



INTERSTATE TECHNOLOGY & REGULATORY COUNCIL

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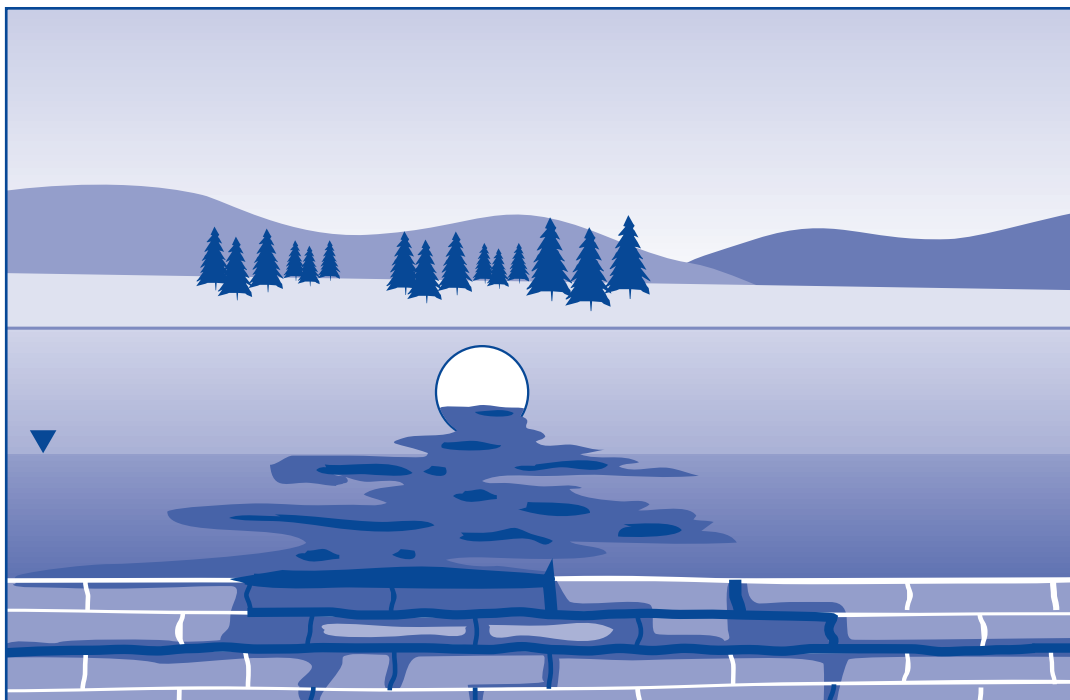


INTERSTATE TECHNOLOGY & REGULATORY COUNCIL



Technology Overview

Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies



June 2000

Prepared by
Interstate Technology and Regulatory Cooperation Work Group
DNAPLs/Chemical Oxidation Work Team

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Established in 1995, the Interstate Technology & Regulatory Council (ITRC) is a state-led, national coalition of personnel from the environmental regulatory agencies of some 40 states and the District of Columbia; three federal agencies; tribes; and public and industry stakeholders. The organization is devoted to reducing barriers to, and speeding interstate deployment of, better, more cost-effective, innovative environmental techniques. ITRC operates as a committee of the Environmental Research Institute of the States (ERIS), a Section 501(c)(3) public charity that supports the Environmental Council of the States (ECOS) through its educational and research activities aimed at improving the environment in the United States and providing a forum for state environmental policy makers. More information about ITRC and its available products and services can be found on the Internet at www.itrcweb.org.

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EXECUTIVE SUMMARY

Because of the mounting interest from ITRC member states in addressing DNAPL contaminant problems, ITRC was asked for input on several sampling and analysis plans commissioned by the Interagency DNAPL Consortium (IDC) as part of its DNAPL demonstration project at Cape Canaveral Air Station in Florida. Initially formed in 1999 to review these documents, the ITRC DNAPL Work Team was expanded to address emerging issues in DNAPL characterization and remediation. The team has prepared this technology overview document to summarize recent developments in this field.

The purpose of this document is to educate regulators and project managers about the DNAPL problem and to spotlight a selection of emerging characterization and remediation technologies for DNAPLs. Traditionally, sites with DNAPL were often dealt with through a ground water containment strategy whereby the recalcitrant source material and/or the resultant plume of dissolved contaminants are physically contained and monitored over the long term to keep them from migrating further. Emerging *in situ* technologies are now being developed that actively target these DNAPL sources for elimination or substantial reduction.

DNAPL Source Characterization. Because the DNAPL source is targeted, additional characterization efforts, focused in the known or suspected source zone, are often needed to go beyond the conventional techniques typically used to delineate a dissolved plume. In addition to modifications of conventional soil and water sampling methods, innovative field characterization methods may in some cases reasonably provide higher reliability in the detection and quantification of DNAPL. Three general types of emerging DNAPL characterization technologies are presented in this document: geophysical techniques (nonintrusive to minimally intrusive); direct push technologies employing one or a variety of DNAPL screening/sampling devices; and *in situ*, large-volume chromatography using chemical tracers.

