Benzene	No	53.2	7	27.32
5	Tetrachloroethene	Yes	51.8	4	31.15
6	Ethylbenzene	No	47.5	11	25.14
7	1,1,1-Trichloroethane	Yes	47.1	9	26.78
8	Chloroform	Yes	45.4	10	25.14
9	Xylenes	No	44.3	--	--
10	bis(2ethylhexyl) phthalate	No	41.8	6	28.42
11	Acetone	No	40.0	20	12.02
12	1,1-Dichloroethane	Yes	39.7	5	28.42
13	Phenol	No	39.4	14	19.13
14	trans-1,2-Dichloroethene	Yes	38.4	8	27.32
15	Naphthalene	No	35.5	18	12.57
16	1,1-Dichloroethene	Yes	33.2	13	20.22
17	1,2-Dichloroethane	Yes	32.7	12	21.31
18	Vinyl Chloride	No	32.1	15	16.39
19	2-Butanone	No	31.8	--	--
20	Chlorobenzene	Yes	31.4	16	16.39
23	Dibutyl Phthalate	Yes	30.3	17	15.30
40	Chloroethane	No	18.1	19	12.57

a/ Table 4.1 after Table 3.3 in Cohen and Mercer (1993a).

Sources of Information: USEPA (1991a); Plumb and Pitchford (1985).

Because traditional groundwater extraction and treatment systems cost millions of dollars to install and operate, innovative remediation strategies present a significant potential for cost avoidance. The remediation of chlorinated solvents is a critical issue within the Air Force environmental program with important long-term financial implications.

1.2.2 Technical Advances

Several technical advances have occurred in the past five years that have improved our understanding of chlorinated solvent fate and transport in the subsurface and how they can be remediated. Each of these advances have been integrated into the technical recommendations of this document. For example:

- Research by Freeze and McWhorter (1997) and others have demonstrated the extreme difficulty of removing chlorinated solvents found in the dense non-aqueous phase liquid (DNAPL) phase, particularly when separate phase solvents have migrated below the water table or into fractured rock formations. Similar limitations on DNAPL removal have been observed in clay soils (Parker, 19XX). Limitations on DNAPL removal can make complete remediation impossible at many sites.

- Research and site case studies (Wiedemeier, 1999) have demonstrated that under proper geochemical conditions a variety of natural

biological processes can account for the destruction of most chlorinated solvents, including TCE. The publication of the EPA protocol for chlorinated solvent natural attenuation has legitamized this alternative and led to a growing number of regulatory decisions to accept monitored natural attenuation as the remedy of choice (EPA, 1998a).

- During this same period, alternative technologies for source reduction and groundwater treatment have been developed. Thermal enhancements to soil vapor extraction, reactive barrier walls, and optimized pumping systems are just a few of the innovative technologies that are beginning to change the way that chlorinated solvent contamination is remediated. This document describes an overall remediation strategy that will assist the reader in appropriately applying natural attenuation as well as emerging and innovative technologies.

1.2.3 Regulatory Changes

The EPA and many State regulatory agencies are now willing to acknowledge the limitations of existing technologies to completely remediate many chlorinated solvent sites. This increasing awareness has resulted in several regulatory changes which are favorable to more site-specific and risk-based remediation objectives for industrial/flightline sites. For example:

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- In 1994, the EPA published guidance that allows for Technical Impracticability waivers for sites where complete remediation is impossible due to the site conditions or the presence of inaccessible DNAPLs. This guidance describes what technical evidence is required and what regulatory procedures exist for establishing more realistic remediation objectives for many chlorinated solvent contaminated sites.

- The EPA "Brownfields" initiative now encourages local governments, environmental regulators, and land developers to work together to establish realistic cleanup goals for contaminated industrial properties. Using risk assessment tools, the actual exposure pathways and receptors are identified for the proposed land use and cleanup goals and remediation activities are specifically tailored to eliminate these risks. Since the risk of exposure at many Air Force industrial sites is limited to occasional excavation activities, this same approach can be applied for establishing chlorinated solvent remediation goals.

- The EPA's Office of Solid Waste and Emergency Response recently published directive 9200.4-17P clarifying how monitored natural attenuation can be applied as an element of CERCLA and RCRA site closures.

- Both RCRA and CERCLA contain provisions for establishing alternate concentration limits or remediation goals based on industrial land use assumptions. Unfortunately, regulatory agencies and Air Force site managers have been far too conservative in their application of residential cleanup standards. Drinking water maximum contaminant levels (MCLs) have been applied at industrial sites where there is little chance of human exposure to groundwater. The strategies outlined in this document challenge the "status quo" and encourage Air Force site managers and regulators to design remediation goals that are realistic for industrial land use.

- Many state agencies are now publishing risk-based cleanup criteria for industrial sites and recognizing "mixing zone" concepts which allow stable chlorinated solvent plumes to attenuate in place so long as surface water and drinking water resources are protected. ASTM is also developing a risk-based corrective action (RBCA) standard for chlorinated solvents that is similar to the very successful standard developed for fuel hydrocarbons.

1.3 REMEDIAL DECISION PROCESS FOR CHLORINATED SOLVENT SITES

This document has been organized to support an overall strategy for chlorinated solvent site remediation based on current technology and regulatory trends. This strategy has been

1-4

developed by AFCEE after evaluating hundreds of sites in varying stages of remedial design and remedial action. Although no remediation strategy can be universally applied, site managers and Air Force consultants are encouraged to use this document as the "default" approach.

Figure 1.1 illustrates the general flowchart for this remediation strategy. This strategy is based on five points of emphasis which are described in each of the remaining sections:

- An accurate Conceptual Site Model (CSM) is critical to understanding remediation possibilities and limitations, and for establishing site-specific cleanup goals.

- The degree of remediation should be based on a realistic assessment of exposure potential (risk) for both the source area and migrating groundwater contamination.

- The remediation of the source of contamination must be based on an understanding of DNAPL accessibility, technology limitations, and the net benefits of only partial removal. The requirements for Technical Impracticability waivers must be integrated into site characterization and pilot testing activities.

- Unless a drinking water supply is endangered, monitored natural attenuation and alternative treatment methods should be fully evaluated before long-term groundwater extraction is selected as a remedy.

- Regardless of the type of remediation selected for a site, the remedy should be subject to an annual performance evaluation. Inefficient systems should be identified for detailed remedial process optimization (RPO) evaluations. RPO documentation should be used to support regulatory milestones such as 5-Year ROD reviews and Operating Properly and Successfully (OPS) demonstrations.

FIGURE 1.1

FLOWCHART FOR REMEDIATION OF INDUSTRIAL/AIRFIELD SITES CONTAMINATED WITH CHLORINATED SOLVENTS

Develop An Accurate Conceptual Site Model

Yes

Could an Exposure Pathway Be Completed Based On The Existing Land Use?

No

Will BRAC Actions Create a Potential for Exposure Pathway Completion?

No

Is There Potential for Off-Base Migration or is Contamination Incompatible with BRAC Land Use?

No

Establish Institutional Controls and Long-term Monitoring Program

Yes

Yes

Yes

Are Default Cleanup Criteria Exceeded for The Current or Proposed Land Use?

No

Document the Potential for Natural Attenuation

Yes

Will Natural Attenuation Prevent Unacceptable Migration and Rapidly Reduce Concentrations?

Yes

Develop Site-Specific Target Levels Based on Realistic Exposure Scenarios

Are SSTLs Exceeded?

No

No

Yes

Are Non-Pumping Groundwater Treatment Alternatives Feasible and Cost Effective?

No

Complete Pilot Testing of Innovative Source Reduction Technology

No

Is the Source Accessible?

Review Table 4.2 for Cleanup Feasibility

Yes

Implement Pump and Treat System for Containment and/or Remediation of Plume

Pursue Technical Impracticability Waiver or Alternate Concentration Levels for Source Area

No

Pilot Test Successful?

Yes

Initiate Proven Source Reductions Methods

Implement Non-Pumping Groundwater Treatment Alternative

Yes

Implement Source Reductions

Does Groundwater Exceed Established Cleanup Levels or Is It Migrating Toward an Exposure Point?

Yes

No

• Complete Annual RPO Evaluation

• Maintain LTM Program

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SECTION 2

DEVELOP OR UPDATE THE CONCEPTUAL SITE MODEL

This section will assist you in:

- Developing a useful conceptual site model or updating an existing one;

- Determining what human or ecological receptors may be at risk and how to limit their exposure to chlorinated contamination.

An accurate conceptual site model (CSM) is critical to evaluating the true risk of chlorinated solvent contamination, as well as the possibilities and limitations of site remediation. A complete CSM should include a visual representation of contaminant source and release information , site geology and hydrology, contaminant distribution, fate and transport parameters, and risk assessment features such as current and future land use and potential exposure pathways and receptors. Figure 2.1 provides an example of a CSM for a chlorinated solvent spill. AFCEE recommends that every site manager prepare a visual CSM for each site they are responsible for.

The CSM will generally be developed as a part of the site investigation or feasibility study phase of site remediation. Many interim remedial systems have been installed and are operating without a well-defined CSM. Other remedial systems were designed based on an initial CSM that requires updating based on recent operations and monitoring data. Changes in land use, or changes in the enforcement of institutional controls, can also alter the exposure and risk assumptions of the CSM. The CSM is intended to be a dynamic representation of site conditions based on a continual influx of information from the site. This section provides an overview of the key elements of a CSM, with emphasis on chlorinated solvent sites.

2.1 ELEMENTS OF A CONCEPTUAL SITE MODEL

2.1.1 Source and Release Information

The CSM should include a description of the source of contamination and what is known about the timing and quantity of the release. Most site characterizations begin by locating areas where chlorinated solvents were originally released to the subsurface. In many cases, the distinct source of contamination is known to be a former underground storage tank (UST), disposal pit, fire training area, etc. However, many

FIGURE 2.1
ELEMENTS OF A CONCEPTUAL SITE MODEL (CSM)

Background Information

- Location of water supply wells.
- Ground-water classification.
- Nearby wellhead protection areas or sole-source aquifers.
- Locations of potential receptors exposure points.

Contaminant Source and Release Information

- Location, nature, and history of previous contaminant releases or sources.
- Locations and characterizations of continuing releases or sources.
- Locations of subsurface sources (e.g., DNAPLs).
- Flux of contamination from DNAPL.

Risk Assessment

- Current and future receptors.
- Exposure scenario's.
- Completed pathways?
- Exposure concentrations.

Geologic and Hydrologic Information

- Description of regional and site geology.
- Physical properties of subsurface materials (e.g., porosity, bulk density).
- Stratigraphy, including thickness, lateral extent, continuity of units, and presence of depositional features, such as channel deposits, that may provide preferential pathways for, or barriers to, contaminant transport.
- Geologic structures that may form preferential pathways for DNAPL migration or zones of accumulation.
- Depth to ground water.
- Hydraulic gradients (horizontal and vertical).
- Hydraulic properties of subsurface materials (e.g., hydraulic conductivity, storage coefficient, effective porosity) and their directional variability (anisotropy).
- Spatial distribution of soil or bedrock physical/hydraulic properties (degree of heterogeneity).
- Temporal variability in hydrologic conditions
- Groundwater recharge and discharge information.
- Groundwater/surface water interactions.
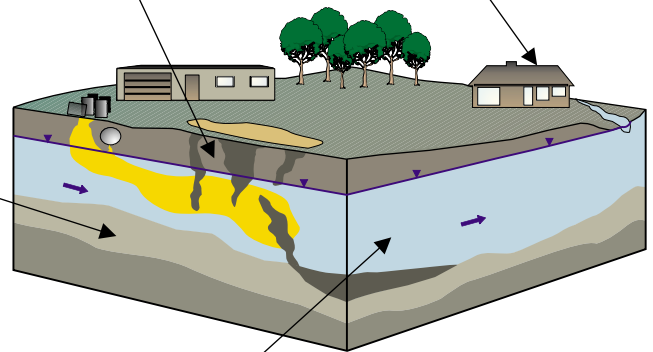
Contaminant Distribution, Transport, and Fate Parameters

- Properties of DNAPLs that affect transport (e.g., composition, effective constituent solubilities, density, viscosity).
- Phase distribution of each contaminant (gaseous, aqueous, sorbed, free-phase DNAPL or residual DNAPL) in the unsaturated and saturated zones.
- Spatial distribution of subsurface contaminants in each phase in the unsaturated and saturated zones.
- Estimates of subsurface contaminant mass.
- Temporal trends in contaminant concentrations in each phase.
- Partitioning coefficients and migration rates.
- Contaminant natural attenuation processes (destructive and non-destructive).
- Geochemical Indicators (aerobic/anaerobic).

Source: Adapted from EPA, 1993.

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industrial source areas are dispersed and difficult to find. For example, oil/water separators, and sanitary and storm sewers have historically received chlorinated solvents from aircraft and other maintenance shops (Figure 2.2). At these sites, it is often impossible to pinpoint the exact source of contamination. Soil gas surveys can be used to locate these dispersed source areas at sites with sandy, permeable soils. However, at sites with low permeability soils, locating dispersed sources will often require excavation and removal of contaminated soils along underground utilities. This level of intrusive characterization may not be possible along active utility corridors.

The timing and the amount of chlorinated solvent released are equally difficult to estimate. Historical records on chlorinated solvent use are difficult to obtain, and if they exist are generally found in Phase I Installation Restoration Program documents developed in the early 1980's. TCE was used by the Air Force for approximately 40 years before it was phased out in the early 1980s. TCE has not been widely used at Air Force facilities for nearly 20 years. This fact is important when evaluating the fate and transport of chlorinated solvents and is especially important when estimating degradation rates based on the breakdown products of PCE or TCE.

In sandy soils, the amount of chlorinated solvent remaining in the subsurface can be roughly estimated based on a comprehensive soil gas survey in a known source area. Average soil gas concentrations of chlorinated solvents can be equated to soil concentrations to estimate the mass of solvents in an impacted volume of soil. Likewise, average groundwater concentrations can be used to roughly estimate the amount of chlorinated solvent dissolved in a volume of impacted aquifer.

These methods are generally ineffective estimators of contaminant mass in low permeability soils or sites where chlorinated solvents exist as dense non-aqueous phase liquids (DNAPLs). Because of the unique challenges posed by DNAPL contamination, Section 4 of this handbook provides more detailed procedures for DNAPL recognition and characterization.

2.1.2 Geologic and Hydrogeologic Characterization

The CSM should include a complete description of the site geology and hydrogeology. At a minimum, the CSM for a chlorinated solvent site should include:

- A general description of site geology including major soil strata that are impacted by or influence the migration of contaminants. Strata thickness, lateral extent, continuity and depositional features should be described.

FIGURE 2.2
CONCEPTUAL SITE MODEL OF DISPERSED SOURCES

Limited Surface Spills

Leaking Sewers

Stormwater Outfalls

Shallow Clay/Silt Unit

Intermediate Sand Unit

TCE and Anaerobic Dechlorination Byproducts 1, 2-DCE, VC, Ethene

Intermediate Clay Unit

Deep Sand Unit

Miocene (Clay and Sand)

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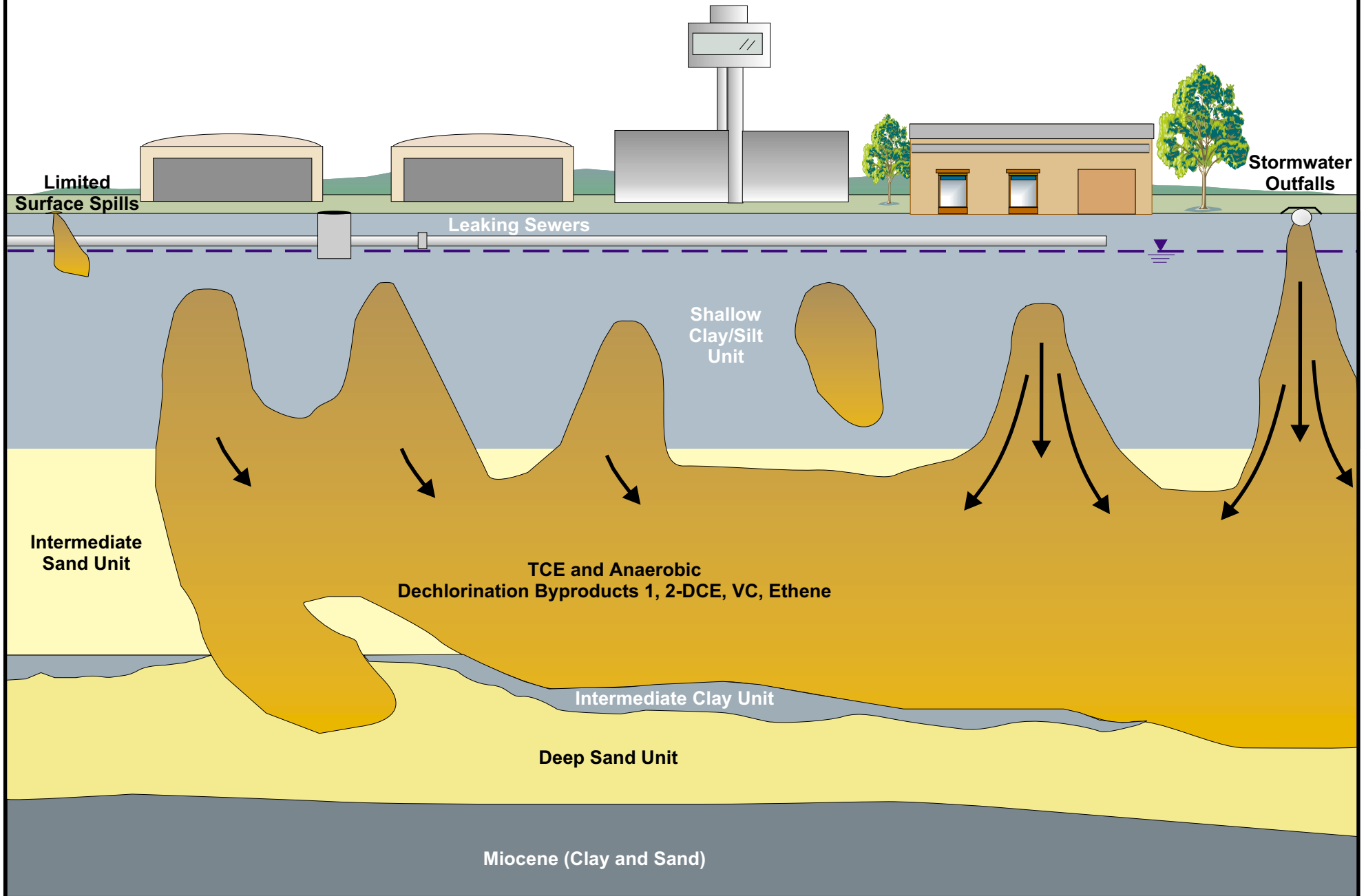
- Physical and chemical properties of subsurface materials such as sieve analysis, bulk density, porosity and total organic carbon.

- Geologic or manmade features which may provide preferential migration of DNAPLs, solvent vapors, or dissolved contaminants.

- Depth to groundwater, seasonal variations, recharge and discharge information including interactions with surface waters.

- Range of hydraulic gradients (horizontal and vertical).

- Range of hydraulic properties (e.g., hydraulic conductivity, storage coefficient, effective porosity, seepage velocity).

- Geochemical properties influencing the natural biodegradation of chlorinated solvents.

The CSM should be updated to reflect current estimates of these properties based on site remediation experience. For example, the hydraulic properties of an aquifer can be more accurately estimated after a groundwater extraction system has operated several months. On sites where natural attenuation has been selected as the groundwater remedy, tracking the movement (or stability) of the contaminant plume provides valuable information that can be introduced into an updated CSM.

> Because many shallow, low-yield aquifers are unsuitable for drinking water production, contamination confined to these aquifers should not be subject to drinking water cleanup standards. The CSM should make a clear distinction between potential sources of drinking water and unproductive, shallow aquifers.

2.1.3 Contaminant Distribution, Transport and Fate

In addition to describing the source of contamination, the CSM should include a summary of the chemical, physical, and biodegradation properties of key contaminants of concern and describe their distribution, movement, and fate in the subsurface environment. At a minimum, the CSM for a chlorinated site should include:

- Chemical and physical properties of chlorinated compounds that impact subsurface transport (e.g., partitioning coefficients, solubility, vapor pressure, Henry's Constant, density, viscosity)

- An estimate of the phase distribution of each contaminant (free-phase DNAPL, sorbed, in soil vapor, or dissolved) in the saturated and unsaturated zone.

- Temporal trends in contaminant concentrations in each phase.

- Geochemical evidence of contaminant natural attenuation processes (destructive and non-destructive).

2.1.4 Geochemistry Impacting Natural Biodegradation

At many sites, geochemical conditions may support the natural biodegradation of chlorinated solvents. The EPA *Technical Protocol for Evaluating Attenuation Protocol of Chlorinated Solvents* provides a detailed explanation of geochemical sampling procedures and methods for interpreting geochemical data to determine if biodegradation is likely to be occurring. Section 5 of this document provides a summary of how site geochemistry can be used to determine biodegradation potential. Geochemical indicators such as dissolved oxygen, nitrate, iron, manganese, sulfate, methane, and hydrogen ion concentrations should be reported in the CSM. The relative distribution of primary solvents such as PCE and TCE, and daughter products such as DCE and vinyl chloride should be discussed in relation to the geochemical profile.

2.1.5 Risk Assessment Site Model

Although the complexity of risk assessment will vary from one site to another and one regulatory environment to another, there are several common elements that should be included in every CSM:

- An analysis of potential receptors (current and future) which could be impacted by contamination.

- An analysis of potential exposure pathways that could allow chlorinated compounds to impact receptors.

- A determination of what level of contaminant exposure will not present an unacceptable risk to impacted receptors (risk-based cleanup goals).

- Measurement of contaminant concentrations at potential exposure points or estimation of exposure point concentrations using fate and transport models. These exposure concentrations are then compared to risk-based cleanup goals.

Section 3 describes the risk assessment process and specifically how to develop risk-based cleanup goals for chlorinated solvent sites. Figure 2.3 illustrates a risk assessment site model for a typical TCE spill in an industrial/airfield area. The primary source of TCE was a leaking UST; the secondary source is the soil contaminated with DNAPL residuals. Potential receptors include utility and construction workers and noninstrusive office workers. Potential exposure pathways include soil gas inhalation, direct soil contact, direct groundwater contact and inhalation of groundwater volatiles. The reduction or removal of risk can be accomplished by limiting contaminant migration pathways or by restricting (or properly protecting) receptors to prevent unacceptable exposure concentrations.

FIGURE 2.3
INDUSTRIAL EXPOSURE SITE MODEL

Solvent UST

Contaminated Soil

TCE   TCE   **Contaminated Groundwater**   TCE

Possible Site Sources	Affected Media	Release Mechanisms/ Migration Pathways		Exposure Routes		Potential Receptors

Soil

- Direct releases of contaminants into soils.
- Contaminants volatilizing into the atmosphere.
- Disturbance of contaminated soils by excavation.
- Leaching of contaminated soil into groundwater.

Human
- Incidental ingestion.
- Dermal contact.
- Inhalation of volatilizing contaminants.
- Inhalation of fugitive dust.

Current
- Onsite intrusive workers.
- Nonintrusive workers.

Future
- Onsite intrusive workers.
- Nonintrusive workers.

Ecological
- No exposed populations, due to industrial land use

- Solvent leaks from USTs.

Groundwater

- Direct releases of contaminants into groundwater.
- Downgradient migration of site contaminants.

Human
- Inhalation of volatiles.
- Dermal contact.

Current
- Onsite intrusive workers.
- Nonintrusive workers.

Future
- Onsite intrusive workers.
- Nonintrusive workers.

Ecological
- No exposed populations, due to industrial land use

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The goal of risk-based remediation is to find the most cost-effective method of reducing present and future risk by combining three risk reduction techniques:

- **Chemical Source Reduction** - Achieved by natural attenuation processes over time or by engineered removals such as excavation and soil vapor extraction.

- **Chemical Pathway Elimination** - Examples include the natural attenuation of a groundwater plume, semi-permeable barrier walls or pumping to stop the migration of contaminants toward downgradient receptors.

- **Restrict/Protect Receptors** - Land use and groundwater use controls such as site fencing, surface capping, digging restrictions, protective clothing , and groundwater well restrictions can eliminate chemical exposure until natural attenuation or engineered remediation reduce the chemical source.

Often at military facilities scheduled for closure, the future land use may differ from the current land use. In such situations the most conservative expected land use should be used to complete the site model. *Industrial or commercial land use should be assumed unless residential land use is specifically included in a future land use plan.*

2.2 LIMITING CURRENT AND FUTURE EXPOSURE TO CONTAMINANTS

Because risk-based remediation methods rely on a clear understanding of how humans or ecological receptors could be exposed to chemicals (exposure pathways), it is essential to have a complete knowledge of the current land use and potential land use changes. Most chlorinated solvent sites on Air Force facilities are located in the industrial/airfield areas of the base. On-site workers typically work 8-hour shifts inside buildings or outside, working on aircraft or support equipment. Excavation in contaminated soils is generally restricted to short-term utility repairs and workers are required to use personal protective equipment (PPE). Most buildings are constructed on abovegrade concrete slabs. With the exception of missile facilities, few Air Force industrial buildings have basements which could be directly impacted by contaminated soil and soil gas. As a rule, current land use is generally industrial in nature with minimal human exposure to contaminated soil, soil gas, or groundwater. This isolation of workers from site contamination (no exposure pathways) is an important element of the Air Force risk-based remediation strategy.

2.2.1 Maintaining Industrial Land Use

On active Air Force installations, future land use is specified in the Base Master Plan. This document is maintained by the Base Civil Engineer, and specifies areas of the base for

2-8

various land uses such as flightline/industrial, warehousing/storage, administration, community services, and residential housing and dormitories. Land use within the flightline/industrial area rarely changes because of the incompatibility of other land uses with flightline noise and aircraft support activities. Most solvent-contaminated sites are located within the flightline/industrial land use category. Check the Base Master Plan to ensure that no significant change in land use or new construction is allowed at chlorinated solvent sites without considering the potential for chemical exposure.

2.2.2 Digging Restrictions and Protection of Workers

The greatest potential for exposure to contaminated soil and groundwater will occur during new building construction or utility repairs or replacement. It is important that the supervisors of utility shops and base construction planners be informed of the known areas of contamination so that any excavation in these areas can be completed with careful air monitoring and proper protective clothing. Digging in contaminated soils should be avoided or minimized. The base digging permit program should alert workers to the potential for contaminated soil and require that all excavation and drilling be completed with adequate health and safety precautions.

2.2.3 Groundwater Use Restrictions

Although most chlorinated solvent spills may be confined to shallow aquifers that are not used for domestic water supplies, there are spills which impact potential drinking water aquifers. It may be necessary to impose groundwater use restrictions in the vicinity of chlorinated solvent spills for two reasons:

- Pumping of groundwater, even for irrigation purposes, will lead to increased exposure to groundwater contaminants.

- Pumping of groundwater outside of the contaminated area may increase the migration of contaminants away from the source and spread contamination to a larger area.

For these reasons, groundwater pumping restrictions should be formally adopted in the Base Master Plan. The area of these restrictions should be determined by a professional hydrogeologist based on the characteristics of the contaminant plume and aquifer.

2.2.4 Institutional Controls for Realignment and Closure Bases

On installations that are scheduled for closure or realignment, the question of future land use becomes more critical. While most flightline areas on closure bases will remain in industrial/commercial land use, formal deed or lease restrictions must be in place to ensure that the new landowner (private or public) understands the extent of remaining

contamination and the need to restrict certain future activities or land uses. In general, Air Force Base Realignment and Closure (BRAC) officials should seek risk-based closures of contaminated sites which make maximum use of deed or lease restrictions to minimize the potential for future human exposure to contaminants. The BRAC Environmental Program Fact Sheet (DoD Policy on Institutional Controls) provides an overview of institutional controls and how they can be applied during BRAC land transfers. This guidance is available on the DoD BRAC Environmental Homepage at http://www.dtic.mil/envIrodod/envbrac. mil.

SECTION 3

DEVELOPING RISK-BASED CLEANUP GOALS

this section will assist you in:

- Determining what risk-based screening levels may be appropriate for an industrial/airfield site contaminated with chlorinated solvents;

- Developing site-specific cleanup goals based on realistic exposure scenarios at this site; and

- Estimating the average exposure concentration as opposed to the maximum concentration at the site.

Once the CSM has defined the source of chlorinated solvent contamination, potential pathways, and potential receptors, the task of defining risk-based cleanup objectives can begin. This is generally a two step process:

- An initial comparison of potential exposure concentrations to conservative industrial screening levels for each contaminant of concern. For sites with potential discharge to surface water, a comparison to ecological screening levels may be appropriate.

- Any contaminant exceeding these conservative screening levels is next evaluated using more realistic, site-specific exposure assumptions to determine if an unacceptable human health or ecological risk could actually exist.

This two-step approach provides the flexibility to replace potentially conservative, nonsite-specific exposure assumptions with site-specific information, while still providing the same level of human health and environmental resource protection. Increasingly complex levels of data collection and risk evaluation may be performed to establish the type and magnitude of remediation required to reduce or eliminate unacceptable risks at a particular site. This is accomplished primarily by replacing nonsite-specific (i.e., default) assumptions about how chemicals behave in the environment and how receptors may be exposed, with site-specific data and assumptions that are more representative of actual site conditions and realistic exposure pathways for human and ecological receptors. This section summarizes how site-specific cleanup goals can be established.

3.1 CONDUCTING A SCREENING LEVEL EVALUATION

A screening level evaluation provides a way of quickly identifying whether a particular chemical warrants additional risk evaluation. Screening levels are conservative (health protective), generic cleanup criteria that define the residual amount of a contaminant that can remain onsite and not present an unacceptable risk to potential receptors. AFCEE recommends the use of industrial land use screening levels for all sites where chlorinated solvent contamination is confined to industrial/airfield areas. For sites with the potential for discharge to surface waters, ecological screening levels also may be appropriate.

3.1.1 Industrial Screening Levels for Human Receptors

Screening levels are generally based on reasonable maximum exposure (RME) assumptions and can be either health protective or designed to mitigate nuisances associated with chemical contamination (e.g., taste and odor). In order to select (or develop) appropriate screening levels, basic information about the current and potential future land and groundwater uses at or downgradient from the site must be thoroughly documented in the CSM. Typically, screening levels for industrial land use scenarios assume prolonged (i.e., 25-year) exposure to all contaminated media. Many published industrial screening levels assume ingestion of onsite groundwater by a specific

receptor group (e.g., industrial onsite workers). While this is seldom the case on Air Force installations, these conservative screening levels may be appropriate if groundwater use can not be absolutely controlled through pumping restrictions (in particular BRAC bases). In general, industrial screening levels are appropriate for an Air Force site if all of the following conditions are satisfied:

- Residential land use currently does not occur at the site;

- A future residential land use scenario is unrealistic (based on the base master plan, local zoning requirements, access control, proposed property transfer plans, etc.); and,

- Historical plume concentrations or modeling indicate that the chlorinated solvent plume will not migrate into a residential area or is not within the pumping influence of a drinking water well. In this case, industrial screening criteria may be appropriate for the on-base portion of the plume, while off-base groundwater may be subject to residential screening criteria.

USEPA (1995a) guidance on establishing land use for CERCLA remedial evaluations provides useful information on how best to define and defend land use assumptions. Any assumptions regarding land use should be included and explained in the CSM (Section 2.2). Once the appropriate land use category has

been defined, the types of exposure pathways to be considered in the screening evaluation should be defined by the CSM. Table 3.1 provides an example of soil and groundwater screening levels for common chlorinated compounds based on two conservative industrial exposure scenarios compared to residential screening standards.

Exposure Scenario 1 - A non-intrusive grounds keeper who is exposed to soils via ingestion, dermal contact, and inhalation and is exposed to shallow groundwater via inhalation of vapors emanating from groundwater. This exposure occurs for 250 days per year over a 25-year period.

Exposure Scenario 2 – An intrusive utility or construction worker is exposed to contaminated soil via ingestion, dermal contact, and inhalation, and is exposed to groundwater via dermal contact and inhalation. This exposure occurs over a single 60-day event.

Exposure Scenario 3 – Residential exposure based on 30 years of soil contact and groundwater dermal contact, vapor inhalation, and ingestion of soil and groundwater.

Two types of soil screening levels may be applicable: a soil screening level that is protective of underlying groundwater quality (commonly called soil leaching screening level) and a direct-contact (health-protective) soil screening level. The soil leaching screening

level typically is more stringent than the soil direct contact screening level. Because soil remediation is often driven by the need to protect underlying groundwater, the potential use of groundwater must be discussed, agreed upon, and documented by the Air Force and regulatory officials.