Geophysical Techniques. Geophysical methods of locating subsurface DNAPL include ground penetrating radar, cross-well radar, electrical resistance tomography, vertical induction profiling, and seismic reflection. Because these technologies do not involve penetrating the suspected DNAPL source zone, they have a conceptual advantage over conventional methods of characterizing DNAPL source zones (e.g., soil borings), in that they do not risk altering the geosystem and disturbing the DNAPL distribution. However, since they rely on properties of the system rather than direct measurements of the contaminated medium, they are subject to numerous interferences and interpretive errors.

Direct Push Probes. Cone penetrometer or direct push probes can be equipped with one or a variety of innovative sensors and/or microsampling devices. These tools may be used to collect *in situ* screening data and/or to sample ground water, soil, and/or soil gas directly, potentially yielding near real-time stratigraphic and contaminant distribution data. Having an array of possible tools to choose from may allow the investigator to customize an application for site-specific conditions. However, as with the geophysical methods, methods employing sensor technologies may be subject to significant interferences and interpretive errors. Furthermore, cone penetrometer/direct push techniques are intrusive and can influence geosystem properties and DNAPL distribution.

Tracer Tests. Finally, *in situ* chemical tracer tests are described, which enable the investigator to map the DNAPL volume and spatial extent, as well as hydraulic properties of the geosystem, based on the measured behavior of contaminant-specific tracers. Such tests are practically nonintrusive, similar to geophysical methods, in that the DNAPL and the source zone geosystem are not significantly altered. In addition, tracer tests contact a large aquifer volume, thus not requiring a large number of samples or measurements to characterize the DNAPL. Finally, these tests do directly contact the DNAPL, thus yielding direct measurement of contaminant mass and distribution. However, tracer tests are complex and costly to perform and require a more thorough understanding of the geosystem up front and, thus, should be used judiciously in a characterization and/or a remedial performance assessment program.

DNAPL Elimination. Emerging *in situ* DNAPL remediation technologies generally fall into one of two categories: extraction or *in situ* destruction. These are briefly summarized.

Extraction. Extraction technologies are primarily intended to effect rapid mass transfer from the immobile residual DNAPL phase into a mobile fluid phase, either a liquid or a gas. The former uses chemicals to enhance dissolution into a mobile aqueous phase for removal, while the latter employs heat to enhance vaporization into a mobile air phase for removal. In both cases, secondary mechanisms may also be involved, such as mobilization of free-phase DNAPL or accelerated chemical or biological destruction of some contaminants. *In situ* flushing, for example, entails the addition of a remediation fluid that can include surfactants or co-solvents, along with other agents such as polymer and electrolytes, to the contaminated zone to lower the interfacial tension between the contaminant and the soil while increasing its solubility in water. This change in phase and control of fluid properties allows the contaminant to be extracted with ground water in an engineered flow field.

The addition of heat to the subsurface likewise effects rapid mass transfer from the residual DNAPL into a gas phase by lowering the DNAPL viscosity and increasing its vapor pressure, making the freed contaminants amenable to conventional vapor extraction methods. Six-phase (electrical resistance) heating and steam injection are two ways of applying heat energy to the subsurface and were developed to address those compounds that are not readily removed with conventional extraction techniques, such as soil vapor extraction, air sparging, or ground water pumping.

To be successful, both these methods share a requirement that the subsurface geosystem be well-characterized and that the remedial system be quantitatively designed so that fluid flow can be controlled, thus capturing the liberated contaminants rather than releasing them into the wider environment. These chemical and thermal extraction technologies are designed specifically for LNAPL and DNAPL removal, and thus these receive the most attention in this review.

Destruction. The second category of *in situ* remedial technology addressed in this review is *in situ* chemical oxidation. Designed and demonstrated to be effective at remediating contaminants dissolved in ground water plumes, the method has also been tried for DNAPLs. The method involves thoroughly permeating a contaminated zone with a sufficient quantity of chemical oxidants, such as hydrogen peroxide, permanganate, or ozone, so that the chemical can contact and fully react with contaminants *in situ*. The advantage of *in situ* destruction is that the process is completed in the ground and no process residuals, requiring further handling or disposal, are formed. However, the reaction occurs in aqueous solution and may be limited by the mass transfer rate from DNAPL to

solution. Oxidants can also be consumed in reactions with other aquifer materials, thus reducing reaction efficiency and potentially requiring much larger amounts of chemical than estimated from simple stoichiometry. Finally, the technique also requires quantitative knowledge of the geosystem properties and DNAPL mass and distribution so that the delivery system can be designed and operated effectively. Because chemical oxidation is primarily targeted at dissolved plumes and is only marginally applicable to DNAPL source zones exhibiting relatively low residual DNAPL saturation, it is treated in summary fashion in this review. Greater detail is provided by a separate ITRC work team focused solely on chemical oxidation for remediation, with a broader view that includes other, more common applications for chemical oxidation.

TABLE OF CONTENTS

ACKNOWLEDGMENTS	i
EXECUTIVE SUMMARY	iii
1.0 BACKGROUND	1
1.1 The Problem of DNAPL Spreading	1
1.2 Problems of DNAPL Detection and Elimination	1
1.3 DNAPL Terminology	2
2.0 EMERGING CHARACTERIZATION TECHNOLOGIES	3
2.1 Geophysical Technologies	3
2.1.1 Ground Penetrating Radar	4
2.1.2 Cross-Well Radar	6
2.1.3 Electrical Resistance Tomography	7
2.1.4 Vertical Induction Profiling	8
2.1.5 High Resolution 3-D Seismic Reflection	10
2.1.6 High Resolution Electromagnetic Resistivity Survey	12
2.2 Direct Push Technologies	13
2.2.1 Soil Probing/Cone Penetrometer-Based Technologies	14
2.2.2 Ribbon NAPL Sampler	16
2.3 <i>In Situ</i> Tracers	18
2.3.1 Partitioning Interwell Tracer Test (PITT)	18
2.3.2 Radon-222	21
2.3.3 Multiphase Multicomponent Equilibrium Partitioning Software for Soil Sample Analysis	22
3.0 EMERGING REMEDIATION TECHNOLOGIES	25
3.1 <i>In Situ</i> Flushing	25
3.2 Dynamic Underground Stripping	29
3.3 Six-Phase Heating™	34
3.4 <i>In Situ</i> Chemical Oxidation	36
3.4.1 Potassium Permanganate/KMnO ₄	37
3.4.2 Hydrogen Peroxide/H ₂ O ₂	41
3.4.3 Ozone/O ₃	45
3.4.4 Safety Considerations	47
4.0 STAKEHOLDER CONCERNS	48
4.1 The Six Principles	49
4.2 Specific Comments on DNAPLs and Remediation Technologies	49
5.0 CONCLUSIONS	51
6.0 REFERENCES	53

APPENDICES

APPENDIX A	Acronyms	A-1
APPENDIX B	Summary of Tribal and Stakeholder Principles	B-1
APPENDIX C	ITRC Contacts, ITRC Fact Sheet, ITRC Product List, and Document Evaluation Survey	C-1

DENSE NON-AQUEOUS PHASE LIQUIDS (DNAPLs): REVIEW OF EMERGING CHARACTERIZATION AND REMEDATION TECHNOLOGIES

1.0 BACKGROUND

One of the biggest challenges to overcome in the field of soil and ground water remediation is the problem of cleaning up sites with dense non-aqueous phase liquids (DNAPLs). As their name suggests, DNAPLs are heavier than water and can be quite difficult to locate and recover once they are released into the subsurface environment. DNAPLs include the common industrial solvents tetrachloroethene (PCE) and trichloroethene (TCE), as well as other hazardous substances like creosote and coal tar. Not ordinarily released into the environment as pure or neat chemicals, DNAPLs are often discharged as spent solvents that contain appreciable fractions of other organic chemicals, such as other dense liquids or light mineral oils. These other components can significantly influence the overall properties of the DNAPL and can both aid detection and complicate remediation. DNAPLs are typically not very soluble in water, and yet some components of DNAPLs are soluble enough to present potential risks to human health or the environment.

1.1 The Problem of DNAPL Spreading

When released in sufficient quantities in the unsaturated or saturated zone, DNAPLs will *actively spread*, primarily due to the influence of gravity, until the point is reached that the free phase is distributed as a discontinuous mass of globules or ganglia, a condition commonly called *residual saturation*. This spreading and ultimate distribution of residual DNAPL is not uniform or readily predictable in the subsurface, as it is responsive to minute variations in pore size distributions due to soil textural variability and soil structure and mineralogy. The residual DNAPL is immobile under normal subsurface conditions, but it can act as a long-term source for continuing dissolution of contaminants into the passing ground water. If, however, the downward movement of a DNAPL encounters low permeability strata in either the unsaturated or saturated zone, lateral spreading can be promoted, and pools or puddles of free-phase DNAPL may even collect along these boundaries. Except in large releases such as may be typical beneath petrochemical plants, pipelines, or tanks that produce, transport or store DNAPL, the latter case of mobile free-phase DNAPL pools is the exception rather than the rule. Thus, investigators usually do not find free-phase DNAPL in soil cores or accumulated in monitoring wells. Based on this lack of observable DNAPL, it is often concluded that no DNAPL is present, when in fact it may be present in substantial quantities at residual saturation, occupying as little as 1 percent of the available pore space to as high as 70 or 80 percent of the total porosity. The classic experiments of Schwille (1988) are helpful to begin to gain an understanding of DNAPL behavior in the subsurface environment. Other helpful references are listed at the end of this document.

1.2 Problems of DNAPL Detection and Elimination

These mechanisms of active spreading, followed by passive spreading through slow dissolution of the DNAPL components into ground water, make DNAPLs difficult to detect and quantify using conventional investigative techniques and even more difficult to eliminate using conventional

extraction technologies. While typical soil gas surveys, soil sampling, and ground water monitoring may effectively enable delineation of the dissolved plume emanating from a DNAPL source and may suggest the possibility that a DNAPL is present, more specialized techniques are often required to locate and quantify the DNAPL source. Similarly, ground water pumping or other methods may contain and recover or treat the dissolved fraction of the contaminant mass, but this fraction can be very small compared to the amount of DNAPL sorbed to soil or pooled beneath the surface of the source area. It can take many years or decades for the majority of the contamination to be recovered by conventional means; thus, cleanup goals can be very difficult to attain when even small amounts of DNAPL are present at a site. Active recovery operations in or near source zones have been aborted at many sites where dissolved ground water concentrations have reached asymptotic levels above the cleanup goals due to the supposed technical infeasibility of recovering more mass by continued pumping.