The last step in defining appropriate screening levels is determining the risk target level. Generally speaking, acceptable target risk ranges for carcinogens (e.g., vinyl chloride) fall between 10^{-6} to 10^{-4} (USEPA, 1991b). These risk ranges correspond to an added lifetime cancer risk of 1 in 1,000,000 to 1 in 10,000 for people exposed to site contamination. Screening levels for carcinogens typically are based on an extremely protective 10^{-6} target risk level (commonly referred to as a *de minimis* risk level, meaning that a 1 in 1,000,000 risk level is so small as to be of negligible concern. A 10^{-6} target risk level should be considered very health protective, given that the "normal background level" of cancer in the general population is about one in three persons (30 to 35 percent) (USEPA Region 8, 1994). For carcinogens, USEPA (1996) believes that setting a 10^{-6} target risk level for individual chemicals and pathways generally will lead to cumulative risks within the 10^{-4} to 10^{-6} risk range for the combinations of chemicals typically found at contaminated sites. Table 3.1 screening values for carcinogens are marked with a "C" and represent a 10^{-6} target risk level.

TABLE 3.1
EXAMPLE SCREENING LEVELS FOR CHLORINATED SOLVENTS

Chemical	Scenario 1 Nonintrusive Site Worker Soil: ingestion, dermal, inhalation Groundwater: inhalation Exposure: 250 day/year; 25 year			Scenario 2 Intrusive Site Worker Soil: ingestion, dermal, inhalation Groundwater: inhalation and dermal Exposure: 60 day/year; 1 year			Scenario 3 Resident Soil: ingestion, dermal, inhalation Groundwater: ingestion and inhalation Exposure: 350 day/year; 30 year		
	USEPA R9[a] Soil (mg/kg)[b]	Soil-to-Groundwater (mg/kg)	Groundwater (µg/L)[c]	Soil (mg/kg)	Soil-to-Groundwater (mg/kg)	Groundwater (µg/L)	USEPA R9 Soil (mg/kg)	USEPA R9 (20 DAF[d]) Soil-to-Groundwater (mg/kg)	USEPA R9 Tap Water (µg/L)
1,1,1-Trichloroethane (N)	1.40E+03	8.05E+05	8.36E+07	2.88E+04	2.47E+03	2.57E+05	7.70E+02	2.00E+00	7.90E+02
1,1-Dichloroethene (C)	1.20E-01	2.32E+01	2.83E+03	3.46E+01	1.03E+01	1.26E+03	5.40E-02	6.00E-02	4.60E-02
1,2-Dichloroethane (C)	7.60E-01	1.98E+02	4.15E+04	2.10E+02	1.22E+02	2.55E+04	3.50E-01	2.00E-02	1.20E-01
1,2-Dichloroethene,total(N)	1.50E+02	2.79E+04	4.58E+06	1.34E+03	1.08E+03	1.78E+05	4.30E+01	4.00E-01	6.10E+01
Carbon tetrachloride (C)	5.30E-01	1.25E+02	9.53E+03	1.34E+02	2.50E+01	1.90E+03	2.40E-01	7.00E-02	1.70E-01
Tetrachloroethene (C)	1.90E+01	4.84E+03	4.19E+05	2.21E+03	2.52E+01	2.18E+03	5.70E+00	6.00E-02	1.10E+00
Trichloroethene (C)	6.10E+00	2.30E+03	2.01E+05	1.24E+03	6.03E+02	5.27E+04	2.80E+00	6.00E-02	1.60E+00
Vinyl chloride (C)	4.90E-02	1.04E+01	1.56E+03	1.43E+01	7.63E+00	1.15E+03	2.20E-02	1.00E-02	2.00E-02

[a] R9 = USEPA Region 9

[b] mg/kg = milligrams per kilogram

[c] µg/L = micrograms per liter

[d] DAF = Dilution Attenuation Factor

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The TCE Controversy

There is significant controversy over the toxic effects on humans exposed to low concentrations of TCE. Appendix A provides a more detailed review of this controversy and summarizes many of the facts regarding toxicity testing. To date, the AFCEE believes that existing evidence supports the following conclusions:

- Epidemiological studies conducted on tens of thousands of workers repeatedly exposed to TCE in the workplace have found little evidence that TCE causes cancer in humans.

- The available toxicity values for TCE are outdated and were based on TCE-induced cancer in mice. The EPA has proposed new methods for evaluating the cancer risk of chemicals which should provide a more rational basis for estimating TCE toxicity. Evidence presented in Appendix A suggests that the pharmacokinetics, modes of action, and toxicity of TCE in laboratory animals may be significantly different from the expected response in humans. Most significant is the growing evidence that TCE-induced cancer occurs as a result of a threshold exposure, below which no cancer formation is expected. Repeated exposure to low concentrations of TCE may result in the metabolism of TCE with little negative impact on the human body.

- Due the lack of evidence supporting the carcinogenic effects of TCE, the EPA withdrew the Integrated Risk Information System (IRIS) database for TCE in 1986 and has not provided updated toxicity values for use in risk assessment.

- Toxicologists employing threshold toxicity response models and available epidemiological data have estimated that a level of 210 µg/L in drinking water should be protective of human health. The current USEPA drinking water MCL of 5 µg/L was based on the reliable detection limits of analytical instruments not current toxicological data.

- Canada has published a Maximum Acceptable Concentration of 50 µg/L for TCE in drinking water and the World Health Organization has established 70 µg/L as a recommended guideline for drinking water.

Equal importance must be given to noncarcinogenic hazard quotients (relevant to analytes that cause non-tumor-related illnesses). The acceptable target hazard quotient for noncarcinogens (e.g., 1,2-DCE) is set by USEPA (1989)] at less than or equal to 1. Table 3.1 screening levels for non-carcinogens are identified with an "N." Sources of published screening levels for human receptors include:

- USEPA (1996) Soil Screening Guidance (EPA/540/R-96/101);

- Regional USEPA RBSLs [some of the 10 USEPA Regions (e.g., USEPA Region 3 or 9) have adopted some type of industrial screening-level criteria].

Although the USEPA (1996) has developed soil screening levels (SSLs) for most chlorinated solvents, a more comprehensive list of SSLs has been developed by USEPA Regions 3 and 9 (USEPA Region 3, 1996: USEPA Region 9, 1999). The Region 3 and 9 SSLs are acceptable to most state regulators in the absence of specific program guidance because these values have been peer reviewed and address industrial as well as residential land use scenarios. The USEPA does not currently provide industrial screening levels for groundwater in a look-up format. The groundwater screening values provided in Table 3.1 are based on dermal contact and/or inhalation pathways, not ingestion. The residential screening values assume groundwater ingestion.

3.1.2 Screening Levels for Ecological Receptors

In addition to potential human receptors, a screening level evaluation should consider potential ecological receptors and other environmental resources that could be impacted by site contaminants. The site CSM should address the potential for ecological receptors to be involved in completed exposure pathways. Most Air Force solvent release sites are in concrete and asphalt covered industrial/airfield areas that lack suitable habitat to support terrestrial ecological receptors. However, shallow groundwater often discharges to nearby surface waters creating a potential exposure pathway for aquatic organisms. Remedial decisions at some chlorinated solvent sites have been influenced by the need to protect ecological receptors found in nearby streams or wetlands. Screening levels for ecological receptors are less readily available and less universally accepted than those for human receptors. At sites where aquatic receptors may be exposed to site contaminants in surface water, state or federal water quality criteria should be adopted as the screening levels. Table 3.2 lists example screening levels applicable to surface water aquatic organisms for several common chlorinated compounds.

Possible sources of published screening levels for ecological receptors include:

- Federal water quality criteria (USEPA, 1991b) and state surface water quality standards developed to be protective of the most sensitive aquatic species. Often there are criteria established for both chronic (long-term) and acute (short-term) exposures. Where available, the chronic values should be used as screening levels. Because the federal criteria are not promulgated, state standards should be used as screening levels for protection of aquatic life whenever they are available.

- Toxicological benchmarks developed in the technical literature for ecological receptors exposed to contaminated media through ingestion or uptake (e.g., no-observed-effect levels (NOELs) for terrestrial wildlife, and agricultural phytotoxicity guidelines for terrestrial plants). Chlorinated solvents are not bioaccumulated in plants or wildlife.

- Sediment quality criteria developed to be protective of benthic aquatic organisms (e.g., Long and Morgan, 1991; USEPA, 1993a).

3.1.3 Comparing Site Contaminant Concentrations to Screening Levels

Once applicable screening levels are identified, the evaluation process is very straightforward. The evaluation consists of comparing representative exposure-point concentrations from recent site sampling events to applicable screening levels. It is important to use the most recent site contamination data. AFCEE generally recommends evaluating the

two most recent sampling events and a comparison of maximum detected site concentrations to applicable screening levels. The use of statistically averaged site concentrations may be appropriate at many sites and is discussed in Section 3.3. Table 3.3 presents an example format that can be used to quickly summarize the conclusions of a screening level evaluation.

Analytical data for soil and groundwater are usually available for most sites. However, one of the most common exposure pathways for the volatile chlorinated hydrocarbons is based on protection of indoor and outdoor ambient air quality. If no ambient and/or indoor air samples were collected during site characterization efforts (which is typical), it is possible to estimate the concentration in air due to volatilization from subsurface sources such as contaminated soils and groundwater, or

TABLE 3.2
EXAMPLE SCREENING LEVELS FOR AQUATIC ORGANISMS

	Federal AWQC [a]		Federal AWQC [a]	
	Freshwater		**Marine**	
	Acute	Chronic	Acute	Chronic
Chemical	(mg/L) [b]	(mg/L)	(mg/L)	(mg/L)
1,1,1 Trichloroethane	- [c]	-	31,200	-
1,1 Dichloroethene	11,600	-	224,000	-
1,2 Dichloroethene	11,600	-	224,000	-
1,2 Dichloroethane	118,000	20,000	113,000	-
Carbon tetrachloride	35,200	-	50,000	-
Perchloroethene (PCE)	5,280	840	10,200	450
Trichloroethene	45,000	21,900	2,000	-
Vinyl Chloride	-	-	-	-

[a] Ambient water quality criteria, value presented is the Lowest-observed-adverse-effect level (USEPA, 1991).
[b] mg/L = micrograms per liter.
[c] A dash (-) indicates a value is not available.

TABLE 3.3
EXAMPLE SOIL SCREENING TABLE

Detected Analyte	Units	Maximum 1997 Concentration	Maximum 1999 Concentration	Risk-Based Screening Levels		
				Nonintrusive Worker Health Based on Ambient Air Inhalation	Intrusive Worker Health-Based (Soil Ingestion/ Dermal Contact/Vapor Inhalation)	Protective of Underlying Groundwater When Groundwater is Ingested
Trichlorethene	mg/kg	7.2*	4.9	6.1	1240	0.06
1,2- Dichloroethene	mg/kg	2.5	2.4	150	1340	0.400
1,1 Dichloroethene	mg/kg	0.09	0.15	0.12	210	0.06
Vinyl Chloride	mg/kg	<.005	<.005	0.049	14.3	0.01
Chlorobenzene	mg/kg	4.6	3.8	94	41,000	0.6

*Shaded boxes indicate exceedence of screening levels.

use soil gas flux measurements (USEPA, 1986) as surrogate comparison levels to inhalation-based screening levels.

> Actual indoor or outdoor breathing zone gas sampling is preferred, because soil flux concentrations are likely to be significantly higher and overly conservative compared to actual indoor and outdoor breathing zone air concentrations.

The comparison of screening levels to site contaminant levels will result in one of the following outcomes:

1. **Maximum Detected Site Concentrations £ Applicable Screening Levels**

   To assess whether an immediate site closure or No Further Remedial Action Planned (NFRAP) decision document can be prepared, measured site concentrations must be equal to or below applicable screening

levels considering on- and offsite receptors under current and future conditions. The screening level selected for comparison to site concentrations must be conservative enough to protect the potentially most exposed human or ecological receptors, under any realistic current or future land use scenario. The burden of proof is on the Air Force to adequately demonstrate that risks to current and especially future potential receptors are acceptable. This may result in an agreement to monitor for some period of time to ensure future site conditions consistently support this finding.

2. **Maximum Detected Concentrations > Applicable Screening Levels**

   The principal requirement is to determine which of the following options is necessary or desirable, to protect human health and the environment:

3-8

- **Option 1** - Take immediate (interim) remedial action to prevent unacceptable hazards. If the screening level evaluation suggests that **current** receptors could be exposed to contamination at concentrations above the screening levels, some type of immediate response action may be necessary. Examples could include an existing indoor inhalation hazard from subsurface vapor concentrations or a groundwater plume rapidly migrating toward a drinking water well.

- **Option 2** - Develop a long-term remedial action plan to achieve screening levels using some combination of source reduction technologies, natural attenuation, and institutional controls. At some sites, soil and groundwater contamination may exist at levels that present a **future** risk to industrial/airfield workers. On BRAC installations, future land use may be uncertain and it may be difficult to control who contacts contaminated media and for how long. In both of these situations, the Air Force may decide to implement remedial actions to reduce contaminant concentrations below risk-based screening levels. Source reduction and plume remediation strategies are discussed in Sections 4 and 5.

- **Option 3** - Conduct a site-specific risk evaluation to more accurately (and realistically) estimate potential risk to human health and the environment and, if necessary, to redefine risk reduction requirements. This option is most appropriate for active installations where the current and future receptor's contact with contaminated soil and groundwater can be limited by enforceable land and groundwater use restrictions. Depending on the complexity of the site, a site-specific risk evaluation may represent a relatively small incremental effort, or it may represent a significant investment in comparison to a screening evaluation. The tradeoff is that long-term compliance costs will be minimized by establishing less stringent, yet health-protective cleanup goals. Section 3.2 summarizes the major elements of establishing site specific target levels (SSTLs).

3.2 CONDUCTING SITE-SPECIFIC RISK EVALUATIONS

A site-specific risk evaluation may be appropriate when the screening levels discussed in Section 3.1 are overly conservative or do not adequately describe the exposure pathways or receptor scenarios at the site. While industrial screening criteria assume only minimal institutional and engineering controls at a site, active Air Force facilities can enforce more rigid controls over excavation activities. Sites are

often covered with concrete or asphalt and are not normally accessible to site workers. SSTLs are alternate cleanup objectives that are more representative of site conditions than screening levels. SSTLs differ from screening levels in several ways:

- SSTLs incorporate site-specific data rather than generic assumptions about land and groundwater use restrictions;

- SSTLs are based on more reasonable exposure routes given the likelihood that reliable and enforceable exposure controls will limit/prevent certain types of receptor exposures to contaminated media;

- SSTLs account for the positive impacts of natural chemical attenuation processes on interrupting potential exposure pathways and/or minimizing exposure-point concentrations; and

- SSTLs may sometimes be based on higher (less conservative) target risk levels than screening levels, once the decreased probability of actual exposure is documented.

3.2.1 SSTLs for Human Receptors

SSTLs can be developed for potential human receptors using site-specific data and exposure assumptions that are more representative of site conditions. A professional risk assessor should be consulted to establish credible SSTLs that are consistent with USEPA-recommended procedures. Technical guidance on developing

SSTLs using site-specific exposure assumptions and defensible toxicity data is provided in USEPA risk assessment documents.

Table 3.4 provides an example of how site-specific exposure assumptions can result in SSTLs which are more attainable then screening levels illustrated in Table 3.1. Example SSTLs for two site specific scenarios are included in Table 3.4:

- **Exposure Scenario 4** - A non-intrusive grounds keeper who is exposed to soils via ingestion, dermal contact, and inhalation and is exposed to shallow groundwater via inhalation of vapors emanating from groundwater. This exposure occurs for only 50 days per year over a 25-year period (versus 250 days/year for screening level).

- **Exposure Scenario 5** – An intrusive utility or construction worker is exposed to contaminated soil via ingestion, dermal contact, and inhalation. There is no groundwater exposure due to the greater depth of groundwater (> 12 feet). This exposure occurs over a 60-day period.

- **Exposure Scenario 6** – A Scenario 5 intrusive utility or construction worker wearing protective clothing to prevent dermal contact and soil ingestion.

- Comparing Tables 3.1 and 3.4 illustrates how an SSTL can differ from a screening level, and still provide the same level of protection

3-10

(i.e., be based on similar target risk levels). Note that changing the assumption about the duration of exposure and level of PPE significantly changes the target cleanup levels for soil and groundwater.

3.2.2 SSTLs for Ecological Receptors and Environmental Resources

Where surface water quality may be degraded by site contamination, and in states that have promulgated surface water quality standards for protection of aquatic life, the state standards that were used as screening levels may also become the SSTLs. However, at such sites it is important to carefully document the receptors present in the affected water body, and to note visible evidence of adverse effects, or lack thereof (e.g., absence of aquatic organisms that are present in unaffected portions of the same or similar nearby water bodies). A discussion of the impacts of natural attenuation on chemicals in the surface water, based on differences in concentrations at the point of contaminant discharge and downstream from the site, also is important. Natural processes such as volatilization, dilution, and photo-oxidation can rapidly reduce CAH concentrations below aquatic life screening levels, making corrective action to address surface water contamination unnecessary. At some sites, more extensive surface water and sediment sampling may be necessary to establish actual exposure concentrations. *Under no circumstances should exposure concentrations be automatically equated to groundwater concentrations.*

Table 3.4
Comparison of Industrial Screening Level and SSTL

Chemical	Scenario 4 Nonintrusive Site Worker Soil: ingestion, dermal, inhalation Groundwater: inhalation Exposure: 50 day/year; 25 year			Scenario 5 Intrusive Site Worker Soil: ingestion, dermal, inhalation Exposure: 60 day/year; 1 year	Scenario 6 Intrusive Worker w/PPE Soil: Inhalation only No dermal contact Exposure: 60 day/yr; 1 yr
	Soil (mg/kg)[a/]	Soil-to-Groundwater (mg/kg)	Groundwater (μg/L)[b/]	Soil (mg/kg)	
1,1,1-Trichloroethane	4.37E+04	4.02E+06	4.18E+08	2.88E+04	4.33.E+04
1,1-Dichloroethene	1.79E+00	1.16E+02	1.42E+04	3.46E+01	3.91E+01
1,2-Dichloroethane	1.08E+01	9.91E+02	2.08E+05	2.10E+02	2.35E-02
1,2-Dichloroethene, total	1.66E+03	1.40E+05	2.29E+07	1.34E+03	1.42E+03
Carbon tetrachloride	1.27E+01	6.25E+02	4.76E+04	1.34E+02	1.52E+02
Tetrachloroethene	1.76E+02	2.42E+04	2.10E+06	2.21E+03	6.13E+03
Trichloroethene	1.19E+02	1.15E+04	1.01E+06	1.24E+03	1.34E_03
Vinyl chloride	7.59E-01	5.20E+01	7.80E+03	1.43E+01	1.69E+01

In the rare instances where it is necessary to develop SSTLs for ecological receptors, a risk assessor can calculate such values for the various affected media to which receptors are exposed by using literature toxicity data to develop safe chemical- and matrix-specific concentrations that are appropriate to the predominant exposure routes involved. For example, exposure concentrations based on chemical properties (e.g., bioavailability) and behavioral characteristics of the affected receptors can be estimated using simple bio-uptake models and exposure models. However, this step is rarely required, and should not be undertaken unless expressly requested by the regulators involved.

3.2.3 Determining Site-Specific Exposure Concentrations

The use of maximum site detections provides an overly conservative estimate of the actual concentrations that site workers will be exposed to. While the use of maximum detections is appropriate for screening analysis, or for small sites with relatively few sampling locations, USEPA's *Supplemental Guidance to RAGS: Calculating the Concentration Term* (1992a) clearly states that the arithmetic mean is the preferred parameter when estimating exposures to site contaminants. An estimate of the average concentration (typically, the upper confidence limit [UCL] on the arithmetic mean) is recommended by USEPA (1989, 1992b) because:

1. Cancer and noncancer toxicity information are based on lifetime average exposures;

2. The average is most representative of the concentration site workers would be exposed to over time; and

3. For site where remediation is necessary, the preferred measure for demonstrating attainment of a cleanup goal is the average contaminant concentration.

- The USEPA documents cited above provide guidance on estimating average site concentrations and comparing average site concentrations to background and/or cleanup levels. While use of an average concentration provides a more technically defensible estimate of exposure, it is important to consider the objectives, requirements, and costs associated with a statistical procedure (e.g., minimum number of samples, acceptable error rates, site-to-background comparisons, location of samples, etc.) when deciding if average concentrations will be used. Generally, average site concentrations are recommended when maximum concentrations fail the screening analysis and the potential costs of remediation based on maximum concentrations exceeds the cost of gathering enough data to produce a statistically valid average concentration. Figure 3.1 illustrates the difference between maximum and average exposure concentrations at a site

FIGURE 3.1
MAXIMUM vs AVERAGE SOIL EXPOSURE CONCENTRATIONS

● (<1)

● (<1)

● (5)

● (<1)   ● (3)   ● (7)
                                              ● (5)   ● (<1)

● (2)

● (11)   ● (3)   ● (2)

● (5)   ● (2)

● (3)   ● (6)   ● (20)   ● (6)

● (4)   ● (9)   ● (3)   ● (<1)

● (4)   ● (4)

● (5)   ● (6)   ● (2)   ● (<1)

● (5)   ● (5)   ● (5)   ● (2)

(<1)   ● (3)
●
● (4)   ● (1)

● (3)   ● (5)   ● (4)   ● (2)

● (<1)   ● (6)

● (<1)   ● (<1)   ● (<1)

● (<1)
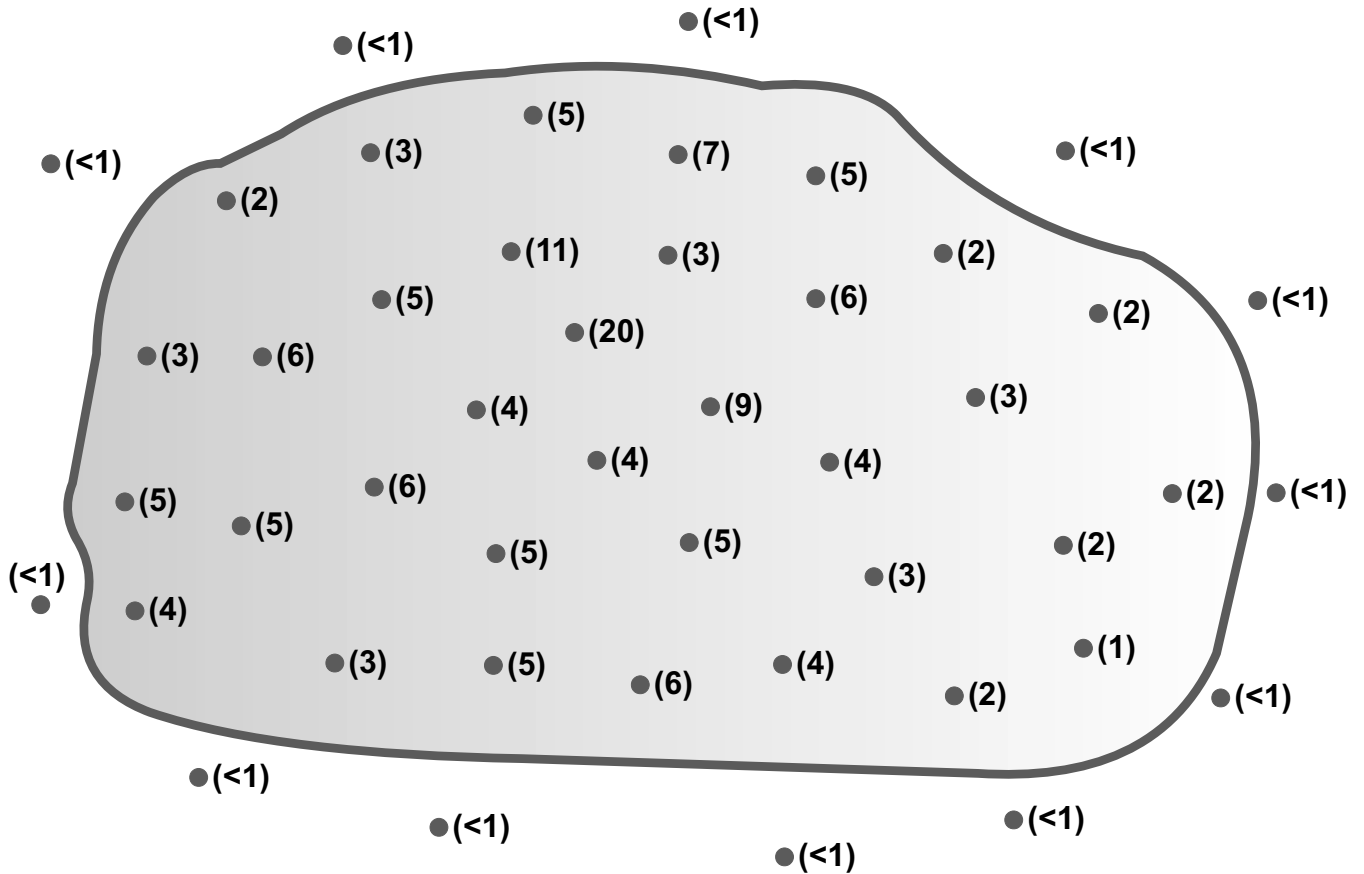
●   Sample Locations (depth 6-10 feet bgs.)

(3)   TCE Soil Concentration in mg/kg

Maximum Soil Concentration   -   **20 mg/kg**

Average Soil Concentration   -   **5.9 mg/kg**
    at 95% UCL*

Non-Intrusive Site Worker   -   **6.1 mg/kg**
    Risk Based Screening Level

* Based on normal distribution

with soil contamination. In this illustation, the maximum detected concentration of TCE (20 mg/kg) exceeds the industrial soil screening level of 6.1 mg/kg, while the average concentration at the 95% UCL (5.9 mg/kg) indicates no exceedence.

3.2.4 Factoring Natural Attenuation Into Exposure Assessment

In addition to developing an SSTL that reflects actual receptor exposure potential, the impact of natural chemical attenuation processes on CAH compounds over time should be considered. Detailed guidance on documenting the natural attenuation of CAH compounds is found in Section 5. This is an important component of the Air Force risk-based remediation strategy because:

- Field-scale evidence of natural chemical attenuation can be monitored over time to confirm the effectiveness of these processes at minimizing contaminant mass, persistence, mobility, and toxicity; and

- The timeframe for achieving various levels of risk-reduction can be estimated and factored into long-term land use decisions.

Natural attenuation can be factored into risk evaluations in many ways, for example:

- Chemical fate modeling results can be used to assess whether existing concentrations can migrate to potential exposure points at concentrations above the screening level or

SSTLs. The role of natural attenuation in reducing the toxicity of TCE is described in Borgert et al. (1995). Borgert indicates that in soils, the half-lives of most chlorinated solvents are less than two years, which will result in a 10- to 40- fold decrease in the soil and soil vapor concentrations used to assess the potential effects on receptors over a 25- to 30-year exposure period. Longer half-lives, but significant decreases in chlorinated solvent concentrations have also been observed in groundwater at many sites (Wiedemeier, 1999). Once chlorinated compounds are released to the atmosphere they are rapidly destroyed by photo-oxidation. For example the photo-oxidation half-life for TCE ranges from 1 to 10 days and the half-life for vinyl chloride is 0.5 to 4 days (Howard, et. al., 1990).

- Chemical fate modeling results also can be used to estimate the timeframe required for more restrictive institutional controls. For example, vinyl chloride concentrations may currently exceed site screening levels or SSTLs, but fate and transport modeling may indicate that vinyl chloride is being degraded at a relatively rapid rate. Restrictions on excavation or new construction on this site may only be required for a relatively short timeframe. This information would be very useful for base master planning or for base realignment or closure actions.

3.2.5 Conducting a More Complex Risk Evaluation

A more complex risk evaluation may be warranted if SSTLs cannot be achieved in a reasonable time frame or at reasonable cost using the primary remedial approaches and technologies. This level of risk evaluation should only be conducted for sites where:

- A quantitative risk assessment using sophisticated modeling (e.g., Monte Carlo simulations) is necessary to define potential site risks with minimal uncertainty;

- Overly restrictive land and/or groundwater use controls would have to be enforced to prevent unacceptable exposure; and

- Expensive containment or isolation remedial technologies (e.g., pump and treat, leachate recovery, or slurry walls) are required to minimize or interrupt potentially significant exposure pathways.

Complex risk evaluations will rarely be required for Air Force sites, and are more likely at mixed-waste sites where soil or groundwater has a high potential to contact human or ecological receptors.

SECTION 4

SOURCE IDENTIFICATION AND REMEDIATION

This section will assist you in:

- Understanding the fate and transport of chlorinated solvents in the source area:

- Determining if DNAPL contamination is likely to be present at the site;

- Evaluating proven and emerging technologies for DNAPL and source area remediation; and

- Justifying a technical impracticability (TI) waiver when source area remediation is impossible with today's technologies.

4.1 OVERVIEW

Once chlorinated solvents have been introduced to the subsurface, their characterization and removal are problematic. Where possible, cost-effective remediation strategies should focus on identifying and delineating those parts of the subsurface environment containing the greatest mass of introduced chemicals, or where chemicals are present at high concentrations. These areas represent potential *chemical source areas*, from which chemicals can leach into groundwater,

migrate to surface-water bodies, or volatilize into soil vapor. These areas can function as long-term contaminant sources, contributing chemical mass to the environment for decades. Identification and reduction of chemical source areas is essential, particularly when natural attenuation processes are slow and the cost of containing resultant groundwater plumes is high. This section provides an overview of chlorinated solvent fate and transport properties, describes current methods for identifying source areas, and discusses several technologies that are being applied to reduce the impact of source areas.

4.2 FATE AND TRANSPORT OF CHLORINATED SOLVENTS

Consideration of the physical and chemical properties of chlorinated solvents is critical in evaluating the migration, distribution, and fate of these chemicals in the environment, developing methods for identifying and delineating source areas, and assessing the possible range in performance of various remedial alternatives (Nyer and Skladany, 1989). In the pure chemical state, most chlorinated solvents are immiscible fluids. Liquid solvents, or solvent mixtures having

4-1

densities greater than water, are known as dense, non-aqueous phase liquids (DNAPLs). Chlorinated solvents comprise the principal category of DNAPL chemicals of concern to DoD. At many sites, the potential for serious long-term contamination of groundwater by DNAPL chemicals is high due to their toxicity, limited solubility, and significant potential for migration in soil vapor and groundwater, or DNAPL migration as a separate immiscible phase. DNAPL chemicals, especially chlorinated solvents, are among the most prevalent groundwater contaminants identified at disposal sites. DNAPL phase has been identified or is suspected at over 50 percent of the solvent-contaminated sites recently examined by the United States Environmental Protection Agency (USEPA, 1999).

4.2.1 Characteristics of Chlorinated Solvents

Chlorinated solvents are manufactured compounds composed primarily of carbon and hydrogen atoms, with one or more chlorine atoms, substituted for hydrogen atoms and attached to the hydrocarbon structure (Dickerson *et al.*, 1970). Alkanes contain only carbon-carbon single bonds, while alkenes contain carbon-carbon double bonds. Double bonds tend to increase the polarity and solubility of the molecule (Schwarzenbach *et al.*, 1993). Chlorobenzene compounds are based on the benzene ring structure of carbon-carbon double bonds with attached chlorine atoms. The number of carbon atoms, the nature of the carbon-carbon bonds, and the number of chlorine functional groups in the hydrocarbon compound have major effects on its properties (Nyer and Skladany, 1989; Schwarzenbach *et al.*, 1993). Figure 4.1 illustrates the molecular structure of several common chlorinated solvents.

Chlorinated hydrocarbons are nonelectrolytes, in that they do not dissociate into cations and anions in aqueous solution, but dissolve as neutral species. Chlorine functional groups and alkene bonds increase the polarity of halocarbon molecules. Chlorine functional groups associate with water molecules by hydrogen bridging, which increases the solubility of polar nonelectrolytes, as compared to non-halogenated hydrocarbons of similar structure (Luckner and Schestakow, 1991). Chlorinated hydrocarbon solubility rapidly decreases as the number of carbon atoms, and/or the number of chlorine atoms in the compound increase(s); vapor pressures also decrease (volatility decreases) as carbon or chlorine numbers increase. For all classes of chlorinated hydrocarbons, aqueous solubility decreases, and the tendency of the hydrocarbon compound to sorb to soil particles (or "partition" to soil), increases as the number of chlorine atoms and molecular weight increase.