Because PCE and TCE are carcinogenic and pose unacceptable threats to human health at very low concentrations in ground water, significant efforts are typically expended trying to remediate these types of sites. Traditionally, it was thought that a containment strategy that may have included ground water extraction and treatment was the best way of mitigating the threat since there were no available technologies to address the elimination of residual DNAPL source material. However, new technologies are emerging for finding DNAPL in the environment and for cleaning up DNAPL contamination. This report presents an overview of some of these emerging technologies.

1.3 DNAPL Terminology

To assist in understanding and communicating on DNAPL issues, it is helpful to establish the definitions of certain terms, as well as to identify and correct common misstatements or misconceptions about DNAPL. Key expressions for DNAPL in the subsurface are presented below:

- DNAPL Saturation [S] is the volume of DNAPL per unit volume of pore space.
- Residual DNAPL [S_r] is that held by capillary forces and is not mobile.
- Free-phase DNAPL is mobile and under positive pressure.

Note that, consistent with its name, *dense non-aqueous phase liquid*, DNAPL is a liquid other than water. While this may seem obvious upon thoughtful consideration, it is not uncommon to hear an environmental professional say “dissolved DNAPL” or refer to a “DNAPL plume.” Certainly, a portion of the chemical components of a DNAPL may become dissolved in ground water, and this solution may spread to form a plume; however, this effect is more properly termed “the dissolved plume” and the components called by their specific chemical names, for example, a dissolved VOC plume or a TCE plume.

While this distinction may appear to be merely semantics, the error in terminology often reflects or begets a misunderstanding of DNAPL behavior. Accustomed to dealing with investigations aimed at delineating the nature and extent of a dissolved plume, environmental professionals will often attempt to apply flow and transport principles developed for dissolved contaminants to multiphase DNAPL-water-air-soil systems, where different or additional principles apply.

2.0 EMERGING CHARACTERIZATION TECHNOLOGIES

When contaminants affect soil and ground water, a key question is whether there is a free-phase and/or residual DNAPL source that could sustain a mobile dissolved or vapor plume. A second question follows. If a DNAPL source is suspected or verified, does this source in the given setting represent a continuing, real, or potential risk to receptors, thus requiring source elimination? To answer these questions, conventional site characterization methods may be useful. However, traditional Phase I and II characterizations at the vast majority of sites initially focus almost exclusively on dissolved plume delineation and on the determination if a DNAPL source *may* exist. Few proceed even so far as DNAPL verification. While this level of information may be adequate for a conceptual evaluation of remedial alternatives, it does not provide the analyst with a sufficient basis for detailed remedial alternatives decision-making, nor does it provide the design engineer with a basis for remedial design.

Characterization of both the site geology and the properties and distribution of the DNAPL is extremely important for successful design and implementation of *in situ* remediation technologies for DNAPL (Pope and Wade, 1995). This applies to all types of *in situ* treatment methods, including flushing, thermally enhanced methods, chemical oxidation, bioremediation, and sparging/vapor extraction. Because the hydrogeology of contaminated sites can be very complex, the subsurface DNAPL distribution can be extremely difficult to delineate. Conventional site investigations are typically not designed to investigate DNAPL; thus, environmental site characterization data is sometimes of limited value, especially when it comes to designing *in situ* DNAPL remediation systems. Such data are typically not sufficient to determine the mass, spatial distribution, or properties of the DNAPL and may not adequately determine the aquifer characteristics and how DNAPLs and remedial fluids will migrate in the subsurface.

In situ remedies involving the recovery or destruction of DNAPL depend on accurate knowledge of the geological media or *geosystem* and the spatial extent of contamination. Thus, the DNAPL characterization phase must be focused to more accurately determine the DNAPL volume and extent, as well as relevant geosystem properties. Traditional methods of determining the DNAPL distribution and relevant geosystem properties rely heavily on the use of monitoring wells and soil borings to obtain actual samples for visual inspection or chemical analysis. Direct push technologies have become more common at augmenting conventional characterization methods. An expanding array of innovative drilling and sampling methods, sensors, and noninvasive tests is available for developing a more focused sampling approach. The following sections discuss these emerging characterization technologies. Citations are provided that should guide the reader to additional information concerning each technology.

2.1 Geophysical Technologies

Geophysical DNAPL characterization technologies employ noninvasive methods of locating subsurface DNAPL, avoiding the risk of additional vertical migration of pooled DNAPL and leading to potentially more complete site characterization. Most of the information contained in this section is derived from the Federal Remediation Technologies Roundtable's (FRTR's) December 1998 report summarizing federally funded projects utilizing geophysical techniques to locate DNAPLs. The report is available for download at <http://www.frtr.gov/pubs.html>.

2.1.1 Ground Penetrating Radar

How the Technology Works

Ground Penetrating Radar (GPR) was originally developed as a means of glacier ice sounding and is similar to methods used for subsurface oil exploration. The GPR technique is similar in principle to seismic reflection and sonar techniques. The basic ground penetrating radar system includes a radio transmitter and receiver, which are connected to a transmitter antenna and a receiver antenna located on the surface of the ground.