Figure 4.1 Common Clorinated Solvent Structures

TCE
(Trichloroethene)

1,1,1 - TCA
(1,1,1 Trichloroethane)

1,2 - DCB
(1,2 - Dichlorobenzene)
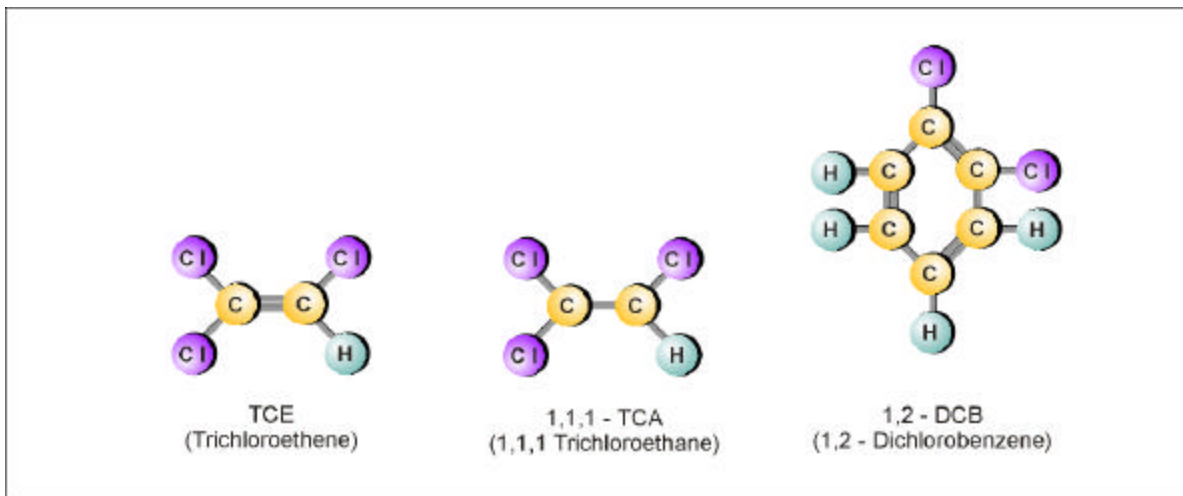
The physical and chemical properties of DNAPLs in the environment can vary considerably from the properties of pure compounds, as a consequence of the presence of complex chemical mixtures, the effects of in-situ weathering, and the fact that much DNAPL waste consists of off-specification materials, production process residues, and spent materials. In general, the chlorinated solvents used in industrial applications are relatively volatile, have relatively low aqueous solubilities (a few hundred to a few thousand milligrams of solute per liter of water [mg/L]), and partition ("sorb") to soil to a moderate degree (Pankow and Cherry, 1996). Table 4.1 summarizes many of the important chemical and physical properties impacting chlorinated hydrocarbon fate and transport.

4.2.2 Physical-Chemical Transport and Attenuation Mechanisms Impacting DNAPL

DNAPL migration in the subsurface is influenced by the characteristics of the DNAPL release (volume, area, and time duration of the release); the properties of the DNAPL; the properties of the porous medium; and subsurface hydrologic conditions. Under particular conditions, chemicals can exist in the environment in any of four different phases - as pure compound or in a chemical mixture; dissolved in water; sorbed to soil particles; or as a vapor. When initially released to the subsurface environment, organic solvents are usually in the NAPL (pure chemical, chemical mixture, or "oil") phase. Once a chemical has been introduced into the environment, it interacts with the surrounding materials (soils, soil vapor, and water). Chlorinated solvents in the subsurface migrate as volatile gases in soil

4-3

TABLE 4.1
PROPERTIES OF SELECTED VOLATILE ORGANIC CHEMICALS

Chemical	Molecular Weight (g/mol)		Henry's Law Constant (atm-m^3/mol)		Vapor Pressure (mm Hg 20°C)		Density (g/cm^3)		Solubility (mg/L)		Koc (mL/g)	
Methane	16.04	(1)	1.83E+01	(6)	2.08E+04	(6)	0.420	(3)	24	(3)	7.60E+02	(6)
Ethane	30.07	(1)	1.92E+01	(6)	2.93E+04	(3)	0.561	(3)	60.4	(3)	7.60E+02	(6)
Ethene	28.05	(1)	8.60E-00	(6)	3.08E+04	(6)	0.566	(3)	131	(6)	4.58E+02	(6)
1,1-dichloroethane	98.96	(1)	4.32E-03	(2)	1.80E+02	(3)	1.176	(1)	5,500	(3)	3.00E+01	(4)
1,2-dichloroethane	98.96	(1)	9.77E-04	(5)	6.10E+01	(3)	1.235	(1)	8,690	(3)	1.90E+01	(4)
1,1-dichloroethene	96.94	(1)	2.07E-02	(2)	5.00E+02	(3)	1.218	(1)	2,250	(4)	6.50E+01	(4)
cis 1,2-dichloroethene	96.94	(1)	2.97E-03	(2)	2.00E+02	(5)	1.284	(1)	800	(3)	4.47E+01	(6)
trans 1,2-dichloroethene	96.94	(1)	7.26E-03	(2)	3.40E+02	(5)	1.257	(1)	600	(3)	5.90E+01	(4)
1,1,1-trichloroethane	133.40	(1)	1.33E-02	(2)	1.00E+02	(3)	1.339	(1)	4,400	(3)	1.05E+02	(4)
1,1,2-trichloroethane	133.40	(1)	1.20E-03	(5)	1.90E+01	(3)	1.440	(1)	4,500	(3)	5.60E+01	(4)
TCE	131.39	(1)	7.19E-03	(2)	6.00E+01	(3)	1.464	(1)	1,100	(3)	1.07E+02	(4)
PCE	165.83	(1)	1.32E-02	(2)	1.40E+01	(3)	1.623	(1)	150	(3)	2.63E+02	(4)
Vinyl Chloride	62.50	(1)	2.18E-02	(2)	2.66E+03	(3)	0.911	(1)	1,100	(3)	2.50E-00	(4)
Benzene	78.11	(1)	5.43E-03	(5)	7.60E+01	(3)	0.877	(1)	1,780	(3)	9.12E+01	(3)
Toluene	92.14	(1)	5.94E-03	(5)	2.20E+01	(3)	0.867	(1)	515	(3)	1.51E+02	(4)
Ethylbenzene	106.17	(1)	8.44E-03	(7)	7.00E-00	(3)	0.867	(1)	152	(3)	2.57E+02	(4)
o-Xylene	106.17	(1)	5.10E-03	(5)	5.00E-00	(3)	0.880	(1)	175	(3)	1.29E+02	(4)
m-Xylene	106.17	(1)	7.68E-03	(5)	6.00E-00	(3)	0.864	(1)	146	(7)	1.59E+02	(4)
p-Xylene	106.17	(1)	7.68E-03	(5)	6.50E-00	(3)	0.861	(1)	198	(3)	2.04E+02	(4)
1,2,4 Trimethyl Benzene	120.19	(1)	5.70E-03	(9)	2.03@25	(9)	0.862	(1)	51.9	(8)	3.72E+03	(9)
Chloroethane	64.51	(1)	9.38E-03	(2)	1.01E+03	(3)	0.898	(1)	5,740	(3)	2.65E+01	(6)
Chlorobenzene	112.56	(1)	3.45E-03	(7)	8.80E-00	(3)	1.106	(1)	500	(3)	1.49E+02	(6)
1,2-Dichlorobenzene	147.00	(1)	1.20E-03	(7)	1.00E-00	(3)	1.305	(1)	100	(3)	1.87E+02	(4)
1,3-Dichlorobenzene	147.00	(1)	1.80E-03	(7)	2.30E-00	(7)	1.288	(1)	69	(3)	1.70E+02	(4)
1,4-Dichlorobenzene	147.00	(1)	1.50E-03	(7)	6.00E-01	(3)	1.248	(1)	49	(3)	1.58E+02	(4)

Sources of Information:

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(7) Howard, P.H., Sage, G.W., Jarvis, W.F., and Gray, D.A., 1990, Handbook of environmental fate and exposure data for organic chemicals, Vol. I -- Large production and priority pollutants: Lewis Publishers, Inc., Chelsea, Michigan, 574 pp.

(8) American Petroleum Institute, 1994, Transport and fate of non-BTEX petroleum chemicals in soils and groundwater, American Petroleum Institute.

(9) Montgomery, J.H., 1996, Groundwater chemicals desk reference: Lewis Publishers, Inc., Chelsea, Michigan, 2nd ed., 814 pp.

vapor, dissolved in groundwater, and as a mobile, separate phase. The major processes affecting chlorinated solvent compounds in the subsurface include dissolution from the NAPL phase, sorption to soil, diffusion, chemical and biological degradation, and volatilization (Nyer and Skladany, 1989).

The subsurface can be divided into three general domains, distinguished by the water content within each. The *vadose zone* or *unsaturated zone* is that part of the soil (or geologic) column which is less than residual water saturation - that is, water is present within the pore spaces of soil in the vadose zone, but not at a degree of saturation sufficient to enable gravity drainage of water. The *capillary zone* spans the region over which the water content in the soil column increases from residual saturation, until all the pore spaces are filled with water (full saturation). The *saturated zone*, or *groundwater zone*, comprises the water-saturated part of the soil column below the water table, where the hydraulic potential ("water pressure") is equal to or greater than atmospheric pressure. DNAPL movement through each of these moisture regions is controlled by different physical and chemical interactions.

Under uncontaminated conditions, moving from the vadose zone to the saturated zone represents a change from a system in which two immiscible fluids (air and water) initially share the pore space, to a system where water occupies the entire pore space. When a DNAPL solvent is introduced, the relationships between the fluids and the porous medium become considerably more complex. In this situation, the vadose zone can contain up to three fluids (air, water, and NAPL); below the water table, two fluids (water and DNAPL) may be present. The physical and chemical relationships among the different fluids will often cause the DNAPL phase to migrate in complex ways, producing a contaminant source beneath a spill area that is very difficult or impossible to fully characterize.

Some of the factors and principles that govern DNAPL migration differ from those that control the occurrence and movement of dissolved-phase chemicals (Kueper and Frind, 1991a; ibid., 1991b). The characteristics of chemical migration as a DNAPL phase are largely a result of interfacial tensions which exist at the interfaces between immiscible fluids (NAPL, air, and water). Interfacial tension between fluids develops because of the difference between the greater mutual electrochemical attraction of like molecules within each fluid and the lesser attraction of dissimilar molecules across the immiscible fluid interface (Cohen and Mercer, 1993a; ibid., 1993b). This unbalanced force draws molecules lying along the interface between two immiscible fluids inward, resulting in a tendency for contraction of the fluid-fluid interface to attain a minimum interfacial area. As a result of

4-5

interfacial tension, non-wetting DNAPLs tend to form globules and irregular ganglia in water and water-saturated media (Cohen and Mercer, 1993b).

Subsurface transport of chemicals as NAPL, dissolved-phase, or vapor-phase, is driven by potential gradients - gravitational, hydraulic, or chemical. In the unsaturated zone, gravitational and hydraulic potential gradients are primarily vertical, so that the direction of movement is generally downward. In most situations, NAPLs denser than water will migrate downward (under the influence of gravity) as a distinct liquid through the soil in the unsaturated zone. This vertical migration is typically accompanied by lateral spreading of the DNAPL due to the effects of capillary forces and heterogeneities in the porous medium. Even small differences in soil moisture content and grain size can provide sufficient capillary resistance to cause lateral DNAPL spreading in the vadose zone. However, downward movement will be enhanced, and lateral spreading limited, by dry conditions or transmissive vertical migration pathways for DNAPL migration (e.g., fractures, coarse-grained material, or boreholes). Figure 4.2 illustrates four common scenarios for DNAPL movement and distribution in the subsurface and the resultant dissolved plume patterns.

Pankow and Cherry have authored a book entitled *Dense Chlorinated Solvents and Other DNAPLs in Groundwater - History, Behavior,* *and Remediation* (1996) which describes the properties of DNAPL solvents and their migration characteristics in detail. This reference is recommended for the reader who is interested in additional information on this subject. The conclusions of this and other references are summarized below:

1. Historically, it was believed that a chlorinated solvent released to the unsaturated zone would readily volatilize to the atmosphere. However, chlorinated solvents are often transported into the subsurface by vapor-phase migration, by infiltration of contaminated water, and as a moving DNAPL phase.

2. The relatively low viscosities of the chlorinated solvents allow relatively rapid downward movement in the subsurface. Chlorinated solvent mobility in the subsurface increases with increasing density/viscosity ratios (Cohen and Mercer, 1993b).

3. The relatively low interfacial tension between a liquid chlorinated solvent phase and water allows a chlorinated solvent DNAPL to enter small fractures and pore spaces, facilitating deep penetration into the subsurface. Low interfacial tension also contributes to the relatively low residual saturation of chlorinated solvents in soil within the unsaturated zone.

FIGURE 4.2

TYPICAL DISTRIBUTIONS OF DNAPL AND DISSOLVED CHLORINATED SOLVENTS
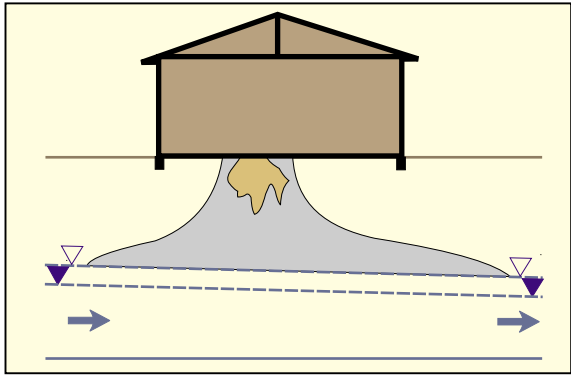
Example A
Schematic of a small spill in a permeable unsaturated zone with a resulting mound of chlorinated hydrocarbon (CHC) gas. Concentration decreases with distance from the spill source.

Example B
Larger spill than in **Example A**, but still not large enough to exceed the retention capacity of the unsaturated zone; no liquid CHC reaches the capillary fringe, but some impact from soil gas.
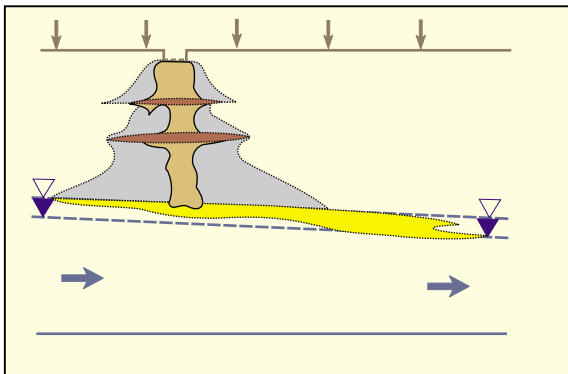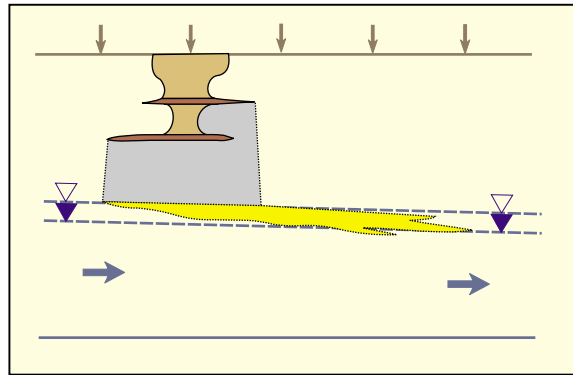
Example C
An envelope of CHC vapor develops around the core of the **Example B** spill, leading to a gas mound. Liquid and gaseous CHC tend to dam up on the top of low permeability layers with some liquid CHC impacting capillary fringe.

Example D
Percolated mass of CHC exceeds the combined retention capacities of the unsaturated and saturated zones. Liquid CHC reaches the bottom confining bed and accumulates there. Groundwater velocity depends on local permeability.

BEDROCK

Source: Modified from Schwille and Pankow, 1988.

draw\730486I.cdr aee 6/23/00
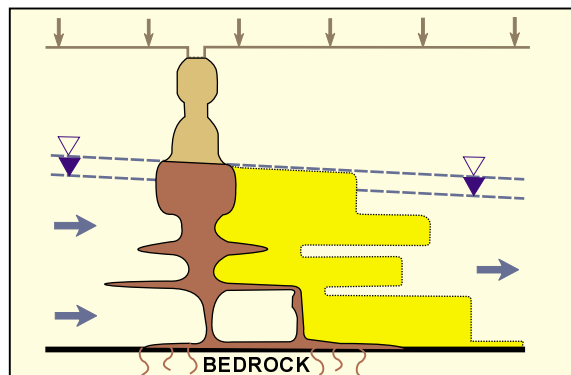
4. The high densities of the chlorinated solvents (1.2 to 1.7 g/cm³) relative to that of water (1.0 g/cm³) mean that if a sufficient volume of chlorinated solvent is spilled, then DNAPL may be able to penetrate the water table. In the saturated zone, capillary forces can immobilize DNAPL at residual saturation in the soil. Alternatively, the unstable nature of DNAPL flow mechanisms can cause the solvent to continue migrating as a continuous body, or in thin "fingers" which can lead to the collection of large amounts of solvent in "pools" on top of less permeable layers.

5. The low absolute solubilities of the chlorinated solvents (typically on the order of a few hundred mg/L) mean that when a significant quantity of solvent is introduced to the environment, liquid solvent will dissolve slowly, and will persist for decades or centuries (Johnson and Pankow, 1992).

6. The relatively low degree of partitioning to soil materials exhibited by the chlorinated solvents means that sorption to soils will not significantly retard the movement of a chlorinated solvent, and zones of contamination can expand quickly.

7. Most chlorinated solvents exhibit low rates of biologic and abiotic degradation and can persist in the subsurface for extended periods of time. For example, natural biodegradation of PCE and TCE is generally limited to sites with high levels of natural organic material where strongly reducing conditions exist. In aerobic aquifers, PCE and TCE are very persistent.

4.3 SITE CHARACTERIZATION FOR THE PRESENCE OF DNAPL

In order to develop rational and cost-effective remediation strategies at sites contaminated with chlorinated solvents, it is necessary to assess whether a DNAPL phase is likely to be present in the subsurface, and if so, to evaluate the nature of DNAPL contamination. The presence and migration potential of DNAPL at contamination sites needs to be characterized because: 1) the properties and principles that govern DNAPL and dissolved-phase transport are quite different; 2) DNAPL can persist for decades or centuries as a significant source of groundwater or soil-vapor contamination; and 3) without adequate precautions or understanding of DNAPL presence and behavior, site characterization activities may result in expansion of the DNAPL contamination with resulting increases in remediation costs.

DNAPL migration is affected by chemical- and media-specific properties, including degree of saturation, interfacial tension, wettability, capillary pressure, residual saturation, relative permeability, solubility, vapor pressure, volatilization, density, and viscosity. DNAPL migration is also controlled by the interaction of these properties and principles with site-specific

4-8

hydrogeologic and DNAPL release conditions. Using information about the types and quantities of chemicals that might be present at a site, together with site-specific hydrolgeologic information, a conceptual site model (see Figure 2.1) should be developed to describe the behavior of DNAPL in the subsurface. Conceptual models should be used to guide site characterization and remedial activities.

Ideally, site characterization is an iterative, continuous process, where each phase of investigation and remediation is used to refine the conceptual model of the site. During the initial phases of the investigation, a conceptual model of chemical presence, migration, and fate is formulated based on available site information, and an understanding of the processes that control chemical distribution and movement. In the second phase, a data collection program is designed based on the initial conceptual model. Data collection efforts should test and improve the site conceptual model. Later phases of site activities may involve full-scale or pilot-scale remediation. Collection of appropriate data during implementation of a remedy provides an opportunity to monitor and evaluate the effectiveness of the remedy, and also to learn more about conditions in the subsurface. Therefore, remediation should be considered an extension of site characterization, yielding information that may allow improvements to the remediation effort.

If chlorinated solvents are known or suspected to be potential site contaminants, the possible presence of DNAPL at a site should be considered in the initial phase of planning for site characterization. Determination of DNAPL presence should be a high priority from the outset of site investigation, and should guide the selection of site characterization methods. Knowledge or suspicion of DNAPL presence requires that special precautions be taken during field work to minimize the potential for inducing unwanted DNAPL migration.

A primary goal in the assessment of a chlorinated solvent site to establish whether significant quantities of a DNAPL phase are present in the subsurface. If present, the site characterization should assess the long-term contribution of DNAPL to site risks and what potential remedies could be used to reduce DNAPL impacts. Specific objectives of DNAPL site evaluation may include:

- Estimation of the quantities and types of DNAPLs released and present in the subsurface;

- Delineation of DNAPL release areas;

- Determination of the zone(s) in the subsurface where DNAPL is present;

- Delineation of site stratigraphy;

- Determination of fluid-media properties; and

4-9

- Determination of the nature, extent, migration rate, and fate of contaminants.

Many lines of evidence can contribute to the diagnosis of a DNAPL site. At most sites, only one or two lines of evidence may be available due to limited data or unknown geologic conditions. The primary lines of evidence that can be used to evaluate the presence of DNAPL include:

1. Compilation and evaluation of the history of chemical use, handling, and disposal practices;

2. Direct characterization of subsurface conditions; and,

3. Indirect observations and interpretations of soil vapor, earth materials, and water.

4.3.1 Historical Use

Evaluation of the operational history of a particular facility can provide valuable information regarding the types and quantities of chemicals that may have been used, and may even provide clues regarding methods and locations of chemical disposal. Assessment of the potential for DNAPL contamination based on historical site use involves careful examination of land use since site development; maintenance operations and processes; types and volumes of chemicals used and generated; and the storage, handling, transport, distribution, and disposal practices used for these chemicals and operations residues. This information is often found in Phase I Site Record Reviews and Site Assessments. Detailed discussions of methods for conducting research on historic use at sites suspected to be contaminated are provided in environmental audit guidance documents (e.g., ASTM, 2000).

4.3.2 Direct Characterization to Determine DNAPL Presence

DNAPL presence can be determined directly by visual examination of samples, inferred by interpretation of chemical analyses of samples, and/or suspected based on interpretation of anomalous chemical distributions and hydrogeologic information.

4.3.2.1 Direct Evidence of DNAPL Presence in Soil Samples

Under ideal conditions, DNAPL presence can be identified by direct visual examination of soil, rock, or fluid samples. Methods that can be used to visually identify DNAPL in solid samples are based on observation and field testing during drilling and recovery of soil and rock samples from the subsurface. Under some circumstances, the presence of a DNAPL is obvious. Abundant dark-colored DNAPL (usually a mixed DNAPL) at high residual saturation, or in layers or pools, is usually readily visible in core samples. Direct visual detection may be difficult, however, where DNAPL is colorless, present at low saturation, or heterogeneously distributed.

Direct visual detection may be enhanced by ultraviolet fluorescence analysis, the addition of dye, and/or separation of fluid phases. These methods have not been widely used, but have been evaluated in controlled laboratory studies (Pankow and Cherry, 1996). The ultraviolet fluorescence (UV fluorescence) method involves examination of soil samples under a portable UV light. Since many unsaturated aliphatic hydrocarbons, including PCE and TCE, fluoresce under UV light, field screening of cores or drill cuttings using this method can be used to enhance the visual identification of some DNAPLs.

Examination by UV fluorescence can be accomplished with the samples enclosed in transparent soil core liners or plastic bags to minimize the loss of volatile constituents. Samples of soil known to be uncontaminated should also be examined as controls, because some minerals and shell fragments also fluoresce.

The soil-water shake test involves the transfer of a soil sample to a clear tube, with addition of an equal volume of water. The tube is stoppered and the mixture shaken by hand. If DNAPL is present, agitation in the presence of water will cause the phases to separate, and the DNAPL can be identified by examination of the tube walls and bottom. The effectiveness of this test can be enhanced by centrifuging the mixture, causing the DNAPL to accumulate at the bottom of the tube. It can also be enhanced

by the addition of a small amount of hydrophobic dye (Sudan IV or Red Oil O) to the mixture. These dyes are insoluble in water, but are soluble in many organic liquids. Any DNAPL present in the sample thereby becomes red in color. These tests can be performed in the field during the normal course of soil sampling.

Many DNAPL chemicals have high vapor pressures and correspondingly high saturated vapor concentrations, and screening a sample with an organic vapor analyzer (OVA) can provide a rapid indication of the presence of a volatile chemical. Field screening of vapor concentrations emitted from soil samples can be conducted in several ways. One way is to remove a soil sample from the sampling apparatus and pass the inlet tip of the OVA slowly along the sample while observing the vapor concentrations indicated by the instrument. Dilution of emitted vapor can be minimized by transferring the sample to a bag or jar equipped to allow access of the OVA inlet tip. To promote volatilization of chemicals from the sample, a sample so enclosed may be warmed (e.g., in a hot water bath). Elevated vapor concentrations detected by an OVA (greater than a thousand ppmv) may be an indication of the presence of DNAPL in a soil sample.

4.3.2.2 Direct Evidence of DNAPLs in Wells

At some sites, DNAPL can be identified in samples from monitoring or extraction wells.

Although such a finding confirms the presence of DNAPL at a site, it is generally impossible to relate the quantity of DNAPL in a well to the vertical distribution or volume of DNAPL in the subsurface. DNAPL layers and pools are generally thin in comparison with the open interval of a boring, and may not be identified during drilling operations. If DNAPL enters a boring, it will sink to the bottom. If the DNAPL accumulation is sufficiently large, it will enter the well screen and may be found by sounding or sampling the well. However, it will not be possible to relate the elevation of DNAPL in the well to the elevation of zones that contain DNAPL in the formation, because DNAPL could have entered at any point along the open interval of a boring.

The accumulation of DNAPL in the bottom of a monitoring well can be evaluated by use of interface probes, or by sampling the bottom of the well. Interface probes are down-hole sensors mounted on a graduated cable or tape. They commonly use an optical sensor for detecting the air-water interface, and a conductivity sensor for detecting a water-DNAPL interface. Under ideal conditions, a DNAPL thickness of about 0.2 inch or greater can be detected.

Sampling the bottom of a well can provide direct visual evidence of the presence of a DNAPL, and can also yield samples for determination of the chemical composition and fluid properties of the DNAPL. Samples can be collected using pumps, bottom-loading bailers,

or discrete-depth cannister samplers. In general, evacuated discrete-depth samplers are the most reliable method for collecting samples of DNAPL. Common DNAPL chemicals can degrade many pump materials. When using a bottom-loading bailer to sample DNAPLs having densities greater than about 1.3 g/cm^3, PVC and Teflon will not provide adequate valve seating, and the DNAPL may be lost through the valve as the bailer is retrieved.

Even though DNAPL has not been detected in any wells at a site, one cannot conclude that DNAPL is not present in the subsurface. At many (or most) sites, the zones containing free DNAPL or DNAPL at residual saturation may be very small in areal extent relative to the spacing of wells or borings. Most DNAPL in the subsurface is present only at residual saturation, and will not be able to move into a boring or well. If a zone containing free DNAPL is not immediately adjacent to the screened interval of the well, DNAPL may not be able to move into the well. Consequently, DNAPL zones may never be intersected by well borings.

Monitoring wells are commonly constructed so that the base of the well screen is some distance above the bottom of the sand pack. DNAPL that enters a boring and sinks to the bottom will not enter the well screen unless enough DNAPL accumulates to enter the bottom of the screen. If the volume of DNAPL that enters a boring is small, it may not be sufficient

to rise up to the well screen. If the formation surrounding the bottom of the boring is relatively permeable, it is possible that the DNAPL may exit the boring before sufficient DNAPL accumulates to enter the well screen. In this situation, not only will the DNAPL be unidentified in the monitoring well, but the boring will become a conduit promoting DNAPL migration deeper into the subsurface. This can be avoided by installing a cement basket and sump at the base of the screen (Figure 4.3) (Pankow and Cherry, 1996). DNAPL migrating down the wellbore is deflected by the cement basket into the well screen and accumulates in the sump. This type of construction may prevent the wellbore from functioning as a preferential pathway for downward migration of DNAPL after well construction, but will not prevent DNAPL migration that might occur during drilling and well installation.

4.3.3 Indirect Evidence of DNAPL

Indirect methods for assessing the presence of DNAPL in the subsurface rely on comparing measured chemical concentrations with effective solubility limits in groundwater and equilibrium partitioning concentrations in soil gas and groundwater. The following indirect evidence can indicate the presence of DNAPLs:

- Concentrations of organic vapors detected in soil-gas samples, at concentrations in excess of 1000 parts per million by volume (ppmv)

may be regarded as indirect evidence of a NAPL phase.

- Where present as a separate phase, DNAPL compounds are generally detected at concentrations less than 10 percent of their aqueous solubility limit in groundwater due to the effects of non-uniform groundwater flow, variable DNAPL distribution, mixing and chemical dilution during migration. When only residual DNAPL is present (not separate phase) dissolved contaminant concentrations greater than about 1 percent of the aqueous solubility suggest that DNAPL residuals may remain in the soil. (Pankow and Cherry, 1996)

- In soil, contaminant concentrations in the range of 10,000 to 20,000 milligrams per kilogram ([mg/kg]; one percent by weight) are generally indicative of the presence of a mobile non-aqueous phase liquid (Mercer and Cohen, 1993). However, NAPL may also be present at much lower bulk concentrations, at a consequence of irregular distribution in soil.

- The presence of subsurface DNAPL can also be inferred from anomalous contaminant distributions or other unusual conditions. Such conditions can include:

  - Dissolved contaminant concentrations that increase with depth beneath a release area;

4-13

FIGURE 4.3

WELL DESIGN FOR DNAPL SITES

Well screen

Sand pack

Cement basket attached to well screen

Grout
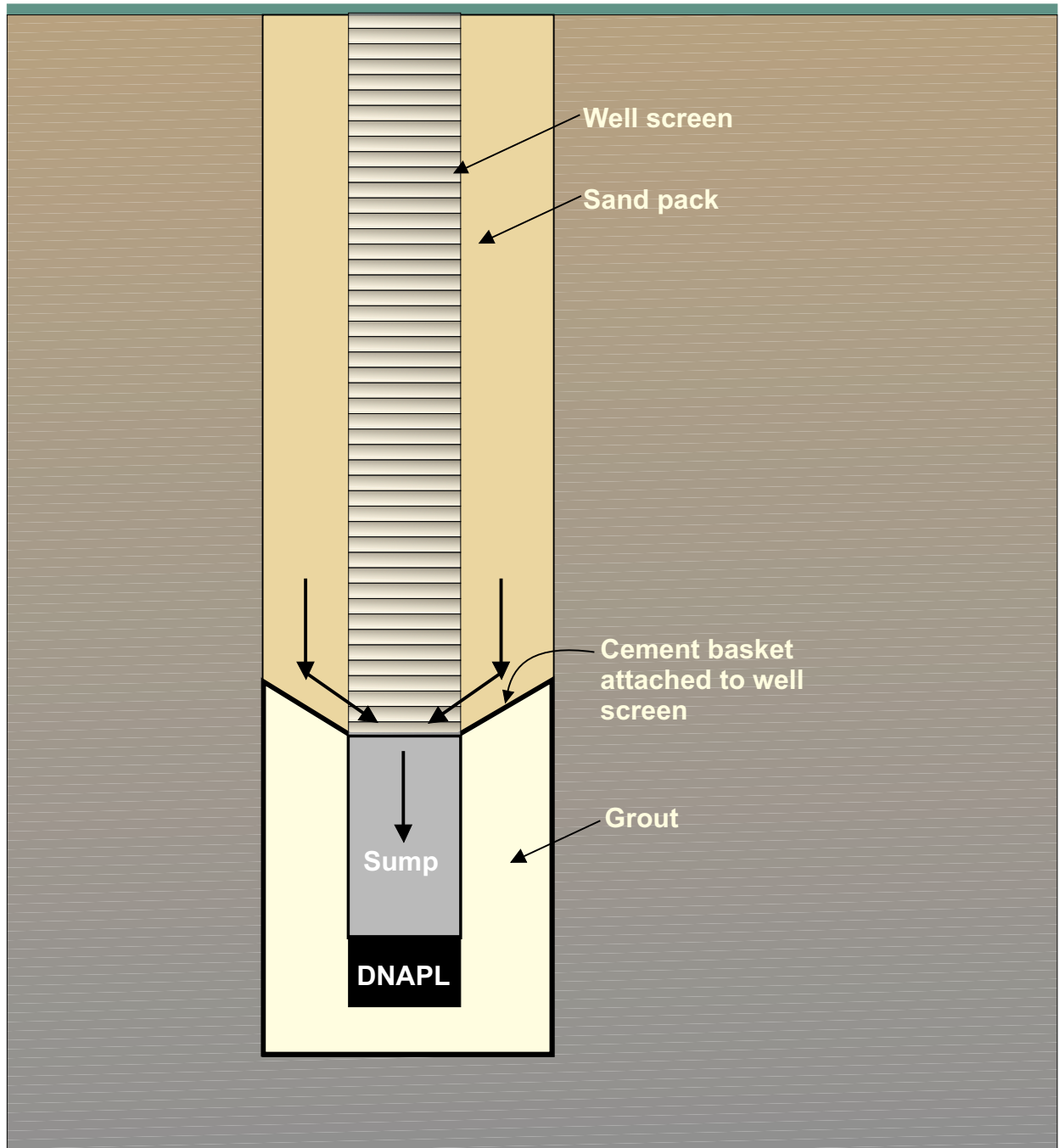
Sump

DNAPL

DNAPL is deflected by cement basket into the well screen and accumulates in the sump.