Pulse mode GPR systems radiate short pulses of high frequency electromagnetic energy into the ground from a transmitting antenna. The propagation of the electromagnetic energy is controlled by dielectric properties in geologic materials. Portions of the radiated energy are reflected back to the radar receiver antenna. Changes in dielectric permittivity of the bulk material will show up in the reflected radiated energy. The reflected signals are amplified, transformed to the audio-frequency range, recorded, processed and displayed. As the unit containing the transmitter and receiver is slowly towed across the ground surface, a continuous cross-sectional “picture” of subsurface conditions is generated. The nonhomogeneous area will be shown on the recorded display.

Electrical conductivity of the soil or rock materials along the propagation paths introduces significant absorptive losses, which limit the depth of penetration. The depth of penetration depends on the soil type, the size of the object, and the material constant. Generally, better overall penetration is achieved in dry sandy soils; reduced penetration is common in moist, clay or conductive soils. The radar frequency selected for a particular study should provide an acceptable compromise between deeper penetration and higher resolution. High-frequency radar signals produce greater resolution but are more limited in depth of penetration. To get accurate information on the depth of signal response, GPR should be calibrated with a core sample.

The primary output information from radar is in a two-dimensional (vertical) profile. These type of data can be immediately interpreted for large subsurface objects; but for more detailed information, it is necessary to use post-processing techniques. By scanning the vertical profiles over the site, a three-dimensional picture can be constructed to better illustrate the overall conditions.

GPR is currently used to identify underground storage tanks, underground utilities, and unexploded ordnance and is used in mineral exploration. Subsurface features, such as soil/soil, soil/rock, and unsaturated/saturated interfaces, can be identified. The presence of floating hydrocarbons on the water table, the geometry of contaminant plumes, and the location of buried cables, pipes, and drums may also be detected. Recently, this technology has been used to attempt to locate DNAPLs; however, the ability to detect DNAPLs consistently and accurately has yet to be determined.

There are two ways to attempt to locate and map DNAPLs with GPR. GPR can be used to assess the natural geologic and hydrogeologic conditions that are controlling ground water flow. For example, when DNAPL is located in fractured bedrock, GPR may be used to determine the most likely location of flow through the subsurface. After the contaminant flow pathways have been identified, direct sampling methods can be used to sample the geologic areas most likely to contain DNAPL. In addition, some DNAPLs (such as PCE and TCE) have dielectric properties. Contaminants with these properties may appear as “bright spots” or anomalies when mapped using GPR, allowing for better delineation.

An investigation by Brewster et al. (1995) was completed in a completely saturated sandy aquifer. PCE was released into the aquifer, and its migration was monitored using GPR and other geophysical methods. Pooling and lateral spreading of PCE on low permeability horizons was observed. The single greatest factor influencing GPR data repeatability was the moisture content of the soil. The highest quality data were produced when the subsurface was the least saturated. The mass of the plume was calculated from radar measurements with an accuracy of 48% to 100%. The study also indicated that the GPR technique was applicable for detecting hydrocarbon pools floating on the water table and also in monitoring their migration.

Limitations of the Technology

- Inability to produce direct readings or measurements.
- Concentration must be fairly high, so may be limited to identifying plume source.
- Observed anomalies must be interpreted based on existing information on subsurface conditions obtained by conventional means.
- Results are highly dependent on soil moisture conditions and soil type, because the radar signal is attenuated by those soils (e.g., clay particles) .

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is a gross characterization technology and is not used to provide quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Dover Air Force Base, Dover, DE

The Groundwater Remediation Field Laboratory (GRFL) at Dover Air Force Base in Dover, Delaware is a national test site. In association with the U.S. Air Force's Armstrong Laboratories, an extensive geophysical site characterization of GRFL was conducted during 1995 and 1996. The main goal of this project was to compare GPR data with data obtained from cone penetrometers, high-resolution seismic data, and soil coring data. Although not used to locate DNAPL, GPR was used to successfully characterize the site geology.

The ground surface is 3.5 acres in size, is grass covered, and consists of minor undulations. Initially, the subsurface was characterized as being relatively homogeneous, consisting of a sandy, fresh-water aquifer with the water table at approximately 8 m. However, further geotechnical work showed the site to possess some heterogeneous properties, including a clay lens, approximately 4 m below ground surface (bgs), located in the north end of the site and an aquitard ranging from 10.5 m to 14.5 m.

The GPR data clearly showed the base of the aquifer at 11 to 15 meters which correlated with the cone penetrometer and seismic data. However, the GPR technology had a more difficult time locating the shallow clay layer at a depth of 4 m using a frequency of 20 MHZ. The clay layer was clearly defined by GPR once the frequency was adjusted to 50 MHZ, which increased the radar resolution.

In addition, a valuable lesson was learned when GPR was used near light towers and fences. The structural properties of these objects reflected the electromagnetic waves emitted by the GPR. As a result, diffraction hyperbolas from such objects appeared in the GPR images.

Overall, the value of GPR data for this site was that it showed the heterogeneous nature of the subsurface. However, GPR does have its limitations, as do other nonintrusive technologies. Therefore, it is recommended that it be used in conjunction with other technologies to establish the geology of the site and that soil coring samples be taken to ensure the proper radar wavelength is used.

2.1.2 Cross-Well Radar

How the Technology Works

Cross-well radar technology is based on the same principle as GPR, but cross-well radar overcomes some of GPR's limitations. It uses antennas that are lowered into sampling wells with a cable. Radar waves are emitted from a transmitting antenna in one well through the ground to a receiving antenna in a second well. The subsurface geology and the pore fluids cause changes in the radar waves. Because the electromagnetic properties of water and DNAPL differ significantly, DNAPL concentrations can be measured by interpreting radar-wave attenuation in the subsurface. However, the DNAPL concentrations must be high for it to have a noticeable effect on the radar waves. Data from cross-well radar systems should be used in conjunction with data collected from dielectric logging to improve data interpretation. Dielectric logging provides detailed information on the geology and pore fluids near the well.

Limits of the Technology

- The technology does not perform as well in the unsaturated zone as in the saturated zone, where the differences in electromagnetic properties of water and DNAPL are discernable.
- The concentration of the contaminant can also be a limiting factor. The concentration must be fairly high, so the technology is often limited to identifying plume sources.
- The distance between the wells strongly influences the effectiveness of this technology. As the distance between transmitting and receiving wells increases, radar wave amplitudes become lower, creating greater difficulty in distinguishing the wave from background noise.

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is a gross characterization technology and is not used to provide quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. M-Area Settling Basin, Savannah River Site, Aiken, SC

Cross-well radar was demonstrated at the M-Area Settling Basin, Savannah River Site, South Carolina. The test demonstrated that cross-well radar could be used to characterize high concentrations of DNAPL in the saturated zone. The wells were 4 to 5 m apart and at various

depths, up to 50 m bgs (the water table was 4 m bgs). Generally, the field-testing, equipment used, and spacing of wells drive the cost of this technology.

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2.1.3 Electrical Resistance Tomography

How the Technology Works

Electrical resistance tomography (ERT), also known as electrical *impedance* tomography, compares the electrical resistivity and phase measurements of materials in the subsurface to distinguish contaminated from noncontaminated soil. The electrical resistivity of a soil is dependent on the soil type, the degree of saturation, and the local geochemistry. An ERT survey is conducted by placing a number of electrodes in separate boreholes. One borehole contains the signal source and a second borehole contains the receiver. The electrical resistivity between the boreholes is then measured and mapped.

ERT is a gross characterization technology and does not provide quantified chemical concentration data. It is effective at mapping leaks from underground tanks, plumes of contamination, and evaluating the effectiveness of remediation technologies. DNAPL can be mapped, because the resistivity of ground water is less than DNAPL, and this difference can be illustrated in ERT displays. These displays are then used to generate a two- or three-dimensional map of the electrical resistance distribution beneath the ground surface.

Limits of the Technology

- Possible adverse effects by steel centralizers in monitoring wells and/or steel well casings. PVC-cased well or open borehole is recommended.
- Possible adverse effects related to pipelines and/or buried power lines located close to borehole. Simple solution would be to relocate technology away from such objects.
- Not as effective in consolidated and unconsolidated rock. Better results in sands, silts, clay tills, etc.
- Unable to differentiate between type of contaminant.

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is used to provide high-resolution site characterization and DNAPL source delineation, not quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Hill Air Force Base, UT

The Lawrence Livermore National Laboratory and Oregon Graduate Institute of Research and Technology used ERT to verify the presence of DNAPLs and monitor DNAPL changes during ground water pumping at Hill Air Force Base, Utah. The removal of DNAPL during pumping produced a drop in electrical resistivity. The ERT difference images provided a two-dimensional view of the zone in which DNAPL was removed from the ground and replaced by ground water over time. ERT implementation costs vary widely with the application. Typically, a 15-array electrode string housed in a single borehole may cost approximately \$1,000. Additional costs include extensive data processing equipment and the installation of monitoring wells if needed.

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2.1.4 Vertical Induction Profiling

How the Technology Works

Vertical induction profiling (VIP), patented by Ground Truth Technology, Inc., is an electromagnetic induction process that provides information about subsurface geophysical conditions. VIP is a minimally invasive surface-to-borehole process that provides a three-dimensional image of subsurface resistivity. Because hydrocarbon and DNAPL contaminants are electrical insulators and displace soil moisture, a resistivity contrast with the indigenous material can be logged by the VIP equipment. The resulting data can be used to develop a three-dimensional model, profiling the lateral and vertical configuration of contaminants in the subsurface.

A continuous vertical electromagnetic (EM) induction profile log is made with surface-to-borehole hardware consisting of an EM transmitter on the surface and tuned receiver placed down a borehole. The transmitter component is placed at each measurement location, and an offset induction log is recorded in the nearby drill hole. The receiver in the probe moving up the drill hole measures the primary and the secondary electromagnetic fields produced at the transmitter location. The large, long wavelength response is due mostly to the primary electromagnetic field. Superimposed on this larger response is a shorter wavelength response, mostly related to the secondary electromagnetic fields caused by eddy currents moving around the boundaries of resistivity contrasts in the earth. These raw data are computer processed to remove the primary field and calculate and verify the secondary

fields. The secondary fields are converted to apparent resistivity to compare directly with the physical properties of the soils. Contour maps of resistivity measurements are used to track geologic patterns and trends and to delineate the configuration of plumes.