* Based on normal distribution

- Higher concentrations at locations that are hydraulically upgradient from a release area;

- Erratic spatial distribution of dissolved-phase chemicals as a possible consequence of the heterogeneity of DNAPL distribution;

- Dissolved chemical concentrations in extracted groundwater that decrease through time during a pump-and-treat operation, but then increase significantly after the system is shut down (the "rebound effect"); and

- Inexplicable deterioration of wells or pumps, possibly caused by solvents present as a DNAPL phase.

4.3.4 Locating DNAPLs in the Subsurface

Techniques for locating and identifying DNAPL chemicals in the subsurface fall into two general classifications - intrusive methods and non-intrusive methods. Intrusive methods include those techniques that involve penetration of the subsurface to some depth (drilling, drive-point or Hydropunch™ sampling; trenching; well installation). Non-intrusive methods involve collection of samples at or near land surface (soil-vapor surveys) or application of indirect data-collection methods (e.g., geophysical techniques).

During site investigations it is particularly important to determine, if possible, the spatial distribution of fine-grained capillary barriers and preferential DNAPL migration pathways (e.g., fractures and coarse-grained strata).

4.3.4.1 Intrusive Investigation Methods

Intrusive methods that may be used to identify chemical source areas or DNAPLs all produce some disturbance of the subsurface environment. Because they permit affected media to be sampled directly, intrusive technologies are capable of generating the most reliable evidence for use in interpreting subsurface conditions. All intrusive technologies require that a piece of equipment (drill string, drive point, backhoe bucket) be driven into the ground. Depending on the technology used, minor or large amounts of earth material are brought to the surface, as cuttings or excavated soil. This can present handling and disposal problems, as soil generated during investigation of DNAPL sites can be classified as a hazardous waste. Current investigation strategies are emphasizing probe technologies that minimize the disturbance to the subsurface environment, while simultaneously minimizing the amount of waste generated.

Test Pits

Test pits in unconsolidated material can provide valuable information that is not easily obtained by other means. Test pits can be

4-15

excavated using a backhoe or power shovel; practical considerations regarding equipment limitations, sidewall stability, and worker safety currently restrict the depth of exploration using this method to a maximum of about 25 to 30 feet. Test pits provide an opportunity for direct visual examination of stratigraphy and geologic structure. In particular, features that may control DNAPL migration, such as vertical fractures and the presence and lateral continuity of fine-grained strata, can be readily identified in test pits, but are more difficult to identify in borings. Shallow test pits can enable the presence and distribution of DNAPL to be visually identified, and the relationship between geologic structure and DNAPL distribution to be assessed.

Excavation of a test pit may generate significant quantities of contaminated material that may require special handling. Whenever possible contaminated material should be returned to the excavation. If new backfill material is required, only low-permeability soils should be used so that the backfilled volume does not create a potential migration pathway for DNAPL.

Conventional Drilling Methods

Conventional drilling methods can be used to penetrate virtually any material to significant depths. Drilling methods enable samples of the soil or rock to be collected as it is penetrated by the drill string, and usually allow a well to be installed within the borehole (Driscoll, 1986).

On the other hand, depending on the sampling method used, visual identification of DNAPL in a soil sample collected using conventional drilling methods may be difficult or impossible, in particular if the drilling method used requires introduction of a fluid (drilling fluid, water or air) to the subsurface. Drilling fluid can dilute any DNAPL moving into the borehole, making detection of the DNAPL impossible. A useful application of conventional drilling methods in locating DNAPL zones involves advancing the drill string to the stratigraphic interval of interest and collecting a soil core using a split-spoon or other coring device. Below the water table, water can be purged from the drill string, allowing ambient fluids (groundwater and/or DNAPL) to move into the drill string for collection of a sample. This technique is applicable when using drilling methods that advance a hollow drill string or casing (e.g., hollow-stem auger).

Drive-Point Methods

Soil and water samples can be collected, and monitoring wells installed, using drive-point methods. The generic term "drive point" encompasses several patented technologies, including GeoProbe™ and HydroPunch™ methods, BAT™ samplers, and cone penetrometers. The drive-point consists of a hydraulically- or pneumatically-driven probe rod that is used to advance a special sampling tool. Depending on the type of sample to be collected, the probe tool may consist of a split-spoon

4-16

sampling device to collect a soil core interval, or a screened or porous point to collect vapor or liquid samples. Following sample collection, the device is removed and the hole may be grouted, or a permanent monitoring well installed. Drive-point methods are suitable for use in sandy and silt materials to depths of about 100 to 120 feet under ideal conditions. The depth of penetration will be limited by dense materials (clays and rock), and by the presence of large gravels and cobbles).

Drive-point methods may be regarded as a refinement of conventional drilling methods, in that the same types of samples may be collected, but more rapidly, at lower cost, and with only minimal amounts of contaminated drill cuttings or water generated during the operation. Drive-point devices can be used to collect discrete samples at intervals as small as a 2-3 inches. Although this intensity of discrete sampling is time consuming, this method greatly increases the likelihood of intersection and recovery of DNAPL.

Preventing Unwanted DNAPL Migration

When a test pit, boring, drive point, or monitoring well installed during an intrusive investigation intersects a DNAPL layer or pool, there is a potential for further migration of the DNAPL and expansion of the zone of contamination. DNAPL may move downward along an open borehole during drilling and sampling prior to well installation, along the

sand pack of a completed well, or along an unsealed boring or probe hole. The potential for unwanted migration is greatest when borings intersect DNAPL accumulations in lenses or pools, especially when the DNAPL is of low viscosity or high density.

The potential for mobilization of DNAPL along borings can be reduced by not drilling in areas that are known or suspected to contain DNAPL. When DNAPL is suspected, emphasis should be given to defining the extent of the dissolved plume first, and then working back to identify the source zone(s). This is referred to as the "outside-in" approach (Pankow and Cherry, 1996). In many circumstances, even the evaluation and design of remedial measures does not require drilling directly through a DNAPL source zone. Information regarding the general spatial distribution of DNAPLs can often be inferred from the results of soil-vapor surveys, and monitoring of wells outside of the source area(s).

In some circumstances it may be necessary to drill directly into the source zone to obtain information regarding the physical and chemical characteristics of the DNAPL, or the nature and distribution of chemical sources. Because of the potential for DNAPL migration, source area drilling should be conducted using suitable precautions, and only when absolutely necessary. Precautionary measures may include:

- Reducing the length of open intervals in borings, and reducing the length of time that borings remain open.

- Ensuring that boreholes, test pits, and probe holes are completely backfilled with an impermeable material, which maintains the integrity of the connection between the backfill material and the borehole wall. This material is generally cement grout, sometimes with a bentonite amendment.

- Using high-density drilling fluids, or maintaining high water levels in borings during drilling. Drilling fluids and elevated water levels inhibit the entry of DNAPL into a borehole. However, large volumes of water introduced to the borehole may hinder data interpretation; and drilling fluid may form a skin on the walls of the borehole that is difficult to remove during well development.

- Terminating the boring at the first evidence of DNAPL. This requires that DNAPL can be accurately and rapidly identified during drilling by visual inspection, vapor monitoring, or field-testing of samples obtained from borings.

- Terminating the boring at the top of geological barriers to DNAPL migration (e.g., fine-grained strata). Application of this strategy is limited to areas where previous investigation activities have identified the presence and location of geological barriers.

- Using telescoping casing to isolate specific stratigraphic intervals from zones above and below. This strategy can be effective in a multi-layer system of water-bearing zones separated by aquitards, and involves the setting of casing in a geological barrier (aquitard) and advancing progressively smaller diameter casing to the required depth of investigation. However, drilling using this technique is slower and more expensive than conventional well drilling and installation; and there is a practical limit to the number of casing segments that can be telescoped within a single boring.

4.3.4.2 Indirect Investigation Methods

Indirect investigation technologies are generally inferential in nature – that is, the property measured or evaluated by the method (e.g., soil gas) is not necessarily the property of interest (e.g., presence/absence of DNAPL). As a consequence of the inferential nature of indirect investigation methods, the results that are generated using these methods are not as definitive as direct measurements. Indirect methods used to locate DNAPLs in the subsurface are of three general types – soil-vapor surveys, geophysical methods, and tracer tests.

Soil-Vapor Surveys

Many DNAPLs, including most chlorinated solvents, have high vapor pressures and will readily volatilize in the vadose zone to form a

4-18

vapor plume around a DNAPL source. Volatile chemicals dissolved in groundwater can also volatilize at the capillary fringe into soil vapor. Volatile constituents in soil vapor diffuse along the chemical concentration gradient (away from the source area), and can move tens of feet or more from a DNAPL source area in the vadose zone in periods of weeks to months (Cohen and Mercer, 1993b). The inference made from the results of soil-vapor surveys is that samples of soil vapor that contain volatile organic constituents originate at sources zones of sorbed, dissolved, or DNAPL-phase chemicals, and migrated away from those areas in the vadose zone, or from very shallow plumes at the vadose zone-water table interface. Higher concentrations of soil vapors are inferred to be closer to the DNAPL source. The sampling grid spacing is generally reduced until a maximum soil vapor concentration is surrounded by soil gas points of lesser concentrations. The DNAPL source is inferred to be co-located with the maximum soil gas concentration.

Samples of soil vapor may be collected from permanent or removable probes installed at a multiple depths. Samples may be collected actively (using vacuum methods to extract the sample) or passively (using a specially-designed "vapor trap", that relies on vapor diffusion to move vapor into the trap). Samples are collected in suitable containers, or within sorbent cartridges, and can be analyzed using on-site equipment (a portable gas chromatograph) or at off-site analytical facilities. Soil-vapor surveys that use laterally-distributed and vertically-distributed sampling points are most likely to provide information useful for the identification of DNAPLs in the vadose zone (Einberger *et al.*, 1998). However, soil-vapor surveys are unlikely to be capable of identifying the location of dissolved plumes that are more than a few feet below the water table (Pankow and Cherry, 1996).

Geophysical Methods

Surface and borehole geophysical technologies are often used to assist in characterization of the subsurface at contaminated sites. Surface methods most commonly used include ground-penetrating radar (GPR), electromagnetic (EM) conductivity, electrical resistivity, seismic, magnetic, and metal detection. Borehole methods include spontaneous potential, electrical resistivity, natural gamma, nuclear logging (generally gamma-gamma, or "density" logging, and neutron, or "porosity" logging), and well-to-well methods (radar and seismic). Geophysical surveys are conducted to evaluate stratigraphic and hydrogeologic conditions; detect and map electrically conductive contaminants; locate and delineate buried waste containers and utilities; identify optimal locations for test pits, borings, and wells; and provide information useful for interpolation of subsurface conditions among boring locations, thereby reducing the number of wells or borings

needed to adequately characterize a site (Ellefsen *et al.*, 1997; Cohen and Mercer, 1993a; USEPA, 1998a).

DNAPL in the subsurface is usually heterogeneously distributed, and if present at residual saturation, may occur as isolated or discontinuous and irregular bodies at the scale of the pores in the subsurface medium (millimeter scale or less). By contrast, the scale of subsurface features that can be resolved by any geophysical method is on the order of one to several feet (Cohen and Mercer, 1993a; Ellefsen *et al.*, 1997). Consequently, DNAPL in the subsurface is generally a poor target for conventional geophysical methods. Although GPR, EM conductivity, and complex resistivity have been used to infer DNAPL presence at a limited number of sites (Sander, 1994; Finci *et al.*, 1998), direct detection and mapping of non-conductive DNAPL in the subsurface using geophysical techniques is regarded as a limited and emerging technology.

Tracer Methods

Tracer methods use the differences in travel time of injected tracers between points in the subsurface to make inferences regarding particular characteristics of subsurface materials. When used in DNAPL investigations, tracer methods rely on knowledge of the partitioning characteristics of the tracers among the sorbed phase, aqueous (dissolved in water) phase, and DNAPL (dissolved in non-aqueous liquid) phase

(Gauglitz *et al.*, 1999). In a partitioning interwell tracer test, a suite of non-partitioning ("conservative") and partitioning tracers is introduced into a well, and is subsequently extracted from other wells. During the advective transport of the tracers in groundwater through the interwell zone, the partitioning tracers travel more slowly than groundwater (are "retarded") as a consequence of their interaction with any DNAPL that is present, while the conservative tracers are not retarded, and travel at the velocity of moving groundwater. The differences in concentrations of tracers recovered at downgradient wells provides information on the presence of DNAPL in the zone between the wells, which can be used to infer the location and volume of DNAPL present. Tracer methods will be less effective in low- and variable- permeability soils where complete contact between tracers and DNAPL is unlikely. Tracer methods represent a promising new site characterization technology suited for additional evaluation at the pilot scale.

4.4   REMEDIATION OF DNAPL SOURCES

At every site where DNAPL has contaminated the local groundwater, there are two principal components to the problem: a subsurface source of residual or mobile DNAPL, and an associated dissolved-phase plume in groundwater. Most of the contaminant mass is in the source zone, although the plume usually occupies a much larger volume of the

subsurface. The DNAPL phase in the vadose and groundwater zones often contains sufficient chemical mass to cause dissolved plumes to persist for centuries (Pankow and Cherry, 1996). Unless essentially all of the DNAPL mass (more than 99 percent) is removed from the source zone, permanent restoration of all groundwater to drinking-water quality will not be achievable (Freeze and McWhorter, 1997). However, reductions of DNAPL that are less than 99 percent may reduce the size and concentration of the groundwater plume and lessen long-term plume containment and monitoring costs.

In 1993, the National Research Council (NRC, 1993) published a detailed report describing the inherent difficulties in site remediation and made recommendations to the EPA regarding the general failure of pump-and-treat technology and the need for new approaches. Table 4.2 was created by the NRC to categorize sites according to the ease of cleanup. As expected, the presence of DNAPL and heterogeneous soils increases the difficulty of site cleanup.

At sites where all DNAPL residuals are situated above the water table, a high percentage of the DNAPL can generally be removed, although long timeframes may be required for in situ methods in low-permeability soils. Remediation strategies for unsaturated zone contamination can include: removal of contaminated soil by excavation; removal of contaminant mass using *in-situ* extraction methods, preventing groundwater contamination by placing an impermeable cover over the source area.

TABLE 4.2
RELATIVE DIFFICULTY OF CLEANING UP OF CONTAMINATED AQUIFERS AS A FUNCTION OF CONTAMINANT CHEMISTY AND HYDROLOGY

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

[a] Relative difficulty of cleanup, where 1 is easiest and 4 is most difficult. Modified from NRC, 1993.

4-21

At many chlorinated solvent sites, the DNAPL mass causing the groundwater plume may be situated below the water table. DNAPL source zones below the water table greatly complicates site remediation and reduces the potential for significant DNAPL reductions and groundwater cleanup. This section describes several technologies with potential application for reducing DNAPL sources above and below the water table. Table 4.3 provides a summary of several proven and emerging technologies with potential application at DNAPL source areas. A brief description of each technology follows.

TABLE 4.3
TECHNOLOGIES FOR DNAPL REDUCTION

Technology*	Status	Capital Cost	O&M Cost	Application
Excavation and Treatment/Disposal	F	H	L	Upper 40 feet of unsaturated zone. Can be extended below water table with dewatering.
Soil Vapor Extraction (SVE)	F	M	M	Most effective in permeable soils. Limited success in clay soils.
Multi-Phase Extraction	F	H	H	Most effective in permeable soils when DNAPL is in upper 10 feet of the aquifer.
Thermally-Enhanced SVE	F/P	H	H	Thermal Options include Steam Injection, RF Heating, Resistive Heating. Can be applied in unsaturated or saturated zone. Heating can improve air permeability of clay soils.
Enhance Bioremediation	F/P	L	M	Primarily for dissolved contamination. Progress may be limited by DNAPL dissolution rate.
Surfactant/Co-Solvent Enhanced Pump-and-Treat	F/P	L	H	Most effective in permeable soils. Must use P&T to contain the plume.
Traditional Pump-and-Treat	F	H	H	Primarily a containment method. Progress is limited by DNAPL dissolution rate.
In-Situ Oxidation	F/P	M	M	Fenton's reagent and permanganate are commonly used oxidants. Limited to proper geochemical conditions
Air Sparging	F	M	L	Success is limited to more uniform sandy aquifers. Channeling and incomplete treatment are common in heterogeneous soils.

*Adapted from Federal Roundtable Treatment Technologies Screening Matrix
F - Full-Scale, P = Pilot Scale, H = High Cost, M = Medium Cost, L = Low Cost

4.4.1 Excavation and Treatment/Disposal of Soil

If a discrete source zone containing DNAPL can be identified and isolated, it is a candidate for remediation by excavation of contaminated soil. Soil excavation methods are well established; after soil containing DNAPL has been removed from a source zone, it may be properly disposed,

or treated in a number of different ways (e.g., hazardous waste landfills, biodegradation cells ,thermal desorption, chemical oxidation). Soils contaminated with chlorinated solvents generally can not be disposed of in landfills unless they can be shown to be non-toxic based on the Toxic Characteristic Leaching Procedure (TCLP).

Practical considerations regarding equipment limitations and sidewall stability can restrict the depth of excavation to a maximum of about 25 to 30 feet in a single lift. If greater depth is required to remove all contaminated soil in the source zone, excavation can be accomplished using a series of progressively-deeper lifts, accessed by ramps. This techniques can extend the maximum depth of excavation in unconsolidated soil to over 40 feet. However, the unit cost of soil excavation increases rapidly with increasing depth of excavation. Excavation may need to be timed to correspond to the "dry season" to prevent weather delays. Excavation cannot be extended below the water table without implementation of methods to control or prevent the movement of groundwater into the excavation. These methods are expensive and can include placement of caissons or driven sheet piling and dewatering. Excavation has a large capital cost but no O&M cost and may have the greatest probability of achieving over 99 percent DNAPL removal at many smaller sites with contamination restricted to the upper 40 feet of the soil. The excavation option should

be seriously considered if the site is not covered with high-value buildings or mission critical facilities.

4.4.2 Soil Vapor Extraction

Soil vapor extraction (SVE) technologies were specifically developed to remove volatile contaminants from unsaturated soils. SVE involves the application of a vacuum to slotted pipes in the vadose zone to draw air through contaminated material. The air flow volatilizes contaminants from the DNAPL, soil, and aqueous phases. The ultimate goal of most SVE operations at DNAPL sites is to remove sufficient contaminant mass so that water percolating through the vadose zone will no longer dissolve contaminants and carry them to the water table at concentrations above regulatory limits. SVE is capable of achieving this goal in relatively homogeneous, coarse-grained material where air can rapidly move through the contaminant zone. However, SVE is not as effective in mobilizing contaminants from the capillary fringe or in fine-grained or very moist strata. Slow diffusion of contaminants from residual DNAPL entrapped in these zones will limit restoration rates. Hydraulic and pnuematic formation fracturing are also being examined to improve the performance of SVE in low-permeability materials, however, rarely are enough fractures created to impact long-term contaminant recovery.

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SVE Optimization – The effectiveness of most SVE systems can be improved by one or more of the following optimization methods:

- Careful characterization of the vertical and horizontal extent of contamination will result in the placement (or replacement) of extraction wells and screened intervals in positions which maximize VOC removal and minimize dilution with clean soil gas.

- For existing SVE systems, downwell logging devices and additional vapor monitoring points can be used to determine the position of remaining DNAPLs and how to design extraction well modifications that can maximize VOC removal.

- Performing shut-down tests for 30-60 days each year to allow the soil gas to equilibrate with DNAPL residuals. Evaluation of equilibrium rebound at various extraction wells and discrete monitoring points provides valuable insights into areas or depth intervals at the site which are clean and those where diffusion is limiting VOC removal.

Additional details on SVE optimization can be found in the recently published Air Force Remedial Process Optimization Handbook (Available at **AFCEE website www.brooks.af.mil\er\toolbox.htm**)

4.4.3 Multi-phase Extraction

Multi-phase extraction is a broad category of remediation methods which combine combinations of groundwater pumping, DNAPL removal, and SVE using a single well to extract both liquid and vapor. At some sites, the depth at which SVE can be applied is increased by lowering the water table with groundwater extraction. At sites with mobile DNAPL, a low rate of groundwater pumping can be used to lower the water table while SVE is applied to enhance liquid migration toward the well and to remove volatiles from the expanded unsaturated zone. Multi-phase extraction is most applicable at sites with permeable soils, where the majority of the DNAPL is trapped within the upper 10 feet of the aquifer. Multi-phase extraction will be less successful in low-permeability soils because dewatering at the well may not result in a significant reduction in the water saturation level of the soil. In this case, the air permeability of the soil will not be improved by simple dewatering (USACOE, 1999)

4.4.4 Thermal Enhancements to SVE

Several in situ heating methods are being tested as means of reducing soil moisture and enhancing SVE effectiveness by extending SVE influence into shallow aquifers. In situ heating technologies have the potential to increase the permeability of silt and clay soils and increase the removal efficiency of SVE. However, heating technologies have limited application for DNAPL zones below the water table. Below the water table, groundwater and DNAPL are in close proximity. The heat capacity of water is much greater than the heat capacity of most

4-26

chemicals. Much of the heat introduced to the subsurface is absorbed by ambient groundwater, and is not available to volatilize DNAPL chemicals. The use of thermal heating methods in layered soils must be carefully monitored to ensure that heating does not result in undesireable lateral migration of contaminants outside of the influence of the SVE collection system.

Steam Injection - Steam injection combined with vacuum extraction can be used to remove volatile DNAPL from the vadose and shallow groundwater zones. When high pressure "dry" steam is injected into contaminated soil, volatile chemicals with boiling points lower than that of water are vaporized. SVE wells are then used to remove the resulting vapor. This process has been successfully applied at smaller sites with relatively uniform permeable soils but may not be as effective in layered soils. (EPA, 1997c)

Resistive Heating - Resistive heating is another emerging technology for increasing soil temperatures and volatilizing DNAPL residuals. The most promising of the resistive heating technologies is a six-phase system which uses metal and graphite electrodes to set up an alternating electrical current in the soil (USEPA, 1999b). This method is limited to sites with soil moisture levels above 10 percent, because water is required to conduct the electricity and to create resistive heating. Resistive heating can reach a maximum temperature of 100° C which boils away the groundwater and can volatilize

residual DNAPLs. Once volatilized, VOCs are removed by a concurrently operating SVE system. Six-phase heating is applicable for DNAPL residuals above or below the water table and will work best in low-permeability soils where the rate of groundwater movement is slow (groundwater velocities > 1 ft/day will cool the saturated zone faster than the electricity can heat it up).

Radio-Frequency Heating - This process uses electrodes placed in the subsurface to deliver radio-frequency energy which excite molecular motion and induce heating (much in the same way that microwave ovens heat food). Radio-frequency heating has the potential to heat soil to temperatures in excess of 200° C and can be used to volatilize higher boiling point compounds such as mixtures of jet fuel and solvents. SVE wells are then used to remove the resulting vapor (EPA, 1997c).

4.4.5 Enhanced Biodegradation

Combinations of anaerobic and aerobic biological degradation are known to completely degrade chlorinated solvents to harmless by products. Although enhanced biodegradation has been primarily applied to the dissolved phase of chlorinated solvent plumes, new biological methods of containing and destroying DNAPL residuals are emerging in full-scale applications. The most promising biotechnology for DNAPL removal is enhanced reductive dechlorination. Under highly anaerobic

conditions, chlorinated solvents such as PCE, TCE and DCE are utilized as electron acceptors by subsurface bacteria. In this process, chlorine atoms are sequentially removed from the chlorinated solvent molecule. A full review of these microbial processes is beyond the scope of this document. The reader is referred to USEPA (1998a) and Wiedemeier *et al.* (1999) for a more complete discussion.

This process can be enhanced by the addition of inert soluble organics which supply a surplus of electrons. Vegetable oil and other food-grade organics are typically injected into the soil volume containing DNAPL residuals and then the site is monitored to track the conversion of "parent compounds" into ethene, chloride ions and water (Boulicault, 2000). One potential advantage of the vegetable oil addition is that the oil also acts as a co-solvent which absorbs DNAPL residual out of the soil/water matrix. Enhanced biodegradation may provide an inexpensive method of containing dissolved contamination and slowly destroying DNAPL source areas. As with any in situ technology, its success depends upon the complete contact between DNAPL residuals and the injected solution. Additional studies are required to determine the long-term cost-effectiveness of this technology.

4.4.6 Traditional Pumping Methods

Large pools of DNAPL have been located in the subsurface at a few chlorinated solvent DNAPL sites. Some pools are large enough to allow pumping of mobile DNAPL from wells screened within the pool. Because DNAPL extraction will leave significant residual DNAPL mass in the source zone, traditional pumping methods are generally regarded as ineffective.

4.4.7 Surfactant/Co-solvent Enhanced Pump-and-Treat

The failure of pump-and-treat remediation of DNAPL source zones (National Research Council, 1994) and the impracticality of excavation in most situations has lead to the development of *in-situ* technologies to enhance the performance of pump-and-treat systems. These include methods that circulate surfactants or co-solvents through source zones containing mobile or residual DNAPL. Flow of fluids is from injection wells to extraction wells where water and entrained liquids (dissolved DNAPL, solvent, surfactant) are extracted from the groundwater system and treated aboveground. Surfactants and co-solvents (e.g., alcohol) are used to increase the effective solubility of DNAPL components by reducing interfacial tension or increasing miscibility so that circulation of the water/chemical mixture through the DNAPL source zone will remove contaminant mass more rapidly that conventional pump-and-treat (Pankow and Cherry, 1996; Sabatini *et al.*, 1996). The chemical additive (surfactant or co-solvent) is usually recycled from the effluent stream, to reduce costs.

As with other technologies, geologic heterogeneities and the distribution and properties of DNAPL may hinder or prevent complete restoration of groundwater quality. The surfactant or alcohol solution must be flushed through the entire volume where DNAPL is suspected to be present. For these technologies to remove DNAPL effectively, the flushing fluid must come into direct contact with DNAPL to cause mobilization, and then carry contaminant mass to the extraction wells. The existence of geologic heterogeneities and residual DNAPL in low-permeability zones will contribute to inadequate contact of flushing fluids and DNAPL.

Introduction of surfactants or co-solvents causes enhanced mobility of the DNAPL phase, with potential adverse effects on groundwater quality. Surfactants tend to mobilize the fine particles in the soil which can lead to clogging of pore spaces and reduced permeability. Contaminated groundwater that contains DNAPL chemicals and surfactants or co-solvents must be successfully extracted. To minimize the potential risks associated with remobilization, these technologies should be considered at sites where deeper penetration of DNAPL is unlikely (e.g., groundwater zones underlain by an impermeable stratum), or where deeper aquifers do not exist.

4.4.8 In-Situ Oxidation

The injection of strong oxidants into the subsurface has the potential to destroy DNAPLs in place. Several oxidants have been extensively pilot tested and are now available for commercial application. Fenton's reagent uses a solution of ferrous iron and hydrogen peroxide to chemically oxidize chlorinated solvents. One drawback is that this method requires that the soil be brought to a pH of 2-4 before application (Watts, 1990). Permanganate (MnO_4) solutions are also available for injection into DNAPL source areas.. Because large quantities of oxidants are required application of these solutions can be very expensive at large sites. As with any in situ technology, its success depends upon the complete contact between DNAPL residuals and the injected solution. In-situ oxidation will be most effective and feasible at small sandy sites. The addition of acids and oxidants can have negative impacts on anaerobic biodegradation processes which must be weighed against the advantages of DNAPL destruction.

4.4.9 Air Sparging

Air sparging is generally not effective for DNAPL treatment due to the limited contact which occurs between injected air and DNAPL residuals. The injection of oxygen (in air) in the source area can also shut down any anaerobic biodegradation processes that may be occurring. Air sparging is best applied for the removal of dissolved VOCs from more uniform and

permeable soils. This technology is discussed in more detail in Section 5.4.5.

4.4.10 Conclusions on Source Removal

The task of removing or destroying sufficient contaminant mass to achieve the complete restoration of a DNAPL source zone is formidable. The petroleum industry has spent billions of dollars on research to enhance the recovery of petroleum (a light non-aqueous phase liquid) from oil fields. Oil companies consider a removal of 40 percent of the formation NAPL to be an exceptional success. In contrast, if groundwater is to be restored to drinking-water quality, at least 99 percent of the DNAPL source must be remediated. The limitations on identification, removal, or control of DNAPL source represent immense obstacles for complete restoration of groundwater.

Groundwater restoration is much different from plume containment. Complete restoration of groundwater requires removal of the source(s) of chemicals from the subsurface, as well as removal of dissolved-phase chemicals to a degree sufficient to allow the original beneficial use of the groundwater. As a consequence of the difficulties of identifying and remediating residual DNAPL, continued dissolution and migration of chemicals from a residual source may necessitate perpetual hydraulic containment at some sites.

4.5 TECHNICAL IMPRACTICABILITY OF DNAPL REMEDIATION

The properties of chlorinated solvents and the characteristics of DNAPL migration and persistence in the subsurface environment suggest that in many circumstances, total restoration of groundwater to drinking-water standards may not be technically or economically feasible. There are provisions in federal and state regulations for exceptions to the application of drinking-water standards as cleanup goals, with establishment of risk-based or other alternative cleanup levels. In particular, non-attainability of drinking-water standards in groundwater can be demonstrated under USEPA's (1993c) technical impracticability (TI) waiver protocol. Applicable and relevant regulations and requirements (ARARs) that might otherwise be used to establish cleanup goals may be waived by USEPA for any six of the reasons specified in CERCLA 121[d][4], including technical impracticability from an engineering perspective.

The TI evaluation must include the following components based on site-specific information and analyses (USEPA, 1993c):

- A proposal of specific ARARs or media cleanup standards for which TI determinations are sought;

- Designation of the spatial area over which the TI waiver will apply;

4-30

- A current conceptual site model that describes contamination sources, site geology and hydrology, and chemical migration and fate processes.

- An evaluation of the restoration potential of the site, including data and analyses that support assertions that attainment of ARARs or media cleanup standards is technically impractical from an engineering perspective. At a minimum, this generally should include:

  - A demonstration that the sources have been identified and have been or will be removed and contained to the greatest extent possible;

  - An analysis of performance of any ongoing or completed remedial action;

  - Predictive analysis of the time frames to attain required cleanup levels using available technologies; and

  - A demonstration that no other remedial technologies (conventional or innovative) could reliably, logically, or feasibly attain the cleanup leaves at the site within a reasonable time frame.

- Estimate of cost of the existing or proposed remedy options, including construction and O&M costs.

- Any additional information or analyses that USEPA deems necessary for the TI evaluation.

The process of applying for a TI waiver, and providing the necessary documentation, is expensive and time consuming. Nevertheless, the relative costs and benefits involved in seeking a TI waiver often compare favorably with the relative costs and benefits associated with installing and maintaining a large pump-and-treat system. As a consequence of the significant difficulties in remediating DNAPL below the water table, this category of DNAPL site should be regarded as a potential candidates for a TI waiver. In fact, the presence of DNAPL at a site is cited in the USEPA (1993b) guidance as a mitigating factor favoring adoption of alternate cleanup goals and/or a TI waiver.

Adoption of a TI waiver will generally require implementation of land-use controls and other institutional measures, to ensure that groundwater is not used as a potable water supply within the area designated in the TI waiver. Effective, long-term land-use planning and zoning are needed to ensure that future remedial actions are compatible with future uses of the land. Institutional controls are considered to be an important complement to other treatment technologies, and in most cases are critical to the successful implementation of a remedial action. Risks from exposure to groundwater contamination can be reduced or eliminated by controlling the migration of the dissolved-phase plume. Section 5 discusses how natural attenuation and groundwater pumping can be used to minimize plume size and migration.

SECTION 5

PLUME REMEDIATION

This section will assist you in:

- Using state-of-the-art site characterization tools to better understand the three dimensional dynamics of the chlorinated solvent plume;

- Assessing if a plume is stable or has the potential to migrate outside of the industrial/airfield area or beyond Air Force control;

- Maximizing the use of monitored natural attenuation (MNA) for plume containment and/or as a final remedy; and

- Evaluating proven and emerging technologies that can be used when MNA is inappropriate.