Limits of the Technology

- Adversely affected by steel centralizers in monitor wells and will not function in steel cased wells (PVC casing or open hole only).
- Adversely affected by cathodic protection on pipelines and buried power lines when in close proximity to the downhole receiver. (Solution is to simply locate holes away from such interferences.)
- Not a panacea or stand-alone process, so it must be calibrated to hard data.
- Less effective in consolidated and unconsolidated rock than in sands, silts, clay, and tills.
- Cannot differentiate between type of contaminant (e.g., petrochemical vs. diesel fuel).

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is used to provide high-resolution site characterization and DNAPL source delineation, not quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Kelly Air Force Base, TX

VIP was used as a site assessment tool at a site contaminated with petroleum fuels and other contaminants at Kelly AFB, Texas. The objective of the project was to evaluate the VIP technology developed by Ground Truth as a tool to locate subsurface contamination. The Kelly AFB demonstration compared the model results to other subsurface assessment methods and subsequent samples analyzed from monitoring and recovery well installations. The results of the demonstration are featured in a report by the Southwestern Research Institute (SwRI) of San Antonio, Texas entitled, “Third Party Evaluation of Surface Induction Profiling and Vertical Induction Profiling Geophysical Methods for Use as a Site Assessment Tool at a Release Site on Kelly Air Force Base, Texas” (June 1996).

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II. Voluntary Cleanup Site, Melville, NY

A VIP survey was conducted by Ground Truth at a voluntary cleanup site to determine whether areas of hydrocarbon contamination (TCE) existed beneath a building foundation, as was long suspected. The survey consisted of 79 VIP soundings and loggings of natural gamma-rays in 18 monitoring wells. The VIP survey was performed over a 12-day period in September 1999. Based

on the gamma-ray logs, the lithology of the site is heterogeneous, comprised mostly of sand and gravel with some silt and/or clay “stringers.” The VIP survey detected a significant anomaly originating inside the building and extending near vertically to approximately 80 ft bgs. This “stove-pipe” shaped anomaly is indicative of a past release of fluids unnatural to the area from inside the building. Another area of VIP anomaly, though not as significant, was near the loading dock.

These findings were used to direct the collection of actual soil and ground water samples from beneath the building to confirm the resistivity patterns observed. A total of eight direct push probes and five angled borings were advanced both inside and outside the building. Based upon the results of the verification sampling, the VIP technology was useful in locating suspected areas of contamination, although some areas identified by VIP as being likely sources of contamination turned out to be only minimally contaminated. In samples collected below the water table, VIP results were generally confirmed by analytical data, and two of the water samples contained NAPL.

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2.1.5 High Resolution 3-D Seismic Reflection

How the Technology Works

High resolution, three-dimensional seismic reflection imaging uses seismic waves to detect materials with different densities at depths of 3 to 3,000 ft bgs. The technology principal is that when an impact is introduced at the surface, acoustic waves will spread throughout the subsurface until they are bounced back (to the surface) when material with different acoustic impedance is encountered. The travel time of these acoustic waves is used to determine the depth and thickness of subsurface features. The technology does not specifically detect DNAPLs, but it can detect fractures and channels that serve as preferred pathways for DNAPL migration after a spill. From this, a site-specific geologic model can be generated for the site. To construct an accurate model, additional pieces of information must be reviewed and incorporated, including previous studies or reports on the facility and its history, regional geology and tectonics, and site-specific hydrology and contaminant distribution. This background work and geologic fieldwork must be completed before geologists can properly interpret the seismic data.

There are a couple of methods that can be used when deploying seismic reflection surveys, which differ by how the seismic source and receivers are placed. In one method, a seismic source and a number of receivers (geophones) are placed on the surface. The source is activated and the refracted sound waves are collected on the surface and recorded with a seismograph. When correlated with available stratigraphic data, the time-distance information makes it possible to map the depth of the water table, clay lenses, and confining layers. In the second method, the source is placed in the bottom of a borehole. The seismic source is activated, and the response to the seismic waves generated is measured by geophones placed in boreholes at known distances from the source. The

data are then recorded with a seismograph. The geophones are moved up the borehole 10 feet, and the process is repeated.

After the data are collected, they are processed in the field and interpreted in a processing center to develop a three-dimensional model of the subsurface. This model is then used to delineate the subsurface stratigraphy and identify pathways of potential contaminant migration. Like all geophysical techniques, confirmation samples should be collected to verify the results of the seismic model.

Limits of the Technology

- The technology does not specifically detect DNAPLs; it merely detects fractures and channels that may serve as preferred pathways for DNAPL migration.
- Spatial resolution may preclude use to delineate DNAPL in ganglia configurations.
- Not a panacea or stand-alone process, so it must be calibrated to hard data.

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is used to provide high-resolution site characterization and DNAPL source delineation, not quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Naval Air Station North Island, CA

Resolution Resources Incorporated performed a two-dimensional and three-dimensional resolution seismic reflection survey at Naval Air Station North Island, California. The Navy estimated it would cost \$2 million for site characterization on a 40-acre site using soil borings. The seismic survey was used to verify the presence of fractures, clay lenses, confining layers, and other stratigraphic features to determine areas of likely DNAPL pooling.