5.1 OVERVIEW

This section will describe several options for both managing and reducing the risks associated with contaminated groundwater plumes that have originated from chlorinated solvent spills. Due to the increased acceptance of natural attenuation as a remedy for groundwater contamination, many options for site remediation and closure are available today that

were not possible five years ago. This section discusses how to determine if a plume is stable or migrating, and how to assess the natural attenuation potential of dissolved plume. For sites where plume migration threatens public drinking water supplies, alternative methods of plume containment and remediation are described including methods of optimizing existing pump and treat systems (Section 6).

5.2 ASSESSING PLUME MIGRATION POTENTIAL

Once the source of contamination has been identified, the next step in site characterization is generally a subsurface evaluation of the extent of plume migration.

At industrial/airfield sites, the potential for off-base contaminant migration is a critical concern. Stable and attenuating plumes may not require active remediation and can often be managed with long-term monitoring. Migrating plumes, particularly at sites where downgradient receptors are contacting groundwater, will require containment or remediation. Therefore, the ability to accurately characterize the plume and predict the future migration of contaminated groundwater is very important to the overall

remediation strategy. There are other references describing general plume characterization methods (USEPA, 1988). This subsection will describe several new tools that are available to more accurately define dissolved contaminant distribution, methods of assessing natural attenuation, and modeling tools that are available to estimate plume migration potential.

5.2.1 Plume Characterization Improvements

Site managers should be aware of several new site investigation and sampling tools that can greatly improve the three-dimensional (3-D) characterization of chlorinated solvent plumes. Many plumes are defined in two dimensions, but lack an accurate vertical profile of contaminant migration. Sites that have been previously characterized using standard, long-screen monitoring wells often provide only a two-dimensional approximation of plume geometry and movement. Several tools have been developed to better define the vertical distribution and movement of dissolved contaminants.

Discrete Interval Sampling Probes - Sampling tools that can collect a groundwater sample from a discrete vertical interval are now available from a variety of vendors (e.g. Hydropunch®, Geoprobe®). These tools are generally advanced into the aquifer and a groundwater sample removed from a discrete interval. Individual samples can be collected at multiple depths at each location, analyzed on

site with a portable gas chromatograph or photoionization detector (PID), and the results used to guide additional investigation and to create a 3-D map of subsurface contamination. For example, the new Geoprobe membrane interface probe system (MIPs) and Simul-probe® system allow for a continuous logging of relative VOC concentrations as the probe is advanced through the unsaturated and saturated zone. The EPA Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Groundwater (EPA, 1998) provides additional details on discrete sampling probes and borehole flowmeter techniques.

In-Well Discrete Samplers – Discrete interval groundwater samples can also be collected inside of existing groundwater monitoring wells. A variety of down-well sampling devices are available including the recently developed diffusion samplers (Vrobleski and Campbell, 2000). Diffusion samplers provide an additional advantage because multiple samplers can be left in each well for weeks or months to evaluate the steady-state contaminant concentrations at varying depths. A major advantage of diffusion samplers is the low cost of sample acquisition when compared to traditional purging and sampling techniques. However, the use of diffusion samplers for vertical profiling of contamination can lead to erroneous conclusions when significant vertical flow is occurring within the well. In this case, the contaminants

entering the diffusion sampler may be entering the well above or below the sampler depth.

Borehole Flowmeters – The depths of greatest hydraulic conductivity generally define the depths where contaminants are migrating the fastest away from the source area. Borehole flowmeters have been developed to assist hydrogeologist in understanding the vertical variations in groundwater flow. Flowmeter tests are performed in existing monitoring wells or long-screened wells that are specially constructed for flowmeter testing (wells without artificial sand packs are preferred). Flowmeters are lowered to the bottom of the well and then raised in 1-5 feet increments. At each depth interval, the flowmeter measures the ambient flow entering the well. Following the ambient flow test, a small pump is placed in the upper part of the well, and water is pumped from the well as the flowmeter is again moved up the well in increments. Flowmeters using small impellers or more sensitive electromagnetic sensors transmit flow data to the surface where a computer prints out a paper log of flow versus depth. These tools allow groundwater flow to be more precisely modeled in 3-D so that plume migration can be predicted with greater accuracy (Molz, et.al., 1994).

5.2.2 Documenting Natural Attenuation

Another important aspect of plume characterization is a thorough documentation of the potential for natural attenuation to limit plume migration and to reduce toxicity. Natural attenuation refers to the decrease in the concentration or mass of groundwater contaminants by natural physical, chemical, and biological processes. More recently, the term "monitored natural attenuation" (MNA) has been used to refer to the use of natural attenuation processes to aid in overall site remediation. The USEPA (1999a) Office of Solid Waste and Emergency Response (OSWER) defines MNA as:

> *…the reliance on natural attenuation processes (within the context of a carefully controlled and monitored cleanup approach) to achieve site-specific remediation objectives within a time frame that is reasonable compared to that offered by other more active methods. The "natural attenuation processes" that are at work in such a remediation approach include a variety of physical, chemical, or biological processes that, under favorable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume, or concentration of contaminants in soil and groundwater. These* in-situ *processes include biodegradation; dispersion; dilution; sorption; volatilization; radioactive decay; and chemical or biological stabilization, transformation, or destruction of contaminants.*

It should be noted that, when relying on natural attenuation processes for site remediation, the USEPA prefers those processes that degrade or destroy contaminants and generally expects that MNA will only be appropriate for sites that have a low potential for contaminant migration.

Scientific understanding of the microbial processes governing chlorinated aliphatic hydrocarbon (CAH) degradation has significantly increased in recent years. Until 1994, the microbial degradation of CAHs was thought to be primarily a cometabolic process (Holliger and Schumacher, 1994). Today, reductive dechlorination is known to be the primary process for CAH biodegradation. In general, reductive dechlorination occurs in anaerobic, reducing environments by sequential dechlorination from the parent CAH (e.g., tetrachloroethene [PCE]) to successively less-chlorinated daughter products (e.g., trichloroethene [TCE], dichloroethene [DCE], vinyl chloride [VC], and ethene) (Figure 5.1). More recently, scientists have also discovered that less-chlorinated CAHs (e.g., DCE and VC) can be degraded aerobically (Figure 5.2) through use as an electron donor

(Bradley and Chapelle, 1998). A full description of these microbial processes is beyond the scope of this document. The reader is referred to USEPA (1998) and Wiedemeier *et al*. (1999) for a more complete discussion.

The procedures for documenting natural attenuation of dissolved CAHs were formalized in the *Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water* (USEPA, 1998) which was based on natural attenuation demonstrations funded by AFCEE. This document describes several lines of evidence that can be used to estimate natural attenuation of CAHs, including:

1. Historical groundwater and/or soil chemistry data that demonstrate a clear and meaningful trend of decreasing contaminant mass and/or concentration over time at appropriate monitoring or sampling points.

2. Chemical and geochemical data can be used to demonstrate indirectly the type(s) of natural attenuation processes active at the site.

3. A comparison of actual contaminant plume migration to potential migration based on known groundwater velocities at the site.

4. Data from field or microcosm studies (conducted in or with actual contaminated site media) which directly demonstrate the occurrence of natural bacteria and their ability to degrade the contaminants of concern.

5.2.2.1 Historical Chemical Data

Historical chemical data are obtained by sampling the same location on multiple occasions throughout time. Historical groundwater chemistry data do not prove that contaminants are being destroyed, because reduction in contaminant concentration could be the result of non-destructive attenuation mechanisms (e.g., advection, dispersion, dilution from recharge, sorption, or volatilization).

FIGURE 5.1

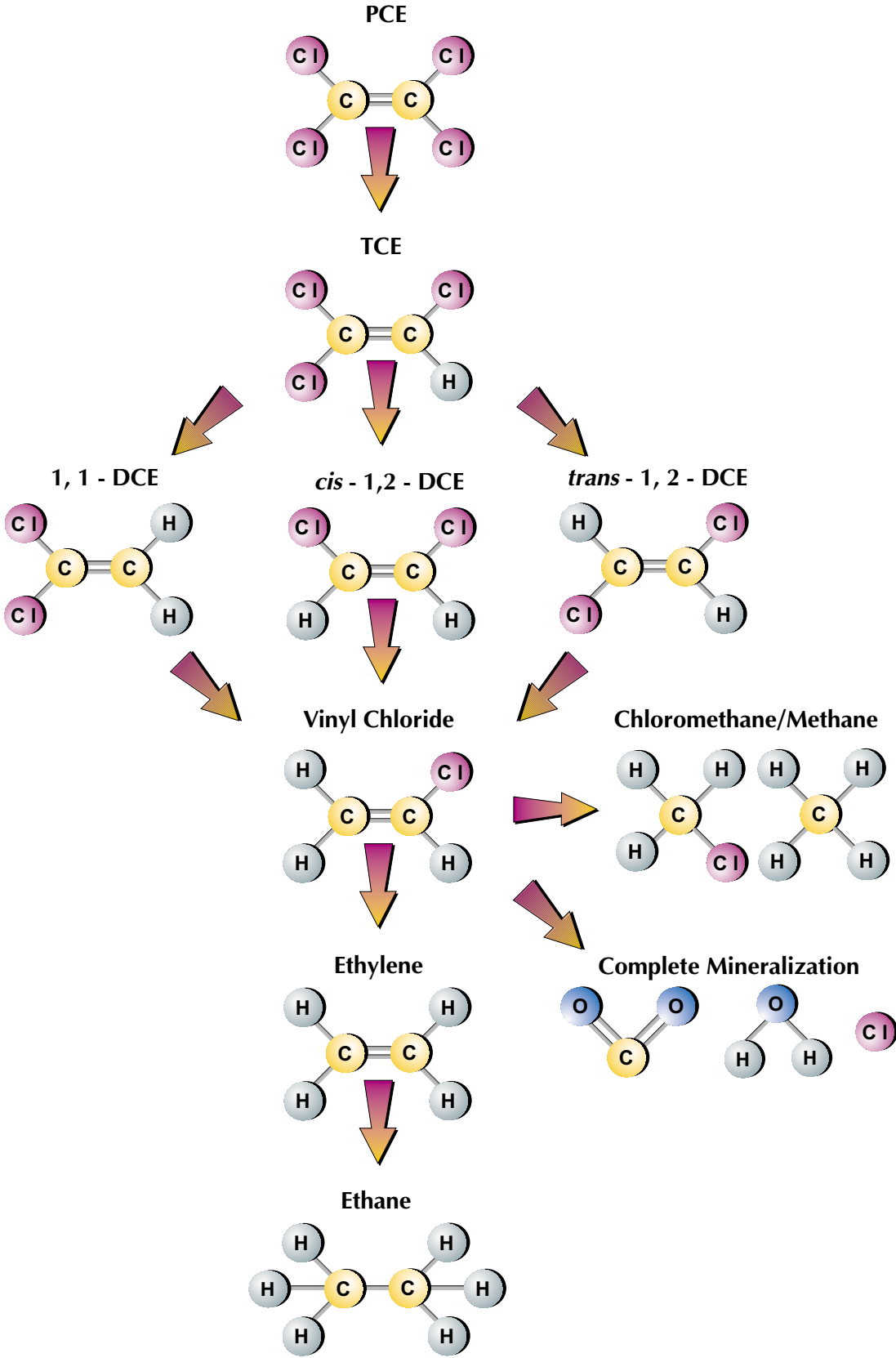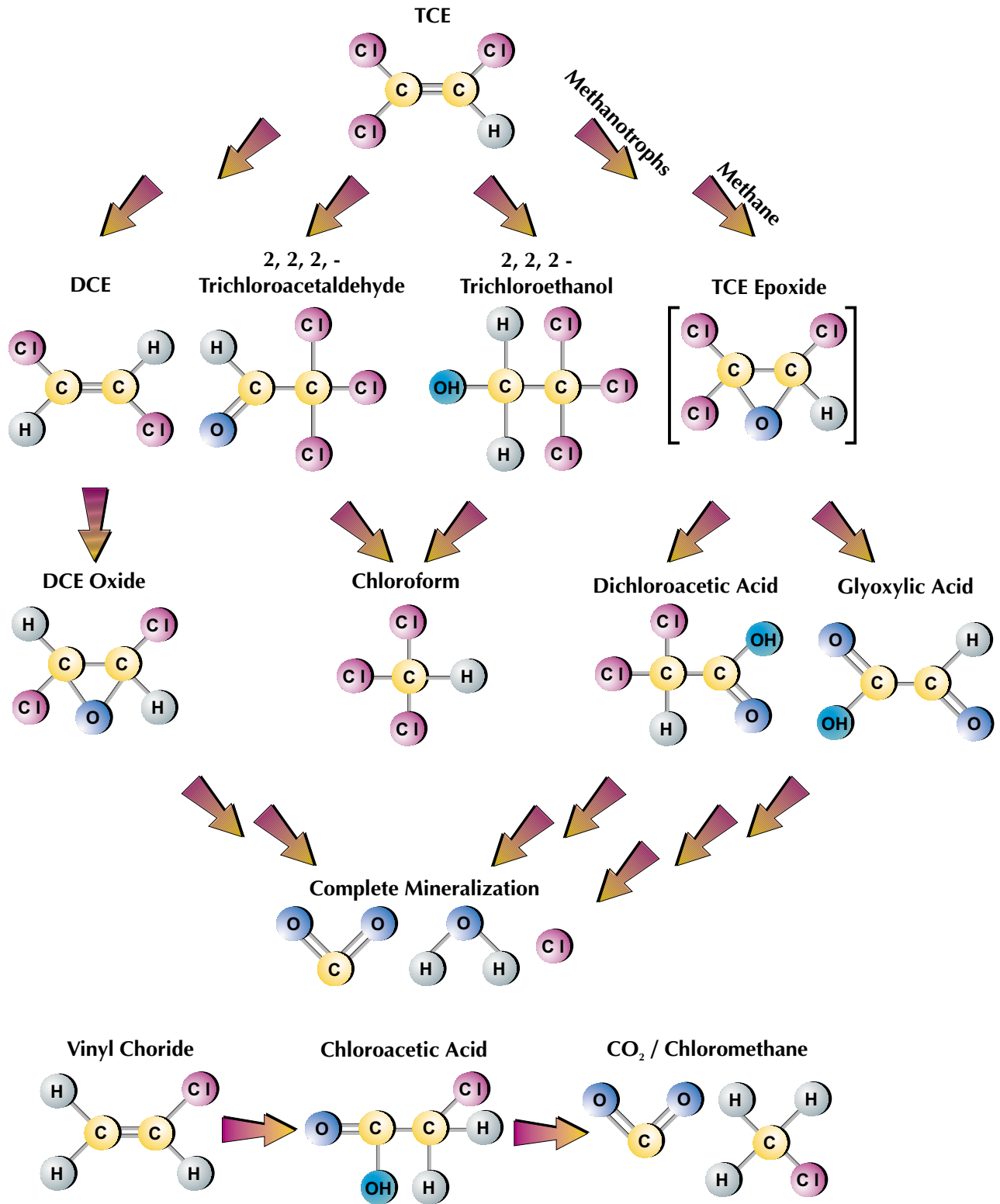**Anaerobic Reductive Dehalogenation**

FIGURE 5.2

Aerobic Oxidation

However, decreasing concentration trends are an indication that biodegradation may be occurring.

The *AFCEE Long-Term Monitoring Decision Support System (LTMDSS)* is a user-friendly software package for designing an efficient long-term monitoring well network for groundwater plumes. This software package can be applied both to natural attenuation situations and to active pumping systems. Using the Mann-Kendall non-parametric test, the LTMDSS evaluates monitoring data from individual wells to determine if plume concentrations are increasing, stable or decreasing. This data can be used to determine overall plume stability and to determine the relative contribution of each monitoring well to the plume monitoring strategy. This software tool will soon be available on the AFCEE website.

5.2.2.2 Chemical and Geochemical Trends

In order to evaluate MNA at most sites, the investigator will have to determine whether contaminant mass is being destroyed. A review of historical chemical and geochemical trends will often indicate that contaminant mass is bring destroyed, not just being diluted or sorbed to the aquifer matrix. Indicators of biodegradation include:

- Depletion of electron acceptors and donors;

- Increasing metabolic byproduct concentrations;

- Decreasing parent compound (TCE, PCE) concentrations; and

- Increasing daughter product (1,2- DCE, VC) concentrations.

5.2.2.3 Comparison of Plume Migration Velocity To Actual Migration Distance

In the absence of biodegradation, the dissolved contaminant migration velocity can be approximated by dividing the average advective groundwater velocity (V_g) by the retardation coefficient (R) for the contaminant of concern. The advective groundwater velocity is defined as the hydraulic conductivity (K) times the hydraulic gradient (dH/dL) divided by the effective porosity (n_e).

$$Vg = \left(\frac{K}{n_e} \right) \left(\frac{dH}{dL} \right)$$

The retardation coefficient is a measure of the degree of retardation of dissolved organic chemical movement through the aquifer. Retardation coefficients are calculated using the following formula:

$$R = 1 + (K_d \rho_b / n)$$

where

$K_d = (K_{oc})(f_{oc})$

K_{oc} = Organic Carbon Partition Coefficient

f_{oc} = Fraction Organic Carbon

ρ_b = Soil Bulk Density of Aquifer Matrix

n = Porosity

Using the calculated contaminant migration velocity, the distance that the dissolved contaminant should have migrated (in the absence of natural attenuation) since the release can be estimated. (The BIOCHLOR model automatically performs this calculation when basic input parameters are known.) This calculated distance will be conservatively low because it does not account for the effects of dispersion, which tend to cause the plume to be elongated in the direction of flow. If the actual contaminant migration distance is substantially less than the calculated theoretical migration distance, then it can be inferred that natural attenuation (especially biodegradation) is occurring and limiting plume migration.

5.2.2.4 Field or Laboratory Microcosm Studies

Microcosm studies are used to show that the microorganisms necessary for biodegradation are present and to help quantify rates of biodegradation. Because microcosm studies are time consuming and expensive, they should be undertaken only at sites where there is considerable uncertainty concerning the biodegradation of contaminants. The results of a microcosm study are strongly influenced by the nature of the geological material submitted for study, the physical properties of the microcosm, the sampling strategy, and the duration of the study. Biodegradation rate constants determined by microcosm studies often are much higher than those observed in the field. Microcosms

are most appropriate as indicators of the potential for natural bioremediation, and to prove that losses are biological, but it is generally inappropriate to use microcosm studies to estimate field biodegradation rates. The preferable method of estimating contaminant biodegradation rate-constants is from field data.

5.2.2.5 Natural Attenuation Screening Process

USEPA (1998a) presents a worksheet to assess the potential for natural biodegradation of chlorinated compounds at a site. A copy of the worksheet is provided as Appendix B. The screening process presented in the worksheet is oriented toward the anaerobic process of reductive dehalogenation, and is designed to recognize geochemical environments where this process is plausible. The objective of the screening process is to allow the investigator to determine if natural attenuation of PCE, TCE, DCE, TCA, or chlorobenzenes is likely to be a viable remedial alternative before additional time and money are expended on a more extensive natural attenuation treatability study (TS).

5.2.3 Predicting Contaminant Migration and Persistence

Contaminant persistence can be estimated by calculating site-specific decay rates and using these rates in conjunction with an analytical or numerical models to predict the future fate and transport of contaminants. These methods are summarized in the following subsections.

5.2.3.2 Estimation of Field-Biodegradation Rates

An estimation of the rates of chemical degradation is necessary to properly evaluate the ultimate fate of chlorinated solvents dissolved in groundwater. Use of first-order kinetics can be appropriate to estimate field-scale biodegradation rates where the rate of biodegradation is assumed to be controlled solely by the concentration of the contaminant. For reductive dechlorination of chlorinated solvents, first-order rates are not always an accurate representation because the degradation of chlorinated solvents depends on the concentrations of electron donors (e.g., fuel hydrocarbons or native organic material) as well as electron acceptors (including competing inorganic acceptors and chlorinated solvents) (Moutoux *et al.*, 1996). Second-order rates would allow more accurate calculations; however, at this time, methods of evaluating or applying second-order rate constants are not well developed. Therefore, first-order rates are generally used to estimate contaminant degradation.

It may be advantageous to calculate two different first order rates for the source area and the downgradient dissolved plume. At source areas containing significant petroleum hydrocarbons (or where organic substrate has been added) the rates of source degradation may be significantly higher than the rates of dissolved contaminant degradation. However,

due to the higher contaminant concentrations in the source area, the time required for plume remediation is often a function of the source area decay rate. The decay rate calculated for the dissolved plume will determine how far the plume will migrate before it stabilizes. Both rates are necessary for evaluating remedial options.

In order to calculate first-order field biodegradation rate constants, the apparent degradation rate must be normalized for the effects of dilution, sorption, and volatilization. Several methods have been derived to estimate first-order biodegradation rates, including:

- Use of a biologically recalcitrant compound present in the groundwater, which acts as a conservative tracer (AFCEE, 1995 and USEPA, 1998a). For many chlorinated solvent plumes, chloride that is released to the groundwater during dechlorination reactions can be used as a tracer if background levels of chloride are low.

- Use of the one-dimensional (1-D), steady-state analytical solution to the advection-dispersion equation presented by Bear (1979) (Buscheck & Alcantar, 1995). The Buscheck and Alcantar (1995) method assumes that the plume is stable and yields a combined destructive attenuation rate that account for both abiotic decay and biological (aerobic and anaerobic) decay. For an expanding plume, this first-order approximation can be

viewed as an upper bound on the destructive attenuation rate. This method requires that chemical suites and concentrations in groundwater at two or more monitoring points be related by having a common source of chemicals migrating along a single flow path between points. Groundwater flow velocity is assumed to be well-defined and constant (i.e., chemical concentrations are related by distance and time).

- Computation of field-scale reductive dechlorination rates using the method of Moutoux *et al.* (1996). This method provides an average total dechlorination rate for all dechlorination steps, including the rapid TCE-to-DCE rate and the slower VC-to-ethene rate. Because abiotic reactions and aerobic biodegradation reactions that involve CAHs in the role of an electron donor are not included in this rate, the rate should be considered a lower bound on the destructive attenuation rate. Consequently, these rates are often an order of magnitude lower than the rates computed for the same site using the Buscheck and Alcantar (1995) or conservative tracer method. Again, groundwater flow velocity is assumed to be well-defined and constant.

- A fourth method of computing chemical degradation rates is described in Parsons ES (1999). This method is applicable for sites with flat or changing hydraulic gradients and groundwater velocities of less than 5 feet per year. In this case, first-order degradation rate constants (see box below) can be estimated using the relative concentrations of TCE and daughter products detected in groundwater samples from several individual monitoring points throughout their monitoring history. Simplifying assumptions must be made to account for the time of chemical introduction, initial mass of chemical introduced, and chemical mass attenuation resulting from processes other than degradation.

One of the most commonly used expressions for representing the biodegradation of an organic compound involves the use of an exponential decay relationship (Wiedemeier *et al.*, 1999):

$$C = C_0 e^{-kt}$$

where   C = biodegraded concentration of the chemical
C_0 = starting concentration
k = rate of decrease of the chemical (units of 1/time).

Exponential, best-fit, first-order trend lines can be fitted to time-versus-concentration data for a specific sampling point (e.g., monitoring well) using common spreadsheet software such as Microsoft Excel®. The estimated time for contaminant concentrations to decrease to below target cleanup levels can then be calculated using the equations for the best-fit lines derived by the software program.

5.2.3.3 Model Selection

Equations that describe groundwater flow and contaminant transport can be solved analytically or numerically. The type of model selected to simulate site conditions will depend on the results of data review and conceptual model development. A balance between simplifying assumptions and actual subsurface conditions must be reached to allow successful and practical simulation of contaminant fate and transport.

Three types of criteria can be used to select an appropriate model code or analytical solution. First, the modeling objectives should be considered (i.e., what is the ultimate purpose of the modeling effort?). If only approximate results are needed, an analytical method or a very simple numerical code may be selected. The more specific and detailed the results must be, the more likely it is that a sophisticated numerical model code will be required. Second, the ability of potential models to adequately represent the dominant flow and transport processes at the site should be considered. Finally, if a model meets the objectives and technical criteria, the scientific and regulatory acceptance of the model should be considered. These criteria can be summarized into three key questions:

- Can the model adequately simulate site conditions including natural attenuation?

- Can the model satisfy the objectives of the study? For detailed studies this could include: predictions of cleanup time, mass removal vs time, plume concentrations vs time, and plume migration under various natural attenuation and engineered remediation alternatives.

- Is the model verified and peer-reviewed, well documented, and field-tested?

The most appropriate choice is often a compromise between the first two considerations, because study objectives typically include time limits and financial constraints. AFCEE has developed a chart to facilitate selection of a model code that meets the minimum requirements for a given situation. The chart can be downloaded from AFCEE's website (www.AFCEE.brooks.af.mil/er/erproducts/ (hydrology)).

Analytical Models

Analytical models are simple and relatively easy to use, and can often provide a good order-of-magnitude approximation of solute transport in relatively simple hydrogeologic settings. Analytical models may be appropriate to use as preliminary, screening-level models or where there is not a sufficient amount of site characterization data available to justify the use of a more sophisticated numerical model. Analytical models can be used to:

- Estimate the migration distance of contaminants at a site over time;

- Predict exposure-point concentrations over time at varying distances from the source; and

- Assess whether natural attenuation may be a feasible remediation strategy at a given site.

Given the widespread acceptance of the effectiveness of natural attenuation for fuel hydrocarbons dissolved in groundwater, simple analytical models such as BIOSCREEN are now accepted by most regulatory agencies for predicting the migration and persistence of BTEX contamination. The analytical model BIOCHLOR (Aziz *et al.*, 1999) may increase the reliability (and therefore the regulatory acceptance) of analytical model results for CAH-contaminated sites. BIOCHLOR is a public domain screening-level natural attenuation model for chlorinated solvent plumes that was recently developed for AFCEE. The model can simulate the reductive dechlorination of common chlorinated solvents and can be downloaded from AFCEE's website.

Other widely-used analytical models include AT123D® (Yeh, 1993) and Solute® (Beljin, 1991). AT123D® is based on an analytical solution for transient one-, two-, or three-dimensional transport in a homogeneous isotropic aquifer with uniform regional flow. The code allows for retardation, dispersion, and first-order decay, with different source configurations and boundary conditions. Solute® is a menu-driven set of five programs that provide the user with nine different types of analytical solute transport models. The nine models include one-, two-, and three-dimensional solutions with differing boundary conditions and options for retardation and first-order decay.

Numerical Models

Because of the inherent complexity of CAH biodegradation, use of a 2- or 3-D numerical model may sometimes be warranted. As with analytical models, numerical models require the user to make some simplifying assumptions about the solute transport system. However, fewer simplifying assumptions must be made, so numerical models can simulate more complex systems. For this reason, numerical models can be used to more accurately simulate complex hydrogeologic systems or contaminant transport affected by complex sets of reactions. Heterogeneous and anisotropic hydrogeologic systems can be more accurately modeled using numerical models, as can transient systems (i.e., systems in which stresses, parameters, or boundary conditions change over time). Another advantage of numerical models is that most codes are capable of simulating contaminant sources that vary over time, allowing more precise simulation of source reduction through weathering or engineered remedial actions.

5-12

Of the available codes, the combination of MODFLOW and MT3D is the most commonly used, due to the number of proprietary software packages that are designed around those programs. Most software codes are unable to simultaneously simulate the fate and transport of multiple dissolved species (e.g., parent and daughter products) that may have a significant presence in groundwater. Recently developed model codes such as RT3D (Clement, 1997) and BIOREM 3D (S.S. Papadopulos & Associates, 1998) are intended to alleviate this concern.

> **Key Question**: Will the Plume Migrate Beyond the Industrial/Airfield Area or Base Boundary? One of the primary purposes of determining the potential for natural attenuation and modeling plume migration is to answer this key question. If natural attenuation is destroying contaminants of concern and modeling indicates that the plume will not migrate beyond Air Force base boundaries, the site is an excellent candidate for monitored natural attenuation.

5.3 ALTERNATIVES TO PUMPING

5.3.1 Growing Regulatory Acceptance of Non-Pumping Alternatives

In 1993, the National Research Council published a report summarizing the results of their study of groundwater remediation in the U.S. The report criticized the use of pump-and-treat as a "default" groundwater remediation technology and cited numerous examples of where pump-and-treat had accomplished little in

the way of permanent aquifer restoration (NRC, 1993). In 1999, the EPA published an overview of the operating experience at 25 Superfund and RCRA sites where pump-and-treat was used as the primary method of groundwater remediation (EPA,1999c). Of the nine systems that had been operating prior to 1989, only one had achieved cleanup goals. The median capital cost of all 25 pump-and-treat systems was \$1.9M and the median annual operating cost was \$190,000. The growing regulatory acceptance of non-pumping alternatives has been strongly influenced by the failure of pumping systems to remediate sites at a reasonable cost.

During the 1990's environmental scientists and engineers made significant progress in understanding and documenting natural attenuation processes for chlorinated solvents and in developing several new technologies for the containment and/or treatment for this group of contaminants. Regulatory agencies, including the USEPA, are now promoting these non-pumping technologies if they provide an equal level of protection.

5.3.2 Monitored Natural Attenuation

This section describes when MNA should be considered as the primary remedial alternative (without engineered source reduction), and when MNA should be used in conjunction with engineered remediation. In addition, situations where MNA is not a realistic option are discussed.

5.3.2.1 MNA as the Primary Remedial Approach

MNA can be used as a long-term remedy for contaminated groundwater when the following criteria are met:

- Biodegradation rates are sufficiently rapid that remedial objectives will be achieved within a timeframe that is acceptable to the Air Force and regulators;

- The plume is not expected to migrate beyond an area where the Air Force can enforce institutional controls; and

- Any significant risks to potential receptors during the treatment period can be prevented using compliance monitoring and institutional controls.

In addition to the above criteria, MNA should be considered in cases where other alternatives (e.g., pump and treat) are significantly limited by low desorption rates. For example, a substantial amount of contaminant mass will be sorbed to aquifer matrices that contain a high percentage of clay minerals or organic carbon, and will therefore be difficult to extract via pumping.

5.3.2.2 MNA in Conjunction with Engineered Remediation

In some cases, it may be necessary to complete engineered remediation to reduce the contaminant source or plume "hotspots", followed by implementation of MNA for the remaining contamination. Targeted source area or plume hotspot remediation can reduce plume migration and the timeframe to achieve remedial objectives in cases where contaminant fate and transport predictions indicate that remedial objectives will not be achieved within a reasonable timeframe, or contamination poses or will likely pose significant risks to potential receptors. Engineered source reduction can reduce risks to future intrusive workers and allows the site to be used with less institutional control. In addition, regulatory agencies are much more likely to accept MNA as a groundwater remedy at sites where active source reduction and/or hotspot pumping has occurred.

Barring removal or reduction of the contaminant source, the distribution and concentrations of contaminants in the plume may not change appreciably through time; therefore the rates of mass removal via groundwater extraction will eventually become asymptotic. Asymptotic mass removal rates also may occur at some sites where source removal has been performed because removal rates are controlled by the rate at which contaminants desorb from the aquifer matrix (e.g., in aquifers containing a significant percentage of clay minerals or organic carbon). When an asymptotic status occurs, the O&M costs for the pump and treat system may outweigh the benefits derived from the system, and implementation of MNA should be considered.

The degree to which engineered remediation will impact the occurrence of natural attenuation processes should be assessed prior to proceeding with this approach. For example, remedial actions that cause the groundwater in the plume area to become more aerobic and oxidizing will inhibit the reductive dechlorination . Such actions may include air sparging, or groundwater pumping that draws relatively oxygenated groundwater into the plume area from outlying, uncontaminated areas. Therefore, caution should be used when scoping engineered remedial actions to ensure that they do not substantially inhibit natural attenuation.

5.3.2.3 When is MNA Not Recommended

MNA is not generally recommended in the following situations:

- Rates of contaminant removal via natural attenuation are very slow leading to uncertainty regarding plume migration;

- Groundwater in the plume area is not sufficiently reducing to promote complete reductive dechlorination of CAHs to ethene, resulting in the accumulation of VC, which is relatively toxic. This situation would only occur in cases where other VC removal mechanisms (e.g., oxidation) are not prominent;

- The chlorinated solvent plume has migrated or has the potential to migrate off-Base and

use of off-Base groundwater cannot be controlled via easements; and,

- Risk analyses indicate the potential for unacceptable impacts to human health or the environment if the plume is not quickly contained.

5.4 ENGINEERED ALTERNATIVES TO PUMP-AND-TREAT

Although MNA should be the first remedial approach considered at chlorinated solvent spills located in industrial/airfield areas, there are several situation (outlined in the previous section) where MNA is not appropriate. This section describes several alternative remedial approaches and technologies that should be considered as a potential substitute or replacement for pump-and-treat.

5.4.1 Point-of-Use Treatment

Point-of–use treatment views groundwater as a non-pristine resource that must be treated to remove impurities before it is provided to the consumer. Impure groundwater is treated when it is needed by the consumer, rather than pumping to contain large volumes of solvent-tainted groundwater and then discharging clean groundwater into non-potable surface water (or attempting to reinject it into the aquifer). This approach is best suited for chlorinated solvent plumes which have migrated at dilute concentrations into deep aquifers that are potential sources of drinking water. Under this approach, the Air Force would agree to fully or

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partially fund the construction and operation of a groundwater treatment system (generally activated carbon) to remove the trace levels of chlorinated organics that may have originated on the Air Force base. Before agreeing to point-of-use treatment, the Air Force should ensure that other non-DOD sources of groundwater contamination share in the treatment cost.

5.4.2 Enhanced Bioremediation

Combinations of anaerobic and aerobic biological degradation are known to completely degrade chlorinated solvents to harmless by products. The most promising biotechnology for chlorinated solvent removal is enhanced reductive dechlorination. Under highly anaerobic conditions, chlorinated solvents such as PCE, TCE and DCE are utilized as electron acceptors by subsurface bacteria. In this process, chlorine atoms are sequentially removed from the chlorinated solvent molecule. The reader is referred to USEPA (1998) and Wiedemeier *et al.* (1999) for a more complete discussion.

This process can be enhanced by the addition of inert soluble organics which supply a surplus of hydrogen molecules. Vegetable oil and other food-grade organics are typically injected into the aquifer near the source area or placed in a "biowall" perpendicular to groundwater flow. Dissolved chlorinated compounds are monitored to track the conversion of "parent compounds" into carbon dioxide, chloride ions and water.

Enhanced biodegradation is a promising and inexpensive method of containing dissolved contamination and slowly destroying DNAPL source areas. This technology could replace pump-and-treat systems at many Air Force sites, particularly industrial/airfield sites where there is sufficient space to allow biological reactions to take place before contaminants migrate off base property. Additional studies are required to determine the long-term cost-effectiveness of this technology.

5.4.3 Air Sparging

Air sparging is the process of injecting air under pressure into an aquifer. The objective is to force the air to move through contaminated aquifer material and groundwater in as many small channels as possible. Treatment may occur either through volatilization or through biodegradation stimulated by adding oxygen. A sparging system often is coupled with SVE to collect the VOCs that have volatilized into injected air. Although air sparging has been applied at numerous sites, the current understanding of air sparging performance and effectiveness is limited. One potential concern is the tendency for injected air to form channels in the aquifer. When one of these channels intercepts a monitoring well, the air then bubbles up through the well, stripping contaminants and oxygenating the well water. As a result, the monitoring well quickly appears "clean", although much of the surrounding aquifer remains untreated. This false indication of rapid

treatment led to early enthusiasm for air sparging, and its indiscriminate application.

More recently researchers have found that many of the early "successes" of air sparging were not in fact successful remediation (Bass *et al.,* 1995). The physics of air flow in an aquifer are more complex than first thought, and a real understanding of air sparging is only beginning to emerge. It is clear that air sparging can have some impact on contaminated soils below the water table, and on contaminated aquifers. Special site conditions may lend themselves to successful use of sparging to address dissolved fuel compounds. Sandy aquifers with shallow groundwater contamination may provide for more uniform treatment than sites with mixed sand, silts and clays. Infeasibility is usually discovered through pilot testing. One common problem is formation of large, horizontal air channels that allow injected air to bypass contaminated groundwater. At other sites, all of the injected air moves up to the vadose zone in the immediate vicinity of the injection point, resulting in a very small radius of influence. In silt and clay aquifers the permeability is too low to inject air.

5.4.4 In-Well Aeration and Recirculation

In-well aeration is the process of injecting air into a well with three intended purposes: the stripping of volatile organics from groundwater that enters the well, the addition of oxygen to groundwater, and the displacement and recirculation of groundwater outside of the well. The first two processes (stripping of volatiles and addition of oxygen) are almost certain to occur at any site, however, the recirculation of groundwater outside of the well has not been consistently proven in sandy aquifers and most certainly will not occur is low permeability soils. The obvious shortfall of this technology is the limited influence that oxygen addition or volatiles stripping will have outside of the well. Because of this limited radius of influence, a large number of recirculation wells may be required to contain a plume and an inordinate number of wells would be required for total plume remediation. Geochemical changes in side of the recirculation well have led to fouling and high O&M costs. This technology has not demonstrated a consistent ability to uniformly treat sandy aquifers, and has no application in stratified or low permeability silt and clay soils (AFCEE, 1997).

5.4.5 Reactive and Permeable Walls

One method of improving the uniformity of groundwater treatment is to install a semi-permeable barrier which can either physically or biologically remove contaminants as groundwater passes through the in situ treatment wall. In situ treatment walls may be particularly effective for preventing plumes from discharging to a drainage ditch or migrating off Air Force property. Several types of physical, chemical, and biological treatment can be completed using semi-permeable barriers.

Barrier wall technologies are best suited for sites where the plume is not stable and is migrating off-base or toward receptors. This technology is more effective in shallow aquifers and can become unworkable and very expensive as the thickness of the aquifer increases.

Volatile chlorinated solvent contamination can be physically removed from shallow groundwater by creating an air sparging curtain of closely spaced sparge wells or by placing a horizontal sparge well in a gravel-filled trench that intercepts groundwater flow. By using a gravel-filled trench, many of the short-circuiting problems common to air sparging can be eliminated. The removal of dilute concentrations of chlorinated compounds can generally be completed without an SVE collection system.

Zero-valent iron barrier walls are currently being applied for the reductive dechlorination of chlorinated solvent plumes. This promising approach has been applied at many sites and is achieving contaminant destruction with only minimal geochemical fouling. (USEPA, 1999d). Initial installation costs for zero-valent iron barrier walls can be high for sites with rapid groundwater movement because of the residence time required for complete dechlorination of vinyl chloride. However, this technology can achieve complete remediation in with just a few feet of iron wall where biological treatment can require hundreds of feet.

Biologically induced reductive dechlorination can also occur in an engineered, semi-permeable barrier wall. A variety of organic material can be placed in a trench creating a flow-through bioreactor where reductive dechlorination can take place. AFCEE is demonstrating this concept on several chlorinated solvent plumes, including a plume at Offutt AFB where a trench filled with organic mulch is successfully biodegrading TCE to cis-1,2 –DCE (Haas, 2000). Other organic additions, such as vegetable oil, are also being pilot tested as potential permeable treatment walls.

5.4.6 Wetlands and Phytostabilization

The migration and ultimate fate of dissolved chlorinated solvents in shallow aquifers can be influenced by vegetation. This influence can be natural, in the case of a plume migrating into an existing wetlands, or engineered if the wetlands or vegetation is purposely placed in the path of the plume. Wetlands provide a biologically active zone in which both anaerobic and aerobic biodegradation can take place as contaminated groundwater moves into the organic sediments and into the surface water. These conditions are often optimal for the sequential reductive dechlorination and aerobic biodegradation of chlorinated solvents.

Trees and shrubs can also be used to stabilize the forward migration of contaminated plumes in shallow aquifers. The evapotranspiration of

closely spaced trees can demand hundreds of gallons a day from a shallow groundwater aquifer. Trees can have the same effect as dozens of small pumps removing contaminated water from a shallow aquifer. This emerging technology is currently being tested by AFCEE and others and several sites with shallow chlorinated solvent contamination (AFCEE, 1999).

REMEDIAL PROCESS OPTIMIZATION

This section will assist you in:

- Evaluating the effectiveness of existing SVE and pump and treat systems;

- Determining if another technology may be required to improve remediation effectiveness; and

- Optimizing the performance of existing pump-and-treats and improving site monitoring programs.

6.1 RPO OVERVIEW

At many chlorinated solvent contaminated sites, pump-and-treat systems have been installed and have been operating for many years. This section describes the overall remedial process optimization (RPO) program that is emerging within the Air Force, with a specific emphasis on evaluating the effectiveness and efficiency of existing pump-and-treat systems and optimizing existing site monitoring programs.

RPO can be defined as a systematic approach for evaluating and improving site remediation processes so that maximum risk reduction is achieved for each dollar spent. Although RPO is frequently associated with the optimization of remediation systems and *how* the cleanup will be completed, it is equally important to review *why* certain cleanup goals have been established and to update those decisions based on new regulatory options. Just as the technical approach to remediation should be upgraded to take advantage of scientific advances, changes in regulatory framework such as risk-based cleanup goals and the growing acceptance of monitored natural attenuation should be considered in the optimization process. An effective RPO program will pursue a wide range of optimization opportunities.

The Air Force Remedial Process Optimization (RPO) Handbook (AFCEE, 2000) has been developed to provide environmental managers with practical guidance on how to evaluate and optimize existing remediation systems. This section provides a summary of the RPO process and how it can be used to improve existing remediation systems at chlorinated sites. The reader is encouraged to consult the RPO Handbook for specific details

on how to evaluate and optimize existing remediation systems.

6.1.1 When Is An RPO Evaluation Recommended?

RPO should be viewed as an ongoing responsibility of the Air Force and its contractors who are hired to operate, maintain, and monitor remediation systems. At least once each year, the operating contractor should complete a Phase I review of key performance data and evaluate the progress toward site cleanup goals, while ensuring remedy protectiveness. Several situations may warrant a more rigorous Phase II RPO evaluation:

- Preparation for mandatory regulatory reviews such as 5-year ROD reviews or RCRA permit reapplications;

- Preparation of an operating properly and successfully (OPS) demonstration document at BRAC sites that are scheduled for transfer from Air Force control;

- Any remediation system that is clearly failing to achieve its designed cleanup objectives based on the annual Phase I RPO evaluation;

- Sites with an opportunity to pursue new cleanup goals based on changes in regulatory policy and/or new understanding of site conditions or chemical toxicity.

Responsible Air Force environmental managers should prioritize sites for Phase II RPO evaluations based on regulatory requirements and the potential cost benefits. For pump-and-treat (P&T) systems, Phase II RPO evaluations are most useful after the initial 2 to 3 years of system operation since the effectiveness of most P&T systems can be evaluated after this period. A Phase II RPO evaluation is always needed for systems that are obviously failing to meet their design objectives, regardless of the age of the system.

RPO can be used to evaluate a wide range of remediation systems and regulatory frameworks. The greatest opportunities for optimization and cost avoidance exist at large pump-and-treat systems. However, a streamlined version of RPO can be applied to other remediation systems.

6.1.2 Expected Benefits of RPO

Multiple benefits are expected from the RPO program (Figure 6.1). RPO is expected to ensure that existing remediation systems remain protective of human health and the environment, to facilitate the reevaluation of cleanup goals, track and report on remedial progress, reduce operating and monitoring costs and ultimately accelerate site closures and transfers.
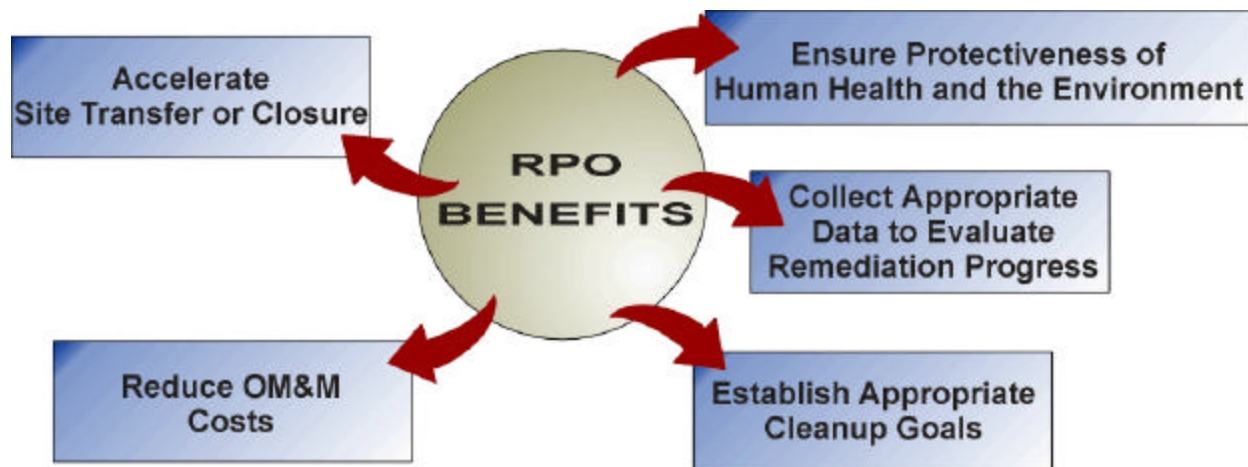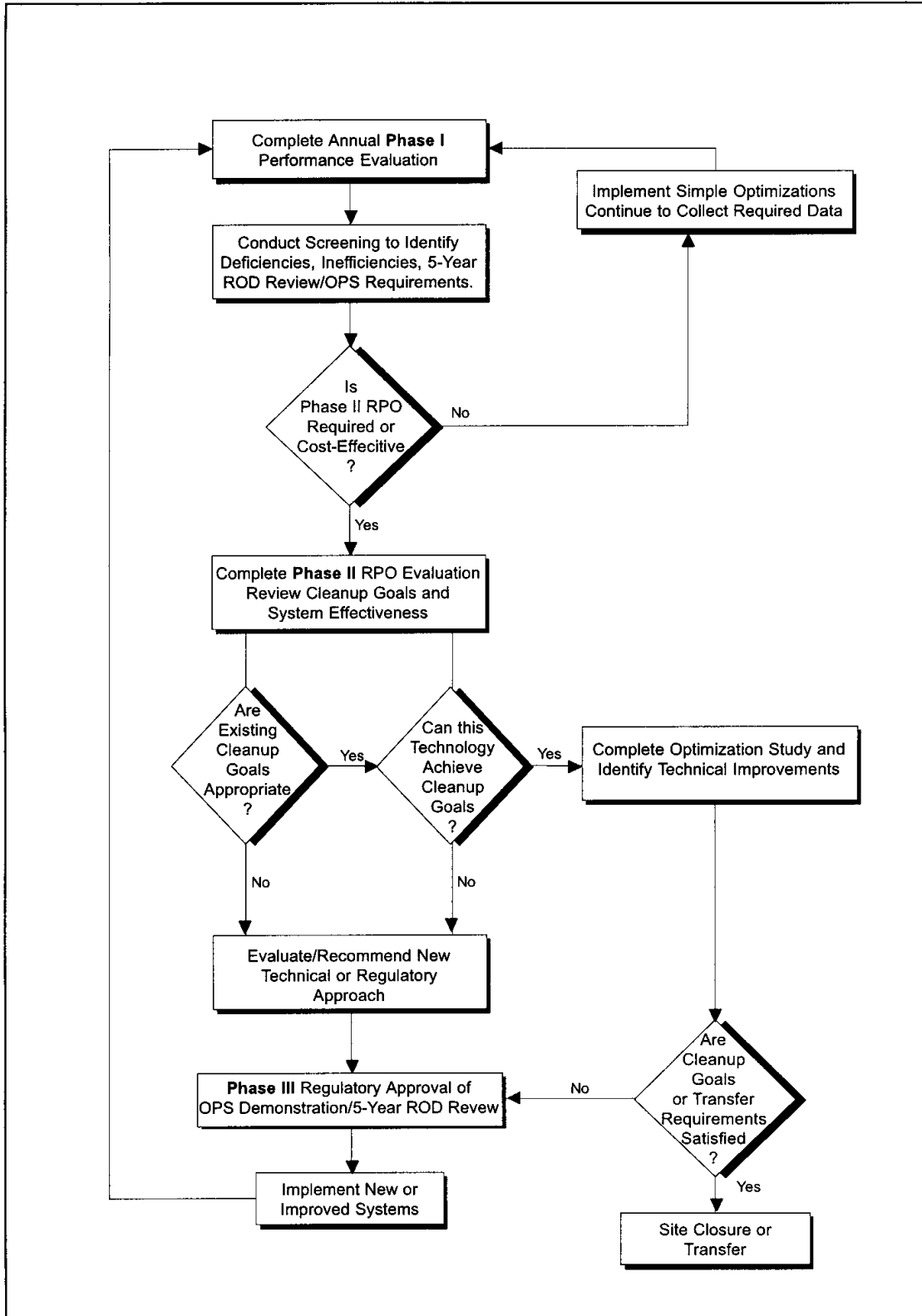
Figure 6.1 Benefits of RPO

6.2 THE RPO PROCESS

6.2.1 Phase I Reviews

Figure 6.2 illustrates the three phases of the RPO evaluation sequence. A major objective of the RPO program is to focus the attention of Air Force environmental managers and their operating contractors toward site cleanup objectives and the performance of existing remedial systems. At least once each year, a Phase I RPO evaluation is recommended to review site monitoring data and treatment system performance to determine if the remediation system is making progress toward cleanup goals. The RPO Handbook describes methods of organizing site data for this purpose. These data collection activities and an annual performance review are critical components of RPO and must be a priority of environmental managers. Based on the results of the annual Phase I evaluation, each site should be screened to determine if a more intensive Phase II evaluation is warranted. In many cases, simple

optimization improvements can be completed as action items from the annual performance evaluation.

Before proceeding into a Phase II RPO evaluation, each site should be screened to determine if the costs associated with Phase II are likely to be recovered through future O&M cost avoidance. This decision must be based on site-specific factors such as the general effectiveness of the system, the cost of the optimization study, the current O&M costs for the remedial system, and the number of years that it is expected to operate. Generally, the longer the system is expected to operate, the greater the potential for payback.

6-3

Complete Annual **Phase I** Performance Evaluation

Implement Simple Optimizations Continue to Collect Required Data

Conduct Screening to Identify Deficiencies, Inefficiencies, 5-Year ROD Review/OPS Requirements.

Is Phase II RPO Required or Cost-Effecitive ?

No

Yes

Complete **Phase II** RPO Evaluation Review Cleanup Goals and System Effectiveness

Are Existing Cleanup Goals Appropriate ?

Yes

Can this Technology Achieve Cleanup Goals ?

Yes

Complete Optimization Study and Identify Technical Improvements

No

No

Evaluate/Recommend New Technical or Regulatory Approach

Are Cleanup Goals or Transfer Requirements Satisfied ?

Phase III Regulatory Approval of OPS Demonstration/5-Year ROD Revew

No

Implement New or Improved Systems

Yes

Site Closure or Transfer

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Figure 6.2 Remedial Process Optimization Sequence

6.2.2 Phase II - Intensive RPO Evaluation

A Phase II evaluation will generally require the formation of an independent RPO evaluation team to more completely study and identify specific optimization opportunities. To minimize conflicts of interest, it is recommended that the Phase II RPO team be directed by an independent team chief who has no contractual relationship to the remedial system operations contractor. On sites with formal Records of Decisions (RODs), or RCRA corrective action programs, Phase II RPO evaluations should begin 18 months prior to mandatory program reviews (5-year ROD reviews, 10-year permit reapplications). For remediation systems located on base realignment and closure (BRAC) facilities, RPO will be useful for reducing long-term operations and monitoring costs and for gathering the data which will be required to demonstrate that a system is operating properly and successfully.

Two parallel activities are envisioned: evaluation of site cleanup goals and risk reduction objectives; and, evaluation of the effectiveness and efficiency of the current remediation and monitoring systems. Phase II will include a thorough review of the cleanup goals that have been established for a site, the regulatory history behind those goals, and the opportunities that may exist for revising cleanup goals without sacrificing the overall protectiveness of the remedy. Emphasis should be placed on the use of engineering and institutional controls to protect site workers in industrial/commercial settings so that more realistic, risk-based cleanup goals can be established. For BRAC facilities, this will require careful negotiation of leases or land sales to ensure that land use controls provide continued protection of human health and the environment.

The Phase II evaluation will also determine if the performance of the existing remedial system can be expected to achieve cleanup goals. In addition to evaluating the effectiveness of the existing remediation system, opportunities for remedial systems and monitoring optimization as well as new approaches such as monitored natural attenuation should be considered. Once the best combination of existing and new technical approaches has been selected, the optimized or new system must be evaluated in terms of its ability to cost effectively achieve cleanup goals within a reasonable timeframe. Complete details on how to conduct effectiveness evaluations and system optimizations can be found in the Air Force RPO Handbook.

6.2.3 Phase III - Implementation of RPO Recommendations

The activities of the final phase of optimization will depend upon the results of the first two phases. For example, if an optimized pump-and-treat system is expected to achieve numerical cleanup goals for dissolved contaminants in a reasonable timeframe, the Air

Force may commit to an extended O&M period, establish intermediate performance goals, and continue to optimize the remediation system and monitoring program until cleanup goals are achieved. This decision will require minimal regulatory involvement because it does not propose significant changes to the approved remedy.

However, if site conditions make source removal technically infeasible, the Air Force may choose to pursue an isolation or plume containment strategy. In this case, the "optimum" remediation system is one that will accomplish long-term isolation/containment at minimum cost. An additional goal may be to reduce the area of the site that must remain under land or groundwater use restrictions. Continuing RPO for isolation/containment remedies will include periodic evaluations of emerging technologies and new regulatory options. Significant regulatory coordination and approval will be required to change primary remedial objectives.

The documentation for Phase II RPO evaluations must be tailored to the specific remedial system and responsive to regulatory requirements. The Phase II RPO evaluation should be structured so that it can be used as a stand-alone document by the Air Force or as a supplement to 5-year ROD reviews, RCRA permit reapplications, or OPS demonstrations.

6.3 EVALUATION OF SYSTEM EFFECTIVENESS

There are two primary criteria to be addressed in a remediation system evaluation: effectiveness and efficiency. System *effectiveness* refers to the ability of the system to achieve the remediation goals at a given site. For example, if plume remediation is the primary goal for the site, system effectiveness will be measured by the mass of contaminant removed from the aquifer and the permanent decrease in concentrations at plume monitoring wells.

The first and primary focus of RPO should be to determine if the existing technology is capable of achieving remediation goals within a reasonable time frame. While it is tempting to "jump into" system-efficiency improvements, this phase of the RPO evaluation should not begin until the fundamental effectiveness of the existing technology has been validated.

System *efficiency* refers to the optimization of time, energy, and costs associated with achieving remediation effectiveness using a specific technology. For example, a groundwater pump-and-treat system may be reducing contaminant concentrations, but pumping at excessive rates. This results in system inefficiencies such as high O&M costs and the over design of aboveground treatment units. Section 3.6 describes how to improve the

6-6

efficiency and "optimize" common technologies in use at Air Force sites.

Effectiveness evaluations can best be completed by direct comparison of actual performance data to established performance criteria. Illustrations such as charts, graphs, and overlay maps provide the most useful tools for evaluating these data. When evaluating treatment effectiveness it is important to graph data from several locations at the site as well as treatment system influent data. Contaminant concentrations at monitoring points in the source area, in the impacted soil and groundwater plume, and from wells at the perimeter of contamination should be plotted. For more complex sites, contaminant levels at several depths may require the use of a 3-dimensional graphics package. The following performance evaluation is recommended for SVE and groundwater extraction systems.

6.3.1 Extraction System Effectiveness

While most *in situ* extraction systems can remove contaminants that are dissolved in groundwater or are volatilized in soil gas, they are limited in their ability to remove contaminants that are sorbed to or trapped within the soil matrix. This situation is known as "diffusion limited" removal and is the most common shortfall of *in situ* soil and groundwater extraction systems. Figure 6.3 illustrates a typical contaminant-reduction curve for extraction technologies such as SVE. Reductions in equilibrium levels of benzene

indicate that progress is being made at this site; however, the performance criteria of achieving a 10-part-per-million-by-volume (ppmv) equilibrium concentration within 3 years has not been achieved in the source area monitoring point (VMP-2). Soils near VMP-2 are experiencing diffusion-limited removal because under normal operations, the rate of benzene desorption is limiting the rate of benzene removal in these source area soils. If rapid remediation is required at this site, another approach to soil remediation (e.g., excavation or thermal enhancement) may be needed for the soil volume near VMP-2.

Figure 6.4 illustrates a contaminant-reduction curve for a groundwater pumping system. TCE concentrations have reached near asymptotic levels in the influent to the air stripper however, MW-B has had much higher levels of TCE and a slower rate of reduction. The effectiveness of this system could be improved by increasing pumping rates near MW-B and decreasing pumping rates near the wells at which the 5-ppb cleanup objective has been achieved.

If little or no NAPL is present, and site soils are sufficiently permeable to allow air or groundwater flow, extraction technologies will often achieve cleanup goals in a reasonable time frame. If residual NAPL is trapped in the soil matrix, diffusion limitation may result in unacceptably long cleanup times. If NAPL is present or suspected, this should be clearly indicated in the conceptual site model, and the

FIGURE 6.3 SVE EFFECTIVENESS EVALUATION

FIGURE 6.4 PLUME REMEDIATION EFFECTIVENESS EVALUATION
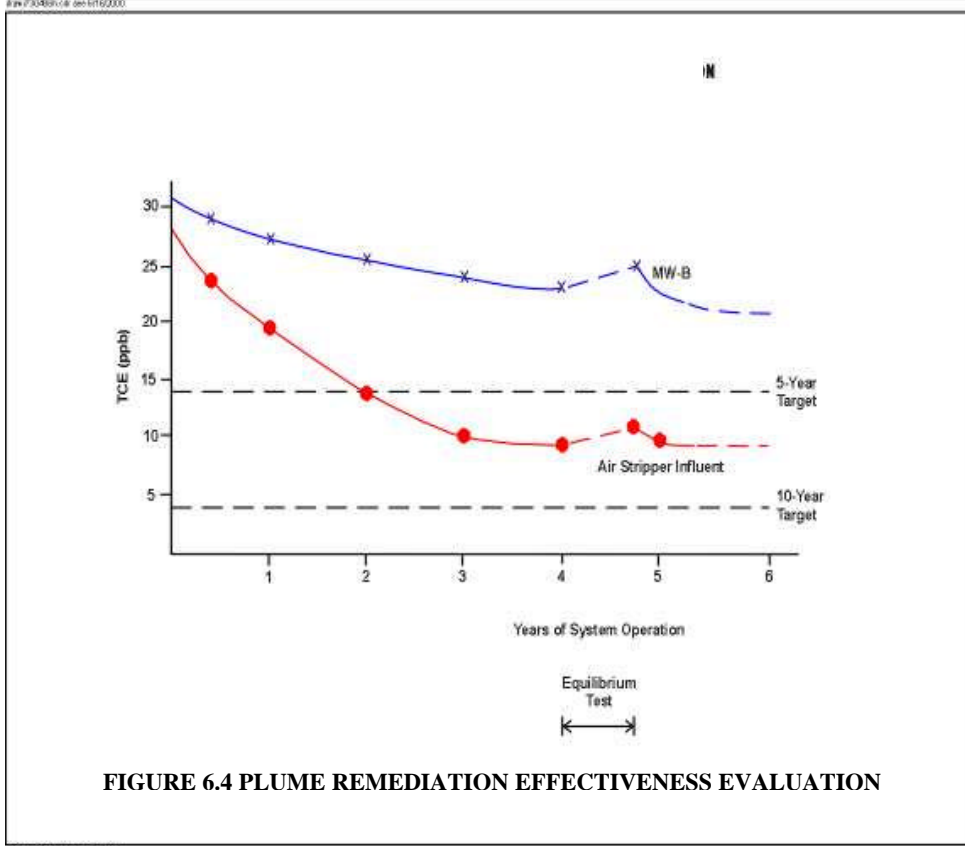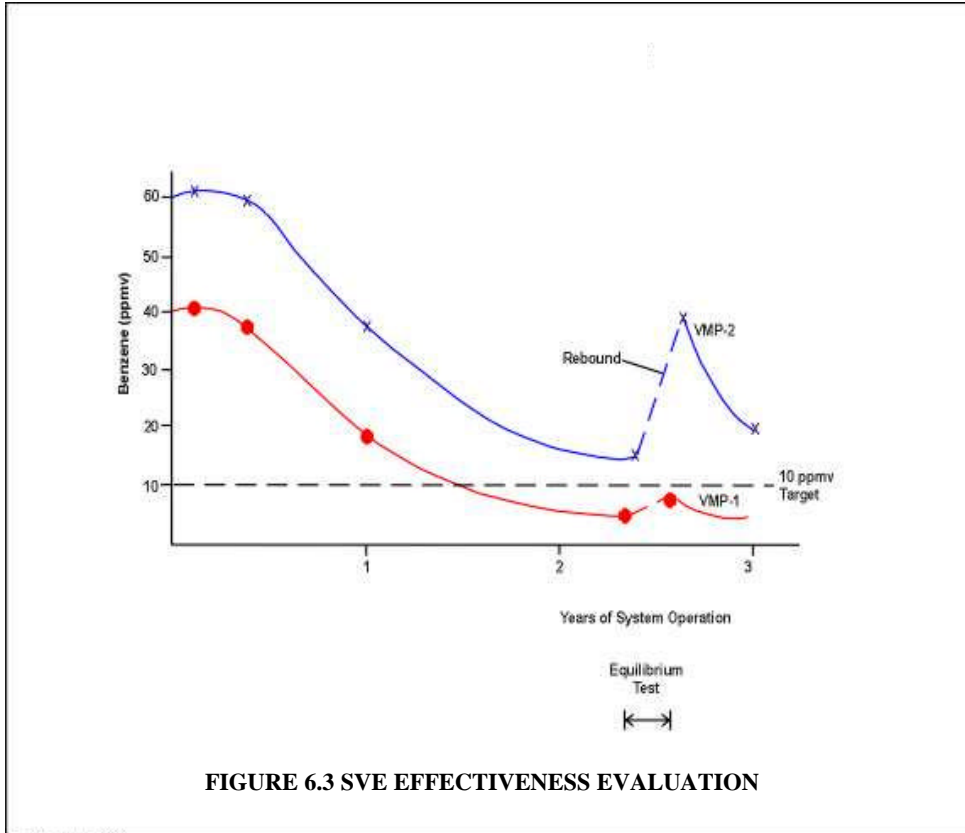
RPO team should evaluate site data to determine if the conceptual site model is supported by operational data. Significant rebounding of contaminants in source area wells during equilibrium testing is one indication that NAPLs may be present in soils or aquifer material. Rebounding can also indicate an area of inefficient treatment where residual contamination is not being impacted by the treatment technology. Figure 6.5 illustrates significant rebounding in source area well MW-1. This situation may require a reevaluation of the system design, or possibly a change of cleanup goals to emphasize source containment rather than total plume remediation.

6.3.2 Containment System Effectiveness

Evaluation of the effectiveness of groundwater containment systems will require a careful analysis of water levels surrounding the pumping system and of contaminant trends, particularly at wells located at the plume perimeter. Figure 6.6 shows typical groundwater drawdown at a pump- and-treat site with the current TCE plume superimposed. Hydraulic containment appears to be effective at this site. In a containment scenario, TCE concentrations in the plume perimeter wells should steadily decrease. Theoretically, the quantity of water pumped from the aquifer should decrease over time as pumping is focused closer and closer to the source area.

The EPA (1994) publication, *Methods for Monitoring Pump-and-Treat Performance* is particularly useful in evaluating the effectiveness of both contaminant extraction and hydraulic containment. The EPA Technology Innovation Office (TIO) has demonstrated that the MODMAN model is particularly effective for determining containment effectiveness under a variety of pumping scenarios. Other models such as MODGA and MODFLOW can be used to simulate pumping containment.

6.3.3 Aboveground Treatment System Effectiveness

A variety of aboveground treatment systems are installed at military installations, primarily to remove or destroy contaminants contained in extracted groundwater or soil gas. Common groundwater treatment systems include air stripping for VOCs and activated carbon for removal of semivolatile hydrocarbons and for polishing air stripper effluent. At sites contaminated with dissolved metals, ion exchange and precipitation processes are frequently employed. Common soil gas treatments include activated carbon and a variety of thermal treatment methods. For each of these aboveground treatment technologies, effectiveness is measured by the ability of the technology to remove contaminants from the extracted groundwater or soil gas so that discharge limits are not exceeded. Aboveground systems can be modified or new technologies can be substituted to maintain the required
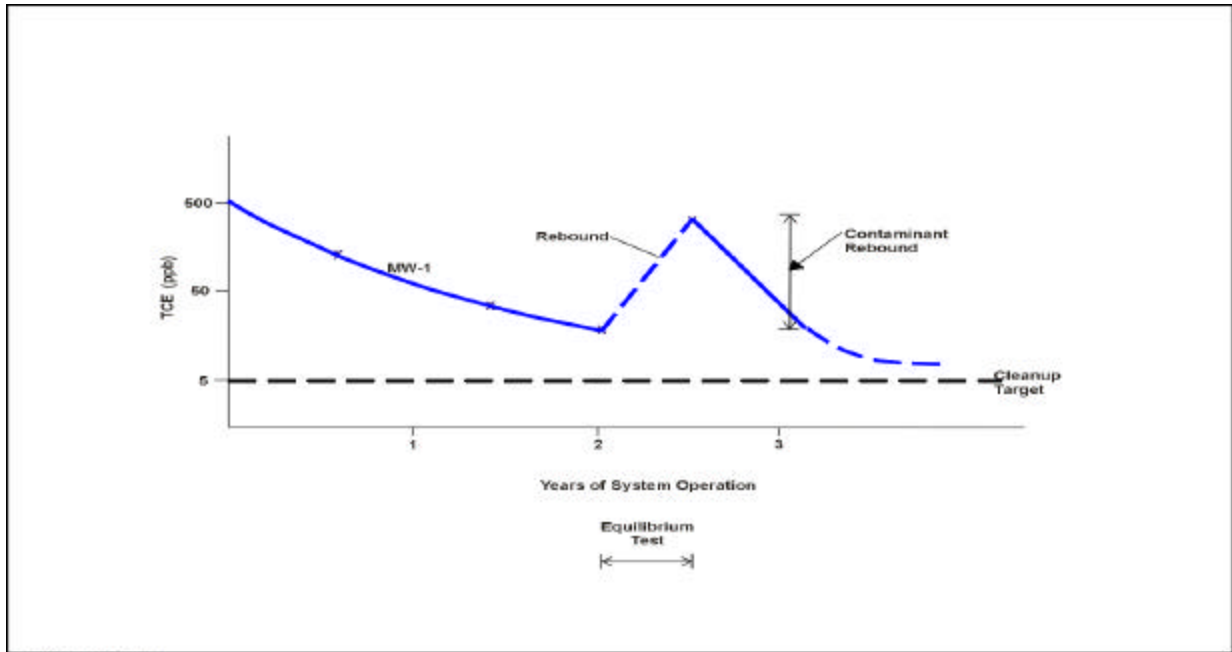
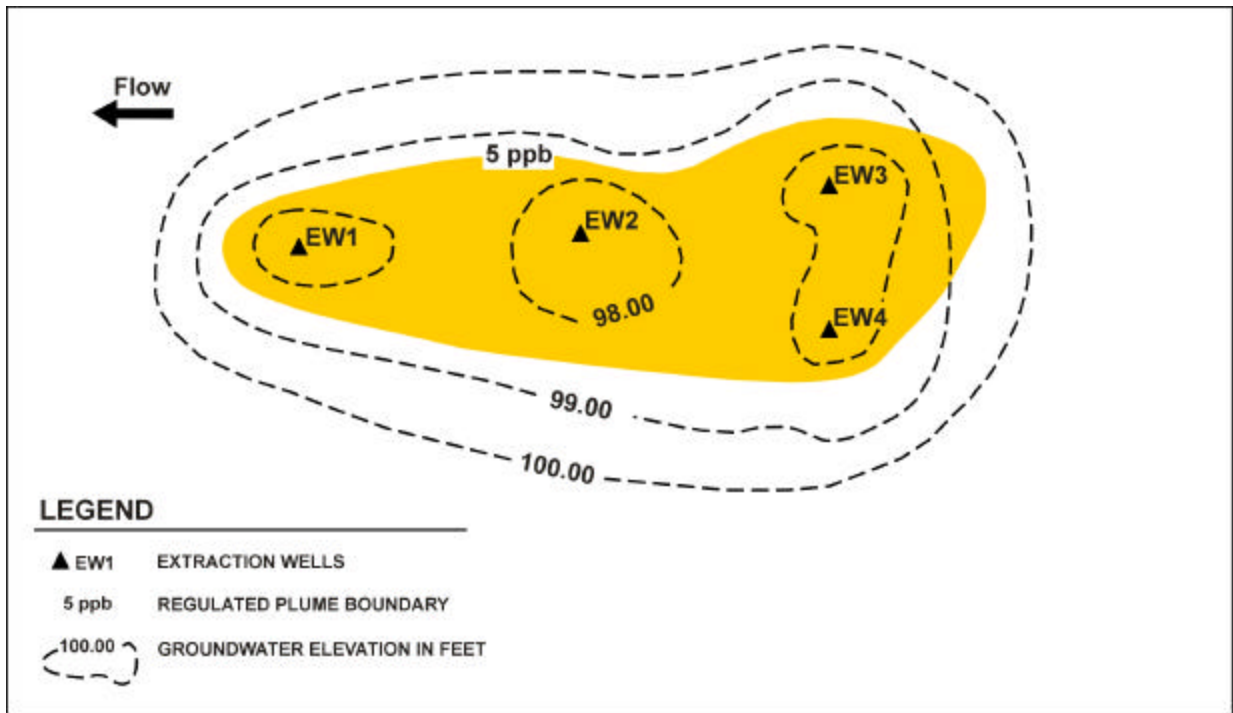**Figure 6.5 Source Area Well with Significant Rebound**

Figure 6.6 Effective Plume Containment

6-10

removal effectiveness. Most RPO evaluations of aboveground treatment systems will focus on improving efficiency through modifications to existing systems or replacement with another technology.

6.3.4 Monitoring System Effectiveness

An effective monitoring system will provide the site engineer with both short-term feedback on the effectiveness of individual aboveground or *in situ* treatment systems, and long-term feedback on the effectiveness and protectiveness of the overall site remedy. Influent and effluent monitoring points should be established for individual treatment systems to determine treatment efficiency and to ensure that the system is effectively meeting regulatory discharge standards. For many systems, this will include frequent calibration of both hand-held monitoring and flow measurement devices, and careful adherence to the field sampling and analysis plan to ensure accurate and reproducible data.

The effectiveness and protectiveness of the overall site remedy is generally monitored at groundwater wells and soil VMPs. These monitoring points must be located so that the remediation response of the entire contaminated soil and/or groundwater volume can be accurately estimated by the monitoring network. An effective monitoring system will reduce the level of uncertainty regarding the spatial and temporal distribution of contaminants. Although

a complete description of how to establish effective monitoring networks is beyond the scope of this document, two references are recommended: the *AFCEE Long-Term Monitoring Optimization Guide* (AFCEE, 1997), Designing Monitoring Programs to Effectively Evaluate the Performance of Natural Attenuation (Wiedemeier and Haas, 2000) and the AFCEE *Bioventing Principles and Practice Manual* **(AFCEE, 1995b).**

An effective monitoring network should:

- Bound the horizontal and vertical extent of contamination and be able to define concentration gradients, including defining an approximate "non-detect" boundary;

- Measure the rate and direction of any contaminant migration to confirm containment or noncontainment;

- Measure the decrease in contaminant concentration resulting from treatment and estimate the mass of contaminant reduction in the subsurface;

- Determine if the source area is decreasing in concentration or how residual contamination may be limiting the rate of treatment.

6.3.5 Estimating Time To Achieve Remediation Goals

The estimated time to achieve remediation goals will dictate the total cost of the project and should be updated during the Phase II RPO evaluation. Although RI/FS and remedial design

documents attempt to predict the time required to reduce contaminant concentrations to cleanup goals, these estimates are often based on limited pilot-test results and unverified assumptions concerning contaminant distribution, hydrogeology, etc. Once the remedial system has operated for several years, these estimates should be refined as a part of the RPO effectiveness evaluation.

Modeling Approach

Most remedial designs for large pump-and-treat and SVE systems include use of a mathematical model to predict the time that will be required to reduce contaminant concentrations to remediation standards. If the input assumptions and numerical code for the original model are available, an experienced modeler should review the input assumptions and compare actual observed pumping (or airflow) rates, capture zones, and contaminant recovery rates to the original model assumptions. The RPO team can then produce a refined model that more accurately predicts future performance.

In some cases, the original model is unavailable or may be judged to be inappropriate for existing site conditions. If the cleanup time is critical to the RPO evaluation, a new state-of-the-art model should be developed for the site. Information on hydraulic control, solute transport, and SVE models can be found on the

EPA website **www.epa.gov/ada/kerrcenter .html** (csmos directory).

Observational Approach

At pump-and-treat sites with 5 or more years of operation (6-12 months for SVE systems), cleanup times can often be estimated from site monitoring data without complicated modeling. This "observational approach" to estimating remediation time is preferred over modeling because it is based on actual contaminant removal rates over time rather than predictions based on unverified assumptions. Additional information on monitoring aquifer restoration can be found in the EPA (1994) publication, *Methods of Monitoring Pump and Treat Performance.* For pump-and-treat systems, the following observations can be used to estimate remediation time frames.

- Based on the potentiometric surface of the groundwater, confirm that the entire contaminated plume is within the capture zone.

- Plot contamination versus time for each monitoring point and extraction well. Figure 6.7 illustrates a situation where the system is approaching asymptotic recovery at all monitoring wells. Using observed data, a simple first-order equation can be solved to estimate the time to attain the 5-ppb cleanup goal.

- Figure 6.5 illustrated a situation where significant rebound is occurring at source area well MW-1, suggesting that DNAPL or LNAPL may be present in the source area. The time frame for achieving cleanup goals is difficult to estimate at these sites. This site may be a candidate for a TI waiver or minimum pumping for source containment.

The same types of observations can be made for SVE systems. Soil gas concentrations in VMPs and extraction vent wells can be plotted against time. Consistent rebounding of soil gas concentrations in source area VMPs can indicate that saturation levels of fuel or solvent are trapped within the soil matrix.

6.4 GROUNDWATER EXTRACTION SYSTEM OPTIMIZATION

If groundwater extraction is determined to be a necessary component of a particular remediation system, the time required for groundwater remediation using extraction techniques generally dictates the overall time frame for site remediation and represents most of the long-term operating costs.

When properly optimized, changes to a groundwater extraction system can yield significant savings without sacrificing protectiveness. Pumping system optimization requires a clear understanding of subsurface conditions, a recognition of the physical limitations of diffusion-limited contaminant transport, and a clear definition of the pumping

objective. There are two primary objectives for pumping: plume containment and mass removal. Plume containment systems are intended to isolate the contaminant and prevent migration. Mass removal extraction systems are intended to maximize removal of dissolved chemical mass, thereby reducing contamination throughout the plume to an acceptable cleanup level. The following sections describe conditions associated with each objective, and a generalized optimization procedure that can be applied to either objective.

6.4.1 Plume Containment Optimization

The purpose of a groundwater extraction system (installed to contain a plume) is to maintain hydraulic control of groundwater so that dissolved contaminants are not transported beyond a compliance boundary. Containment of groundwater using extraction technologies ("pump-and-treat") may be a preferred remedial option in cases when a DNAPL phase is suspected to be present, or when a plume is moving offsite. In many cases, containment pumping may be cost effective as compared with other containment options (e.g. deep slurry walls or reactive walls). Because groundwater containment systems need only contain a plume, it is necessary to extract groundwater at a rate only slightly greater than the rate at which groundwater is moving naturally through the plume volume. Groundwater extraction rates frequently incorporate large safety factors that, based on the operational history of the system,
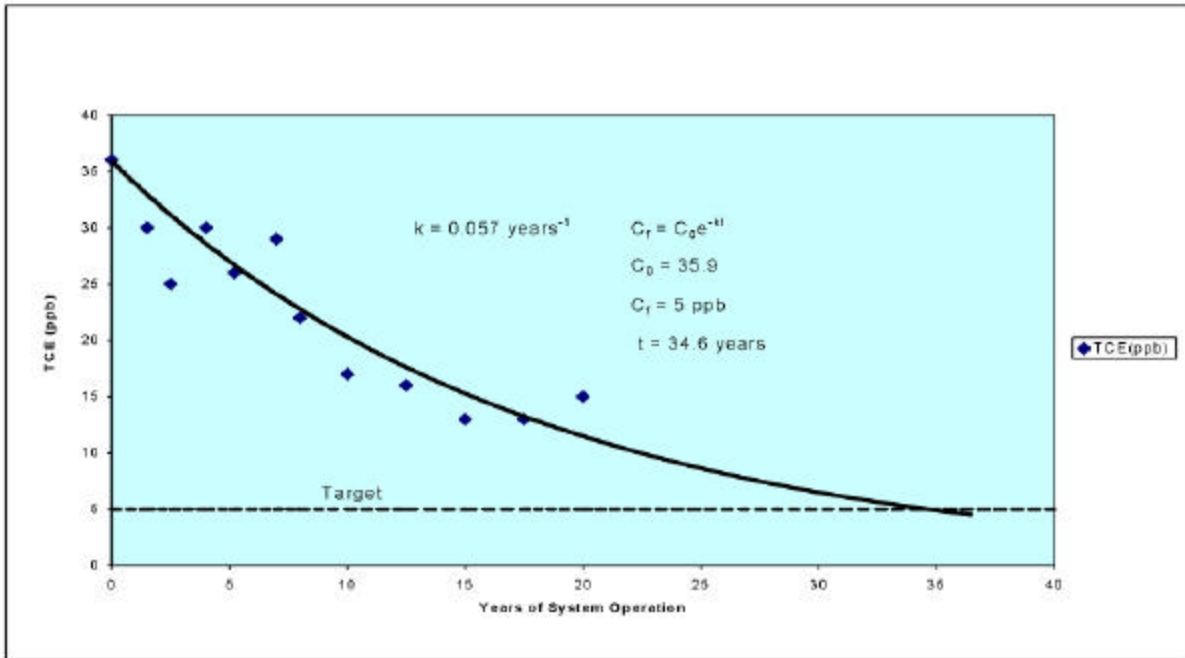
Figure 6.7 Predicting Cleanup Time Frame

may not be justified. In some cases, the groundwater extraction rates are the maximum the formation and/or wells can achieve, regardless of what is required for containment. These, and similar situations offer opportunities for optimizing the plume containment system.

6.4.2 Mass-Removal Optimization

Pump-and-treat systems designed for removal of contaminant mass are intended to extract groundwater containing dissolved contaminants from the subsurface and deliver the water to the surface for treatment, while maximizing the rate of contaminant removal. This typically requires maximizing mass removal rates while minimizing the volume of groundwater requiring treatment (locating the extraction well(s) in areas where contaminant concentrations are highest). However, since this process is mass-transfer limited; a number of factors can adversely affect system performance, and groundwater extraction systems intended for mass removal have not typically been successfully applied as stand-alone remediation systems. For example, the presence of DNAPLs can render a mass-removal system ineffective, because the rate of contaminant removal is limited by the rate of chemical dissolution from the DNAPL phase. Furthermore, in older plumes, the soluble contaminants have diffused into dead-end pores, low-permeability zones and even the aquifer matrix. In these cases contaminant removal is limited by diffusion rates.

6-14

6.4.3 Optimization Procedures for Groundwater Extraction Systems

Although the objectives of groundwater extraction systems may differ, depending on site-specific conditions or requirements, the general procedures for optimizing systems designed for plume containment, and systems designed for maximizing mass removal, are similar, and are described in the following sections. Where differences exist, these are noted in the discussion.

1. Has the extent of the dissolved-phase plume been adequately defined, and a conceptual site model constructed and validated using geologic, hydrologic, and chemical data adequate for site characterization? A better understanding of site hydrogeology, and lateral and vertical distribution of contaminants, will assist in optimizing the locations of extraction wells, and in optimizing the placement of the extraction interval(s) (well screens) of individual wells. If this level of characterization is not available, direct-push probes and discrete sampling can often be used to collect stratigraphic and/or water-level information and fill in data gaps regarding subsurface conditions or contaminant distribution.

2. Are source-control measures appropriate or necessary? A typical groundwater containment system extracts groundwater from the downgradient edge of a plume, preventing further migration of contaminants.

By contrast, a system designed for removal of contaminant mass will focus extraction efforts on those areas of the plume where contaminant concentrations are highest. However, without removal or reduction of the contaminant source, the distribution and concentrations of contaminants in the plume may not change appreciably through time; and therefore the rates of mass removal will eventually become asymptotic. In this case, addition of a source-control well, or implementation of other source removal or control measures, can reduce the volume of water pumped in downgradient areas and assist system optimization. Other control measures to be considered may include *in-situ* chemical destruction (e.g., injection of carbon sources to enhance reductive dechlorination), or construction of *in-situ* barriers or treatment walls.

3. Has the potential for natural attenuation been evaluated? Natural attenuation should be incorporated into all fuel-related plume remediations and considered for chlorinated solvents. If the site-specific occurrence of natural attenuation can be demonstrated, other source-control or mass removal measures may not be necessary, and natural-attenuation mechanisms, in combination with plume containment measures, may be sufficient to prevent further chemical migration while removing chemical mass from the subsurface. The EPA technical

protocol (USEPA, 1998a) describes how to document and incorporated natural attenuation into plume remediation.

4. Have the design and extraction rates of individual wells in the extraction system been optimized? Based on the objectives of a particular extraction system, identification of the appropriate completion intervals for individual extraction wells can greatly enhance the effectiveness of the extraction system. Changes in well design, construction techniques, or well materials can result in improved extraction efficiencies of individual wells. For additional information on improving well design, refer to *Groundwater and Wells* (Driscoll, 1986) or *Handbook of Ground Water Development* (Roscoe-Moss, 1990).

5. Based on drawdown and chemical data from individual monitoring wells (not data from extraction wells, which can be misleading), is the entire volume of the plume contained by the groundwater extraction system? If mass removal is the primary objective of the system, are extraction wells located in areas having historically elevated concentrations of contaminants? These concerns can only be evaluated if groundwater monitoring wells are located appropriately throughout, and down-gradient of the plume, and in the vicinity of extraction wells. The performance of a groundwater extraction system cannot be evaluated without an adequate number of appropriately-located monitoring wells. Therefore, prior to commencing optimization of the extraction system, (e.g., the wellfield), the groundwater monitoring network should be evaluated and optimized. Optimization of monitoring systems is more fully discussed in Section 3.6.5.

6. If mass removal is the primary objective of the extraction system, collect groundwater samples and extraction-rate information from each extraction well (during operation) to evaluate the relative mass removal from each point (extraction well, wellpoint, trench). These data will generally demonstrate that some wells are significantly less productive at removing contaminant mass. These data can then be used in conjunction with Step 5 (above), to identify simple adjustments that can be made to decrease extraction rates at unproductive wells, and increase extraction rates within the more contaminated areas of the plume.

7. If mass removal is the primary objective of the extraction system, is the contaminant removal rate limited by either chemical solubility or diffusion? If so, an extraction system designed to achieve contaminant mass removal may be pumping at a much higher rate than is necessary. These systems can be optimized by reducing groundwater extraction rates to better match the chemical dissolution/diffusion rates, while still preventing plume migration. Cycling all or a

part of the system (i.e., systematically turning pumps on and shutting them down) can also be used to reduce extraction rates to match dissolution/diffusion rates.

8. Complete equilibrium tests. If possible, turn off the entire extraction system for a period of three months to allow the concentrations of dissolved contaminants to equilibrate with contaminant residuals in the soil. Longer equilibrium times will be required for low-permeability and more heterogenous soils. Sampling of extraction wells and monitoring wells after a period of equilibration, and observing concentration "rebounds" (if any) will allow the true progress of remediation to be evaluated, enable the identification of remaining "hot spots", and assist in identifying stratigraphic intervals or areas in the plume where extraction should be focused.

9. If necessary, complete vertical profile testing on each extraction well to evaluate how extraction rates and contaminant recovery rates vary with depth or particular hydrostratigraphic intervals. Borehole flowmeters and discrete sampling devices, such as diffusion samplers, can be used to develop flow and contaminant profiles for each extraction and monitoring well. This will provide additional information regarding the hydraulic conductivity of particular intervals, and enable identification of intervals containing the greatest mass of

recoverable contaminants. Based on test results, the RPO evaluation team may recommend "packing off" unproductive intervals in particular extraction wells, or installation of new extraction wells, completed in more-productive and contaminated intervals.

10. Are individual wells in the extraction system optimally located to control plume migration, or are individual extraction wells optimally located to maximize mass removal, and is the cumulative pumping rate of the entire system the minimum necessary to achieve such control (or removal)? These questions are best addressed using drawdown calculations and/or simulation techniques. Using site-specific hydraulic, hydrologic, and groundwater monitoring information, the radius of influence and extent of the capture zone of individual extraction wells can be estimated. Groundwater capture zones for individual wells can then be projected onto a map of the plume and drawdowns superimposed so that the degree of plume containment can be estimated. This exercise should be completed using several different extraction rates for each well, within the range of extraction rates that can physically be achieved, depending on the aquifer characteristics at particular locations. Well locations and extraction rates can then be adjusted to improve the effectiveness of containment or removal, and reduce

6-17

groundwater extraction rates. Extraction system optimization can subsequently be refined, using analytical or semi-analytical techniques, or numerical models of groundwater flow (such as MODMAN), combined with trial-and-error or numerical optimization methods.

11. The aboveground water treatment system should be evaluated to determine whether it remains the most economical technology for the optimized extraction rates and contaminant concentrations. Often, as influent concentrations decrease, a particular treatment technology may become comparatively less efficient (air stripping may eventually be replaced with carbon treatment). Techniques for optimizing aboveground treatment systems are discussed in the following section.

6.5 ABOVEGROUND TREATMENT OPTIMIZATION

Although a wide variety of aboveground systems exist for groundwater and vapor treatment, these systems have common objectives and operating principles. The optimization of aboveground treatment systems can be achieved by following the general steps outlined in this section. The equipment manufacturer should be consulted for additional, system-specific optimization recommendations.

1. Review influent and effluent data to determine if each component of the treatment

system is achieving both its design removal efficiency and the regulatory discharge limits. Note any efficiency problems and call the equipment manufacturer to discuss possible maintenance or aging problems that could lead to inefficient operation. Correct these problems and monitor to ensure that efficiency improves.

2. Many systems are over-monitored and under maintained. If the system has a history of frequent shutdowns, it may not be receiving adequate preventative maintenance. Make sure that the labor hours being expended at the site are productive, and that required system maintenance is not being overlooked. An audit of O&M hours, and what activities are charged to O&M, is an essential Phase I activity.

3. Many treatment systems are over designed for current site conditions. Once the influent flow rate and/or contaminant concentrations begin to decrease, the contaminant mass loading to these systems is much less than design capacity. While total replacement of installed systems may not be economical, many of the energy-consuming components such as transfer pumps and blowers can be replaced with smaller, more efficient motors without sacrificing treatment efficiency.

4. In some cases, optimization will require a more complete cost-benefit analysis that compares continued operation of existing

equipment to replacement with more efficient, state-of-the-art equipment. This is particularly true of vapor treatment equipment that uses thermal destruction to remove VOCs. These units are very inefficient when operated below design mass loadings and consume large quantities of auxiliary fuel such as natural gas or propane. Replacement of these units will often generate fuel savings that rapidly pay back the cost of the new equipment.

5. Significant savings in remedial systems O&M will be realized through labor reductions. Improved remote control systems and modern telemetry/computer interfaces allow many simple treatment systems to operate for weeks without on-site labor. For large treatment systems with decades of future operations, these system enhancements can translate into significant savings. A systems controls expert should be consulted to determine what remote monitoring and control opportunities exist. There should be an appropriate balance between automation and human oversight of the system.

6.6 MONITORING OPTIMIZATION

Remedial action monitoring will have several goals that should be clearly stated in DQOs:

- Assessment of remediation progress;

- Operational performance of remedial system;

- Confirmation of remediation effectiveness; and

- Final confirmation of cleanup goals.

Long-term monitoring of soil, groundwater, and aboveground treatment systems represents a significant percentage of the total O&M cost for the current Air Force remediation program, and that percentage is expected to rise significantly over the next 10 years. Considerable emphasis has been given to reducing the overall cost of monitoring without sacrificing the reliability of monitoring programs. Several helpful references have been developed to assist site environmental managers and consultants with the optimization of site monitoring and analysis procedures. The primary reference for this topic is the *AFCEE/AFBCA Long-Term Monitoring Optimization Guide,* (AFCEE, 1997) which can be consulted for a variety of monitoring optimization ideas. The following monitoring optimization checklist has been summarized from this reference.

1. Review the existing site monitoring program and determine if all of the monitoring wells/VMPs are useful for tracking remediation progress or are required by regulatory decision documents. Identify redundant wells for elimination and abandonment. Monitoring well elimination typically will require regulatory approval.

2. Is the sampling frequency appropriate based on the rate of remediation progress? At many sites groundwater is monitored quarterly or semiannually based on requirements that were established during the initial site investigation. Once seasonal variations have been established, annual monitoring of subsurface conditions (during the same month each year) typically is sufficient to track remediation progress. Aboveground treatment systems may require more frequent monitoring to ensure desired system effectiveness and that discharge limits are being achieved.

Is the sampling and analytical protocol appropriate for monitoring remediation progress? Sampling and analytical protocols for remediation system monitoring are not as rigorous as those required for the initial site investigation. Check to ensure that the analytical methods can detect contaminants of concern at the desired quantitation limits and at levels that are appropriate for the use of the data. For example, only the treatment system effluent and point-of-compliance monitoring wells may require low detection limits and the strict quality assurance/quality control. The new *AFCEE Remedial Process Optimization Field Procedures and Quality Assurance Protocol* (AFCEE, 1998) provides guidance on appropriate data quality objectives (DQOs) for remediation scenarios.

The Phase II monitoring optimization could include the use of several advanced tools:

- The *AFCEE Long-Term Monitoring Decision Support System (LTMDSS)* is a user-friendly software package for designing an efficient long-term monitoring well network for groundwater plumes. This software package can be applied both to natural attenuation situations and to active pumping systems. Using the Mann-Kendall non-parametric test, the LTMDSS evaluates monitoring data from individual wells to determine if plume concentrations are increasing, stable or decreasing. This data can be used to determine overall plume stability and to determine the relative contribution of each monitoring well to the plume monitoring strategy.

- Borehole flowmeters and discrete-level monitoring devices, such as diffusion samplers, are useful for determining the vertical intervals of groundwater flow and of maximum and minimum contamination. This information can be used to redesign extraction wells for optimum plume containment or mass removal and to place monitoring wells at the appropriate interval(s) to monitor remediation progress.

- Monitoring for Site Closure - The Phase II RPO evaluation should determine, with input from responsible regulators, the statistical method to be used to demonstrate that site

cleanup goals have been attained. The monitoring program must be designed to provide the data set that will be required to determine if soil or groundwater has been remediated to cleanup standards.

In many cases, the 95 percent upper confidence limit (UCL) on the mean concentration can be compared to cleanup goals in lieu of maximum concentrations detected on the site. A clear understanding of statistical sampling and data analysis methods will help to determine when active remediation can be terminated at a site. EPA's (1996) *Soil Screening Guidance Document* provides a variety of statistical approaches for sampling soils and comparing results to generic, risk-based soil screening levels (SSLs). Statistical methods for evaluating groundwater remediation are described in the EPA (1992d) publication, *Methods for Evaluating the Attainment of cleanup standards, Volume 2: Groundwater.* This publication describes how monitoring well data should be collected to evaluate progress toward site cleanup goals.

6.7 IDENTIFYING AND ESTIMATING COST SAVINGS

6.7.1 Identifying Cost-Reduction Opportunities

While cost saving is not the only objective of RPO evaluations, cost savings are the natural outcome of more efficiently operated and maintained systems. Recall that remedial system optimization should seek to maximize the protectiveness and risk-reduction of each dollar spent. To accomplish this, the RPO evaluators should:

- Review the major contributors to O&M costs and determine if each expenditure is adding value through increased protectiveness or risk reduction.

- Determine what system improvements will reduce O&M costs or reduce the remediation time frame without sacrificing protectiveness.

- Compare the cost of implementing these improvements to the future cost savings that will be realized.

- Prepare a simple cost-benefit analysis for presentation to funding authorities.

SECTION 7

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APPENDIX A

TCE TOXICITY INFORMATION

THE TOXICITY OF TRICHLOROETHYLENE AND ITS BREAKDOWN PRODUCTS - IMPLICATIONS FOR REMEDIAL DECISIONS AT USAF SITES

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THE TOXICITY OF TRICHLOROETHYLENE AND ITS BREAKDOWN PRODUCTS - IMPLICATIONS FOR REMEDIAL DECISIONS AT USAF SITES

1.0 INTRODUCTION

The purpose of this document is to provide an overview of the important toxicological issues surrounding the regulation of trichloroethylene (TCE) and its natural breakdown products and to offer recommendations on how the remediation of TCE-contaminated groundwater should be addressed based on existing toxicological information. This information should be considered by Air Force and regulatory agencies when establishing or reviewing remedial objectives at TCE-contaminated sites. The document presents a summary of several studies which have attempted to determine if human exposure to TCE has led to a statistical increase in the incidence of human cancer. The primary findings of laboratory toxicity studies on animals exposed to TCE and how these studies relate to human toxicity are also explored. Finally, this document describes the results of several new studies on the potential toxicity of TCE to humans and a discussion of how this data may influence future regulatory standards and risk evaluations involving this compound.

This document is intended for the reader who is interested in gaining a general understanding of the key toxicological issues surrounding TCE and its breakdown products. It is not intended as a thorough review of the complex toxicological issues surrounding this subject.   Another document, *Remediation of Chlorinated Solvent Contamination on Industrial and Airfield Sites* has been prepared for a broader audience and includes other topics such as evaluating TCE exposure pathways, the role of natural attenuation and institutional controls, and alternatives to aquifer pumping. The goal of these documents is to assist Air Force environmental managers in determining the best course of action at chlorinated solvent-contaminated sites.

TCE was widely used as a cleaning solvent by the Air Force and the electronics industry for over 40 years. Prior to environmental regulations, TCE was frequently disposed of in sanitary and storm sewers, disposal pits, and fire training areas at hundreds of Air Force facilities. The Department of Defense (DoD) has identified chlorinated solvents at nearly 50 percent of its 3,212 contaminated waste sites, and TCE appears as a major groundwater contaminant at 35 percent of all DoD sites (USEPA, 1997a). The appropriate regulation and remediation of TCE is a critical issue within the Air Force and Department of Defense environmental programs and has significant long-term financial implications.

Because the U.S. Environmental Protection Agency (USEPA) considers TCE to be a probable carcinogen, a maximum concentration limit goal (MCLG) of zero has been recommended. Since an MCLG of zero cannot be achieved, an MCL of 5 µg/L has been stipulated as the

lowest achievable concentration. The MCL of 5 µg/L was established in the early 1980's based on the lowest concentration of TCE that could be reliably detected in water.

In May of 1995, a group of DoD and EPA toxicologists gathered to determine if there was sufficient information to warrant EPA to complete a new Health Risk Assessment for TCE.   A "TCE Workgroup" was later formed under DOD and USEPA sponsorship. The focus of this cooperative workgroup was to review the latest literature on TCE toxicity and to assess if and how TCE acts as a human carcinogen. The goal of this group was to reexamine risk factors associated with TCE and to recommend changes in the MCL, if appropriate.   A review of several important toxicological studies on TCE that are under consideration are presented in this document. Many of these studies indicate that the risks associated with TCE exposure may not warrant an MCL of 5 µg/L. In fact, several toxicological studies support a risk-based MCL in a range between 50 µg/L and 210 µg/L.

This document is divided into six sections including this introduction. Section 2 reviews the environmental fate and natural attenuation of TCE and the potential human exposure pathways for TCE. Section 3 presents the findings of several epidemiology studies to determine if any link exists between TCE exposure and human cancer. Section 4 describes the metabolic fate and toxicity of TCE and its metabolites in both humans and animals. Section 5 presents information regarding the toxicity of TCE and its environmental breakdown products. Section 6 describes the current regulatory classification of TCE and Section 7 concludes with a summary of key toxicological findings and several recommendations on appropriate remedial actions at Air Force sites contaminated with TCE.

2.0 ENVIRONMENTAL FATE AND EXPOSURE PATHWAYS

2.1 The Impact of Environmental Fate On Risk

TCE is a nonflammable, colorless liquid at room temperature with a somewhat sweet odor. In the Air Force, it was primarily used in metal cleaning and degreasing. TCE is released into the environment during its use as a degreaser or from waste sites where it has been disposed. TCE will rapidly evaporate, but is more persistent in soil and groundwater.

Perchloroethene (PCE) was also used as an industrial solvent by the Air Force, although to a lesser extent than TCE.   PCE is significant in this discussion because in anaerobic aquifers, TCE can be an environmental breakdown product of PCE.   Under anaerobic conditions, TCE continues to breakdown to cis-dichloroethene (c-DCE). Under highly anaerobic conditions, c-DCE will be completely dechlorinated to vinyl chloride (VC) and ethene (ETH). Figure 5.1 in the main document presents a schematic of the breakdown of PCE and TCE in the environment under anaerobic conditions (Semprini, 1995; Cox et al., 1995).

Aerobic aquifers are generally not conducive to the microbial degradation of PCE and TCE. However, an aerobic aquifer will often support the microbial degradation of c-DCE, VC, and ETH to ultimately yield CO_2 and/or hydrochloric acid (HCL) (Semprini, 1995).

The impact of natural attenuation on volatile organic compounds (VOCs) should be taken into account when cleanup levels are determined. If impacted groundwater is currently used as a source of drinking water, cleanup criteria should be protective of current conditions. However, most Air Force TCE-contamination is found in relatively shallow and unproductive aquifers that are not used for drinking water. At these low-risk sites, the potential for natural attenuation of chlorinated solvents should be evaluated before active remediation is pursued. The AFCEE Technical Protocol for Evaluating the Natural Attenuation of Chlorinated Solvents in Groundwater (AFCEE, 1997) has been prepared to assist in this evaluation.

The role of natural attenuation in reducing the toxicity of TCE is described in Borgert et al. (1995). Borgert indicates that in soils, the half-lives of most chlorinated solvents are less than two years, which will result in a 10- to 40- fold decrease in the soil concentrations used to assess the potential effects on receptors over a 25- to 30-year exposure period. Longer half-lives, but significant decreases in TCE concentration have been observed in groundwater at many sites (Wiedemeier, 1999).

2.2 Common human exposure pathways

The majority of TCE in the environment is released into the atmosphere by evaporation from dry cleaning and vapor degreasing operations. Once in the atmosphere, the estimated half-life is approximately seven days, indicating that TCE is not a persistent atmospheric compound. Generally, atmospheric levels of TCE are highest in areas of concentrated industry and population, and lower in rural and remote areas. Workers, especially those employed in the degreasing industry, are likely to be exposed by inhalation to the highest concentrations of TCE (1 to 100 ppmv) (ATSDR, 1995a).

The most likely routes of exposure to TCE for the general population are inhalation of ambient air and ingestion of drinking water. Exposure to TCE in ambient air varies according to location: background levels in the low parts per trillion (ppt) in rural and remote areas, and values in the high-ppt and low-ppb range in urban and industrial areas (ATSDR, 1995a). Given a typical background air range of 100-500 ppt (0.54-2.7 (μg/m3) and a daily respiratory volume of 20 m^3/day, the average daily inhalation of TCE in air is 11-54 μg/day for the moderately active adult.

Between 9% and 34% of the drinking water supplies in the United States have some TCE contamination. In fact, TCE is the most frequently reported organic contaminant in groundwater (ATSDR, 1995a). Affected populations have had an average daily intake of 4 -14 μg of TCE per day (calculated from a typical water concentration of 2-7 μg/L and a consumption of 2 L

water/day) (ATSDR, 1995a). Long-term ingestion of water containing these concentrations of TCE has not been associated with adverse health effects (ATSDR, 1995a).

3.0 EPIDEMIOLOGY STUDIES FOR TCE

Epidemiology measures the risk of illness or death in exposed populations when compared to that risk in otherwise identical unexposed populations.   Unfortunately, chemical exposure has not always been controlled in the work place, and thousands of workers have been exposed to TCE in their industrial jobs. Numerous epidemiology cohort studies have evaluated past human exposure to TCE to determine if these exposures are associated with a statistically significant increase in cancer or other diseases.

Of the 20 studies that have investigated human health effects of TCE exposure, none have found a statistically significant association between TCE exposure and cancer. Table 1 presents an example of several large epidemiological studies completed with cohort groups exceeding 1000 with at least 25 years of followup monitoring.

TABLE 1
EXAMPLE EPIDEMIOLOGICAL STUDIES OF TRICHLOROETHYLENE

Cohort	Number	TCE Exposure	Years of Followup	Reference
Workers monitored for TCE and other solvent exposures	3,089	Inhalation	27	Antilla et al, 1995
Medical records of workers at a TCE plant	1,670	Inhalation	31	Axelson et al., 1994
Workers at Hughes Aircraft since 1950	4,733	Inhalation >50 ppm in one subgroup	42	Morgan et al, 1998
Workers exposed at Hill AFB between 1952 and 1956	14,457	Inhalation and dermal contact	37	NCI, 1997.

Burg et al. (1995) evaluated the National Exposure Registry, focusing on the subregistry for TCE, to assess the long-term health consequences for the general population following long-term, low-level exposures to TCE. The health outcome rates of the TCE Subregistry (4,280 people) were compared with morbidity (disease) data in the 1989 National Health Interview Survey (NHIS) of the general population. Overall, the results do not identify an association between long-term, low-level TCE exposure and adverse health effects, although the need to continue follow-up surveys was emphasized.

Epidemiological studies evaluating potential carcinogenic effects associated with occupational exposure to TCE were also reviewed by Weiss (1995). Four studies were evaluated: NCI (National Cancer Institute) study (Spirtas et al., 1991); Swedish study (Axelson et al., 1994); Finnish study (Anttila et al., 1995) and an earlier Hughes Aircraft study (Wong and Morgan, 1990). These studies suggest a slight increase in the rate of liver cancer, but in all four studies, a total of only 16 cases out of 14,457 (9.5 cases expected) were identified. Thus, the size of the increase was small, and increasing TCE exposure was not associated with an increase in cancer cases (i.e., a dose-response relationship was not established). Only two of the studies reported an increase in kidney cancer (NCI study and Finnish study), with no significant increases reported in the remaining two studies. Rates of lung cancer were not shown to increase in any of the four studies.

In 1997, the NCI published a followup report on the 14,457 workers exposed to TCE at Hill AFB. The report concluded that out of the 5,727 deaths experienced by these workers there was no association between any form of cancer and TCE exposure at any dose. Bogen et al. (1994) and Steinberg and DeSesso (1993) also assessed the results of several epidemiological studies for TCE. It was concluded that none of the studies provided convincing evidence that environmental or occupational exposures to TCE have caused cancer in humans.

In contrast to the results of the studies discussed above, an increased incidence of kidney cancer was observed in workers with occupational exposure to TCE in a cardboard manufacturing factory in Germany (Henschler et al., 1995). Four verified cases of kidney cancer were reported in the exposed group, with no cases of kidney cancer observed in a control group. However, the validity of this study is questionable due to the small cohort group (only 169 people) and its failure to account for a higher general incidence of cancer in this region of Germany.

In 1995, the International Agency for Research on Cancer (IARC) reevaluated the toxicity and carcinogenicity data for TCE. For the analysis, IARC reevaluated the three cohort studies that were considered to be most relevant for TCE carcinogenicity at that time: the Swedish cohort (Axelson et al., 1978, 1994), the Finnish cohort (Antilla et al., 1995) and the United States cohort (Spirtas et al., 1991). Although no significant increase in the incidence of cancer was found in any of the studies alone, the combined results of these studies indicated an excess relative risk for cancer of the liver and biliary tract, with a total of 23 cases observed and 12.87 expected. In addition, a modest excess relative risk of non-Hodgkin's lymphoma was reported with 27 cases observed and 18.9 expected. An increased incidence of kidney tumors was not observed in these cohort studies. Based, in part, on the increased incidence of liver and biliary tumors and non-Hodgkin's lymphoma in the cohort studies, IARC reclassified TCE as a 2A carcinogen (probably carcinogenic to humans).

4.0 TOXICITY STUDIES

In addition to human epidemiology studies, laboratory testing of animals has been used to evaluate TCE toxicity. Animal toxicity data must be extrapolated to estimate human risk factors. This section summarizes some of the similarities and differences in the pharmacokinetics and toxicity of TCE among humans and rodents.

4.1   Pharmacokinetics and Mode of Action of TCE

Pharmacokinetics is the study of chemical disposition within the body over time (the absorption, distribution, metabolism and excretion of a chemical in the body).
Pharmacokinetic studies on TCE have produced varied results among species, which has greatly complicated the determination of risk. For example, a comparison of how TCE is metabolized by humans, rats and mice, suggests that humans have a slower metabolism than mice but a slightly higher rate of metabolism than rats (IARC,1995). The primary site for metabolism of TCE for humans and animals is in the liver, although the exact metabolites, ratio of metabolites, and rate of metabolite formation varies between species (Maull and Lash, 1998). Differences in TCE metabolism make it difficult to predict the carcinogenic impact of TCE on humans based on animal studies. Most significant is the growing evidence that TCE-induced cancer occurs as a result of a threshold exposure, below which no cancer formation is expected. Repeated exposure to low concentrations of TCE may result in the metabolism of TCE with little negative impact on the human body.

The primary target organs for TCE for carcinogenic effects in rodent studies are the liver, kidneys and lungs. Limited studies have also tied TCE exposure to testicular tumors in rats . The target organs, however, differ between species: the liver and lung are targets in mice and the kidney and testes are the targets in rats. In humans, no significant link has been determined between occupational exposure to TCE and the incidence of cancer in any of these organs. The differences in the pharmacokinetics of TCE in rodents and humans may, in part, be responsible for the differences in carcinogenic effects.

Several proposed modes of action are being considered to describe the toxicity and carcinogenicity of TCE on specified target tissues (liver, kidney, lung) (Clewell and Andersen, 1995):

Peroxisome proliferation. Two TCE metabolites, tricloroacetic acid (TCA) and dichloroacetic acid (DCA), have been shown to be peroxisome proliferators, which are a class of chemicals that may cause liver cancer in mice. With the induction of perioxisomes in the liver, the liver is subjected to oxidative stress resulting in the production of reactive oxygen species which have been shown to cause DNA damage and, therefore, may contribute to the carcinogenic process (Rao and Reddy, 1991). While perioxisome proliferation has been associated with tumor production in rodents, this process does not occur in humans and can not be linked to liver cancer in humans.

Genotoxicity. Genotoxic agents directly impact DNA, resulting in mutations that may lead to carcinogenicity. In mice, TCE can be metabolized into choral hydrate (CH) and may induce genotoxicity and tumors in their lungs. In the lungs, Clara cells metabolize TCE to CH, which then may cause tumors via genotoxic effects. Humans are not able to metabolize TCE in the lungs and are not at risk for developing lung tumors. Although choral hydrate (CH) is also formed in the liver, it is rapidly transformed to TCA, and genotoxicity is not considered to be a significant mode of action in the induction of liver tumors (Clewell and Andersen, 1995).

Cytotoxicity. Cytotoxicity is the repeated damage, and death of, cells followed by cell regeneration. The tissue is exposed to repeated damage which leads to cycles of cellular death and regeneration, ultimately resulting in tumors. Experimental data on laboratory rats and mice indicate that one of the primary modes of action of TCE for the induction of cancer is cytotoxicity rather than damage to the DNA (Clewell et al, 1995). The cell damage only occurs following exposure to high doses over a long period of time, indicating that a threshold effect occurs.

Clewell et al. (1995) evaluated TCE using a physiologically-based pharmacokinetic (PBPK) model for tumors in the lung, kidney and liver in rats and mice. The conclusions of this study were that:

1. Carcinogenic target organs differ among species:

> Mouse: Liver and lung
> Rat: Kidney

2. The mode of action in liver cancer appears to be regeneration following cytotoxicity resulting from TCA and DCA (TCE metabolites). Liver tumors were reported in mice, but not rats, exposed to TCE. The greater sensitivity of mice to liver toxicity likely results from an increased metabolism of TCE to TCA/DCA in mice as compared to rats.

3. The mode of action for lung cancer appears to be both cytoxicity and genotoxicity, primarily resulting from metabolism of TCE to CH in lung Clara cells. Lung tumors were reported in mice, but not rats, exposed to TCE. Lung tumors have not been associated with TCE exposure in any human epidemiological study. Clara cells are less prevalent in rats and humans than in mice, which may explain the difference in target organs among species.

4. The mode of action for kidney cancer appears to be exposure to a reactive thiol intermediate that results in both cytotoxic and genotoxic effects in the rat kidney. Kidney tumors have not been reported in mice. Differences in metabolism of TCE to the thiol intermediate between rats and mice appears to be responsible for the difference in the species response. It is unclear how this data can lead to a conclusion that TCE exposure can lead to kidney cancer in humans.

In summary, TCE has been reported to be associated with liver and lung tumors in mice and kidney and testicular tumors in rats following chronic exposure to high doses (ATSDR, 1995a). The differences in target organs among animal species may, in part, be explained by differences in the pharmacokinetics of TCE among these species.   While humans and rodents may produce the same metabolites, they produce them at different rates and in different ratios which will likely have different effects on human tissues.

As described in Section 3, the majority of human epidemiology studies have found no significant link between TCE and cancer in humans. There is little evidence linking cancer induced by high doses of TCE in laboratory animals with humans exposed to low levels in the workplace or in drinking water. Based primarily on the evidence of carcinogenicity in rats and mice, USEPA considers TCE to be a human carcinogen.

Despite these "missing links", human and animal data has been combined by the USEPA to derive provisional slope factors for ingestion and inhalation for human risk assessment purposes.

4.2 Human Risk Estimates Based on Toxicity Data

The study completed by Clewell et al. (1995) reported that the human cancer risk estimates for liver, lung, and kidney tumors obtained for TCE using the PBPK model (with a threshold approach) are less conservative than the risk estimates derived using the provisional USEPA toxicity values (USEPA, 1997b), which assume a no-threshold approach. Depending on the target tissue, the Clewell study indicated that exposure levels associated with an increased excess lifetime cancer risk of 10^{-6}, ranged from 0.35 to 300 ppbv in air (estimate using USEPA toxicity values based on a no-threshold approach is 0.11 ppbv). In water, the Clewell study indicated that 5.6 to 4500 µg/L of TCE could be associated with an increased excess lifetime cancer risk of 10^{-6} (compared to USEPA toxicity value of 3.1 µg/L based on a no-threshold approach estimated a lifetime exposure).   Clewell concludes that the USEPA toxicity values may be lower than necessary to protect human health.

Bogen et al., (1994) used a PBPK model to evaluate the appropriateness of the current USEPA drinking water MCL of 5 µg/L for TCE. Using chemical-specific pharmacokinetic and epidemiological data, the model estimated a value of 210 µg/L in drinking water to be protective of human health. For air exposure, a protective level of 16 ppbv was derived using the PBPK model. Bogen et al. (1994) concluded that the use of this PBPK model was appropriate because TCE carcinogenicity appears to be caused by TCE-induced cytotoxicity, which is likely to have a threshold response. Bogen et al. (1994) also concluded that the current USEPA drinking water MCL value of 5 µg/L may be overly conservative and a higher MCL value may be protective of human health.

5.0 TOXICITY OF TCE BREAKDOWN PRODUCTS

As indicated in Figure 1, c-DCE, VC and Ethene (ETH) are all potential breakdown products of TCE in the environment and should be considered when evaluating the long-term toxicity of a TCE plume. According to the USEPA, TCE and VC are considered to be carcinogenic and c-DCE is considered to be toxic but noncarcinogenic. ETH has not been classified by USEPA for carcinogenicity. A brief discussion of the toxic effects associated with c-DCE and VC is presented below:

5.1 Cis-Dichloroethene

The most likely routes of exposure to c-DCE in the general population are inhalation in air and ingestion of water. Inhalation of high concentrations of DCE (>1000 ppmv in the 1000s) can result in nausea, drowsiness, fatigue, increased pressure inside the head and eye irritation. In studies in rats and mice, longer-term inhalation of c-DCE (100 ppmv to 1000 ppmv) has been reported to result in effects on the liver, lung, and heart. Following subchronic oral exposure of rats to c-DCE (>100 mg/kg-day doses), effects on the blood, liver and kidney were reported. c-DCE has not been reported to result in carcinogenic or developmental effects (ATSDR 1996).

A USEPA Reference Dose (RfD) is available for c-DCE (USEPA, 1995). The RfD of 0.01 mg/kg-day is based on hematogenic effects (decreased hematocrit and hemoglobin) in a subchronic oral study in rats. This value is currently under review by USEPA, but is not considered to be provisional. The federal drinking water MCL of 70 µg/L has been established for c-DCE.

5.2 Vinyl Chloride

Inhalation of VC is uncommon outside of workplaces where VC is used. VC may be ingested in contaminated drinking water, but given its high Henry's Constant, it will rapidly volatilize out of the water as it exits the faucet, and ingestion is unlikely (Easter and Von Burg, 1994). Inhalation of VC while showering with VC-contaminated groundwater may be the most likely exposure pathway for this chemical.

VC is rapidly and completely absorbed through the lungs and the gastrointestinal tract and is metabolized primarily in the liver. Metabolites are excreted in the urine (ATSDR, 1995b). Acute inhalation exposure to high vapor concentrations of VC (8,000 - 20,000 ppmv) results in a feeling of dizziness, giddiness, euphoria, ataxia, headache and narcosis (Easter and Von Burg, 1994; ATSDR, 1995b). Exposure to lower concentrations of VC over longer periods of time has resulted in adverse effects on the liver, nervous system, immune system, and circulatory system (ATSDR, 1995b).

VC has been classified as a carcinogen by USEPA (Class A - human carcinogen), IARC (Group 1 - carcinogenic to humans), MAK (Group A1 - capable of inducing malignant tumors as shown by experience with humans), NIOSH (carcinogen with no further categorization), NTP (Group 1 - known to be carcinogenic), OSHA (carcinogen with no further categorization) and ACGIH (A1 - confirmed human carcinogen) (ACGIH, 1993).

In humans, VC exposure is associated with an increase in the incidence of tumors of the liver, brain, pulmonary, blood and lymphatic system (IARC, 1987; ATSDR, 1995b).

Epidemiological studies have reported a causal relationship between VC exposure and an increased incidence of rare liver tumors (ATSDR, 1995b; Lelbach, 1996). Studies in animals have also reported VC to be carcinogenic (ATSDR, 1995b). VC has been reported to be genotoxic in both human and animal systems (Giri, 1995; Hollstein et al., 1994; Fucic et al., 1995, 1996; Du et al., 1995; Trivers et al., 1995; Zhao et al., 1994).

Clearly, of all of the compounds associated with TCE, VC is the most toxic and deserving of strict regulation in drinking and showering water. EPA has established a Cancer Slope Factor of 1.9 (mg/kg-day)$^{-1}$ and a drinking water MCL of 2 µg/L. Fortunately, VC is often biodegraded in aerobic aquifers before it can migrate to municipal well fields or surface waters. If VC-contaminated groundwater is removed from the aquifer to be used for domestic or commercial purposes, it will rapidly volatilize into air, making inhalation the most likely exposure pathway.

6.0 CURRENT REGULATION OF TCE

There is considerable discussion among professional toxicologists and occupational health specialists regarding the proper classification of TCE as a carcinogen. For example, TCE has been classified as a carcinogen by NIOSH (Group B) and IARC considers TCE to be a Group 2A (probably carcinogenic to humans). ACGIH considers TCE to be an A5 carcinogen (not suspected as a human carcinogen) (ACGIH, 1993).

The IARC and ACGIH classifications were modified over the last several years, but in different directions. The discrepancy between the classifications results from the differing data sets used as the basis of the classification. The following discussion provides a summary of the fundamental differences in TCE classification.

6.1 IARC Classification

IARC evaluates the potential of any agent to cause cancer in humans or animals, even if animals are chronically exposed to high levels of TCE. IARC considered all carcinogenicity data available in both humans and animals and concluded that TCE is a Group 2A carcinogen.

6.2 ACGIH Classification

ACGIH evaluates human data and animal dose-response data available within occupational exposure limits. Because the reviewed epidemiological data were equivocal, and because the animal studies associating TCE exposure with an increased incidence of tumors were not within occupational exposure limits for humans, ACGIH considered TCE a Group A5 (not suspected carcinogen).

6.3 Other Studies

Two workshops (1993 and 1995) have been held to assess the state-of-the-science for TCE (Clewell and Andersen, 1995). Two PBPK models were the outcome of the 1993 meeting, and the results of those models were the topic of the 1995 meeting. The workshops concluded that "It is both possible and desirable to begin a cancer risk assessment for TCE within the next year." It was emphasized that the assessment should focus on liver, lung and kidney tumors in animals and non-Hodgkin's lymphomas in humans.

6.4 USEPA Toxicity Values

Neither IRIS (USEPA, 1998) nor HEAST (USEPA, 1995) provide toxicity values for TCE. The carcinogenic evaluation of TCE was removed from IRIS in 1989 and was never replaced, and is not forthcoming. The provisional values provided by the USEPA (1997b) Superfund Technical Support Center are an oral slope factor of 1.1×10^{-2} (mg/kg-day)$^{-1}$ and an inhalation slope factor of 1.7×10^{-6} (μg /m3)$^{-1}$. These provisional values have been used for quantitative risk evaluation since 1989. The official documentation obtained from the Superfund Technical Support Center does not discuss the basis for these values, but refers to previous USEPA documents (1985 Health Assessment Document (HAD) and 1987 Addendum to the HAD). These values were based on the incidence data for lung tumors in female Swiss mice together with tumor incidence data from other rodent studies (ATSDR, 1995a). A linear, dose-response model (no-threshold model) was used in the derivation of these provisional values. USEPA Regions 3, 6 and 9 provide screening level values for tap water of 1.6 μg/L for an increased cancer risk of 1×10^{-6}. This value is based on the EPA slope factor for TCE that was derived using the conservative, no-threshold methodology.

To date, the USEPA has not come to a consensus regarding an appropriate weight-of-evidence classification for TCE. In 1996, EPA proposed new weight of evidence methodology that will consider the modes of action of carcinogenic agents and the toxicokinetic and metabolic processes when comparing animal toxicity to potential human affects. In addition, new criteria for assessing the adequacy of human epidemiologic studies are provided. The proposed guidelines also require a new approach for relating the dose response of animal studies to the extrapolated dose response in humans. Although the final impact of these changes on the 5 μg/L MCL for TCE is unknown, the proposed changes will allow for consideration of threshold effects which should provide a more accurate and realistic framework for assessing

the toxicity of TCE and other chemicals. (From Federal Registrar Vol 61, No. 79, April 23 1996) .

Because the EPA currently classifies TCE as a carcinogen, the recommended maximum contaminant level goal (MCLG) is zero (USEPA, 1987). As previously discussed, the current drinking water MCL for TCE is 5 µg/L, which is based on the reliable detection limit in water (USEPA, 1987; USEPA,1996). To date, there is no human toxicological evidence that indicates the 5 µg/L MCL is needed to be protective of human health. Adverse human health effects due to exposure to TCE near the MCL have yet to be documented.

6.5 International Regulation of TCE

The World Health Organization established 70 µg/L as a recommended guideline for TCE in drinking water (WHO, 1993). Canada provides a Maximum Acceptable Concentration (MAC) of 50 µg/L for drinking water (Health Canada, 1992; Health Canada, 1998). Based on the lack of conclusive carcinogenicity data, Canada classified TCE as a Group IIIB carcinogen, indicating that it is possibly carcinogenic to humans. This value is based on a No-Observed-Adverse-Effect-Level (NOAEL) of 217 mg/kg-day and a Lowest-Observed-Adverse-Effect-Level (LOAEL) of 393 mg/kg-day for decreased water consumption, enlarged livers and increased urinary protein and ketone levels. The NOAEL value was adjusted by an uncertainty factor of 10,000 (10 for inter-species variability, 10 for intra-species variability, 10 for use of a less than chronic study, and 10 for limited evidence of carcinogenicity) and converted to units of µg/L. The result is a maximum acceptable value of 50 µg/L for drinking water. It should be noted that Health Canada reassessed the TCE carcinogenicity issue in 1997, and again concluded that the value of 50 µg/L is acceptable for drinking water (Health Canada, 1998).

7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

Although there is significant controversy over the toxic effects on humans exposed to low concentrations of TCE, AFCEE believes that existing evidence supports the following conclusions:

- TCE is known to attenuate over time via many destructive and nondestructive natural processes. The impact of natural attenuation should be considered when estimating the concentration of TCE that future populations will be exposed to.
- Vinyl chloride production is a natural step in the degradation of TCE. VC is a known carcinogen and the degradation of VC to ethene should be carefully monitored to ensure that this chemical does not come into contact with humans.
- Epidemiological studies conducted on tens of thousands of workers repeatedly exposed to TCE in the workplace have found little evidence that TCE causes cancer in humans.

- The available toxicity values for TCE are outdated and were based on TCE-induced cancer in mice. The EPA has proposed new methods for evaluating the cancer risk of chemicals which should provide a more rational basis for estimating TCE toxicity. Evidence presented in this paper suggests that the pharmacokinetics, modes of action, and toxicity of TCE in laboratory animals may be significantly different from the expected response in humans. Most significant is the growing evidence that TCE-induced cancer occurs as a result of a threshold exposure, below which no cancer formation is expected. Repeated exposure to low concentrations of TCE may result in the metabolism of TCE with little negative impact on the human body.
- Toxicologists employing threshold response PBPK models and available epidemiological data have estimated that a level of 210 μg/L in drinking water should be protective of human health. The current USEPA drinking water MCL of 5 μg/L was based on the reliable detection limits of analytical instruments not current toxicological data.
- Canada has published a Maximum Acceptable Concentration of 50 μg/L for TCE in drinking water and the World Health Organization has established 70 μg/L as a recommended guideline for drinking water.

7.2 Recommendations

AFCEE recognizes that this document and the following recommendations are based on a limited literature review and that additional and perhaps more definitive recommendations will be forthcoming from the EPA/DOD TCE workgroup review and other toxicological studies. However, based on the findings of this initial literature review there is uncertainty with regards to the appropriateness of the USEPA drinking water MCL of 5 μg/L for TCE. There is a general lack of scientific data linking TCE exposure to the occurrence of cancer in humans. In addition to this conservative statement of cancer risk, most regulatory agencies have incorrectly applied the drinking water MCL as an aquifer cleanup standard to aquifers that are not being used for drinking water and have little potential for future domestic production. This misapplication of drinking water standards has also been cited by the National Research Council (NRC,1993). Finally, current regulations do not adequately account for natural attenuation processes and their long-term impact on risk.

In light of these facts, AFCEE believes that several recommendations are in order to ensure that the intensity and type of remedial actions undertaken at TCE-contaminated sites are appropriate given the unknown toxicity of this chemical and the limited potential for human exposure to contaminated groundwater.

1. Historically, the Air Force position on most TCE-contaminated sites has been to attempt to restore contaminated groundwater to the 5 μg/L MCL. Although the federal MCLs were intended to apply to drinking water "at the tap", this standard has been extended to "potential" sources of drinking water even when the aquifer in question is unsuitable for domestic pumping. Given the lack of toxicological evidence supporting this standard, AFCEE recommends that all TCE-contaminated sites be reevaluated to determine if the 5 μg/L MCL is an appropriate .

Sites where TCE contamination is not threatening drinking water supplies should be considered for less stringent cleanup criteria.

2. For sites with maximum concentrations of less than 200 µg/L, and no evidence of DNAPL contamination, AFCEE recommends that pump and treat systems not be installed unless a natural attenuation study has concluded that the plume is migrating and is within a twenty-year travel distance of leaving the base property (or is already off-base). This recommendation is intended to discourage expensive pump and treat systems (or continued pumping) at sites with dilute concentrations of TCE which pose little risk to on- or off-base populations. (The twenty-year timeframe should allow time for EPA to reevaluate the MCL for TCE.) Pump and treat systems may be appropriate if the TCE-contaminated aquifer is threatening on-base or off-base potable water wells.

3. Sites with active pumping systems which do not meet the above criteria should be reevaluated to determine if there is a need to remediate TCE to the 5 µg/L MCL. If a system has reached asymptotic levels below 50 µg/L, an alternate cleanup standard between 5 and 50 µg/L should be evaluated. This recommendation should be implemented at sites where the impacted aquifer is not used for domestic production. At the relatively few sites where a TCE-contaminated aquifer is currently used for domestic production, AFCEE recommends 5 µg/L remain the cleanup goal until this level is achieved through remediation or the MCL is revised.

4. The final recommendation relates to recent developments in our understanding of the natural biodegradation processes affecting PCE and TCE and their breakdown products, c-DCE and VC. In anaerobic aquifers, PCE and TCE are likely to be degraded to c-DCE and VC. In aerobic aquifers, c-DCE and VC can be further degraded to harmless ethene.   If historical information indicates that VC is being degraded with minimal migration, then natural attenuation, institutional controls, and long-term monitoring may be an appropriate groundwater remedy. At sites with a historical buildup of VC concentrations, and a potential for significant downgradient migration, it may be prudent to pump and treat the PCE/TCE source to remove the potential for future VC formation. The recent emphasis on adding inert hydrogen or carbon sources to enhance reductive dechlorination of PCE or TCE should be carefully evaluated.   This engineered reductive dechlorination should only be attempted at sites where the application can ensure that c-DCE and VC can be biodegraded to ETH without significant migration.

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APPENDIX B

**USEPA WORKSHEET FOR
REDUCTIVE DECHLORINATION POTENTIAL**

EXAMPLE
REDUCTIVE DECHLORINATION SCORING SHEET
SITE 1
ANOTHER AFB, CA

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value	Site 1 Score
Oxygen	<0.5 mg/L	Tolerated, suppresses the reductive pathway at higher concentrations	3	0
	>1 mg/L	VC may be oxidized aerobically	-3	
Nitrate	<1 mg/L	At higher concentrations may compete with reductive pathway	2	0
Iron II	>1 mg/L	Reductive pathway possible	3	3
Sulfate	<20 mg/L	At higher concentrations may compete with reductive pathway	2	0
Sulfide	>1 mg/L	Reductive pathway possible	--	--
Methane	<0.5 mg/L	VC oxidizes	0	0
	>0.5 mg/L	Ultimate reductive daughter product, VC Accumulates	3	0
Oxidation Reduction Potential (ORP)	<50 millivolts (mV)	Reductive pathway possible	1	0
	<-100mV	Reductive pathway likely	2	2
pH	$5 < pH < 9$	Optimal range for reductive pathway	0	0
	$5 > pH > 9$	Outside optimal range for reductive pathway	-2	0
TOC	> 20 mg/L	Carbon and energy source; drives dechlorination; can be natural or anthropogenic	2	1
Temperature	> 20°C	At T >20°C biochemical process is accelerated	1	0
Carbon Dioxide	>2x background	Ultimate oxidative daughter product	1	1
Alkalinity	>2x background	Results from interaction of carbon dioxide with aquifer minerals	1	1
Chloride	>2x background	Daughter product of organic chlorine	2	2
Hydrogen	>1 nM/L	Reductive pathway possible, VC may accumulate	3	--
	<1 nM/L	VC oxidized	0	
Volatile Fatty Acids	> 0.1 mg/L	Intermediates resulting from biodegradation of aromatic compounds; carbon and energy source	--	--
BTEX	> 0.1 mg/L	Carbon and energy source; drives dechlorination	2	2
PCE		Material released	0	0
TCE		Material released	0	0
		Daughter product of PCE	2 [a/]	
1,2-DCE		Material released	0	0
		Daughter product of TCE.	2 [a/]	2
		If *cis* is greater than 80% of total DCE it is likely a daughter product of TCE		
VC		Material released	0	0
		Daughter product of DCE	2 [a/]	0

(Concluded)
EXAMPLE
REDUCTIVE DECHLORINATION SCORING SHEET
SITE 1
ANOTHER AFB, CA

Analysis	Concentration in Most Contaminated Zone	Interpretation	Value	Site 1 Score
Ethene/Ethane	>0.01mg/L	Daughter product of VC/ethene	2	2
	>0.1 mg/L		3	0
Chloroethane		Daughter product of VC under reducing conditions	--	--
1,1,1-Trichloroethane		Material released	0	--
1,2-Dichlorobenzene		Material released	0	--
1,3-Dichlorobenzene		Material released	0	--
1,4-Dichlorobenzene		Material released	0	--
Chlorobenzene		Material released or daughter product of dichlorobenzene	2 [a]	--
1,1-DCE		Daughter product of TCE or chemical reaction of 1,1,1-TCA	2 [a]	--
		TOTAL	**38**	**16**

[a] Points awarded only if it can be shown that the compound is a daughter product (i.e., not a constituent of the source NAPL).

INTERPRETATION OF POINTS AWARDED DURING NATURAL ATTENUATION SCREENING

Score	Interpretation
0 to 4	Inadequate evidence for biodegradation of chlorinated organics
5 to 12	Limited evidence for biodegradation of chlorinated organics
13 to 17	**Adequate evidence for biodegradation of chlorinated organics**
>17	Strong evidence for biodegradation of chlorinated organics