The seismic data found a discontinuous clay layer 35 to 40 ft bgs and a confining layer 100 ft bgs. Temporary wells were drilled into the discontinuous clay layer, and no DNAPL was found. Additional borings indicated that the DNAPL plume was located at the lower confining layer at 100 ft. The information from the seismic survey was used to optimize the remedial system design and placement. The cost of the seismic survey was \$250,000.

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2.1.6 High Resolution Electromagnetic Resistivity Survey

How the Technology Works

The electromagnetic resistivity (EMR) survey uses an above-surface source coil to induce a low frequency magnetic field. The source coil transmits a long wavelength/time-varying magnetic field signal into the ground. An EMR receiver is located in a well hole and measures magnetic field flux signals. The signals are continuously emitted, and the receiver records voltage measurements at 0.1-ft intervals from the near-surface to the bottom of the well (up to depths of 300 ft). The process is repeated with the source coil situated at other grid points, with the ability of locating the coil up to 300 ft away from the well.

The surveys serve to identify high resistivity anomalies. These anomalies are representative of locations that may contain DNAPL. The reasoning behind this assumption is based on the difference in resistivity between the contaminant and the surrounding medium (DNAPL having a higher resistivity than the surrounding soil).

Advantages of the Technology

- Can be used in metal buildings.
- May be deployed over steel-reinforced concrete or asphalt floors, highways, and runways.
- When properly floated, can be used over water.
- Can be used to monitor remediation operations (before and after surveys).
- Ability to tune transmitter and receiver allows for technology to be used in, over, and around structures with extreme electrical noise.

Limits of the Technology

- Requires an in-depth review of all subsurface geology and hydrogeologic data to ensure proper interpretation of surveys.
- Receiver well should not be located in contaminated area. Placement of receiver in uncontaminated media will provide a better background level or baseline for comparing resistivity levels.
- May only identify 60 to 80 percent of the plume due to complex subsurface lithology.

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is used to provide high-resolution site characterization and DNAPL source delineation, not quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Whiteman Air Force Base, MO

Whiteman Air Force Base used the technology four times and realized a cost savings of \$6,000 to \$30,000 per project. A DNAPL plume at a small-to-average site (800 to 1000 square ft) can be defined in less than two weeks compared to traditional methods, which might take up to seven weeks. The technology identified the plume from a leaking oil/water separator and enabled the remediation contractor to complete the site cleanup under budget. The 7-ft-diameter plume was located within 1 ft of a building, 3 ft from an electrical transformer and 12 ft from a mature tree.

The EMR technology eliminated the “guess and dig method” to remove the plume.

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II. Alameda Naval Air Station, CA

The technology was used at Alameda Naval Air Station in California without much success, however. The EMR method did not detect any DNAPL, despite the fact that over 500 gallons of mixed NAPL (DNAPL and LNAPL) were subsequently recovered from the area surveyed.

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2.2 Direct Push Technologies

The emerging DNAPL site characterization technologies reviewed in this section are termed *direct push*, because the tools or probes that penetrate the subsurface are deployed relatively quickly (using hydraulic rams or percussion hammers) and are withdrawn once the required data are collected. Direct push technology (DPT) describes a variety of methods for obtaining subsurface data in a quick, minimally invasive manner. With a few modifications, these direct push tools can also be used to screen or quickly assess the extent of ground water and soil contamination present at a contaminated site.

The DPTs discussed below are based on commonly used systems like percussion soil probing machines (Geoprobe systems) and cone penetrometer-based systems, which are quick, cost-effective means of opening up holes into the subsurface through which various sampling devices or sensors are deployed. These sampling devices can provide continuous, real-time information on soil stratigraphy and contaminant distribution, as well as extract ground water and core samples for *ex situ* analysis. Direct push technologies are also being used in conjunction with flexible membranes fitted with absorbent liners to detect DNAPL directly.

2.2.1 Soil Probing/Cone Penetrometer-Based Technologies

How the Technology Works

The cone penetrometer is an example of a direct push tool traditionally used in the civil engineering

field for cone penetration testing (CPT) and adapted for the environmental field. CPT is an expedient method for stratigraphic profiling and developing soil engineering parameters for geotechnical design. Standard cone penetrometers collect stratigraphic information using embedded sensors to measure cone tip pressure and sleeve friction. The ratio of the tip resistance to the sleeve friction provides information that can be used to classify soil type.

The typical CPT system consists of a vehicle-mounted hydraulic ram which forces a steel probe (cone) into the ground. Figure 2 shows a typical vehicle-mounted cone penetrometer system. The data acquisition system uses electronic signal processing equipment and a computer to store and process data. Penetration rates are typically 40 to 50 ft/hr but can be as high as 200 ft/hr (DOE EM-50, 1996). ASTM standards (D 3441-86) require 2 cm/sec as the maximum push rate for data collection. Measurements are conducted at the cone portion of the penetrometer probe. The electronic circuitry inside the steel cone is the heart of this device. Many different state-of-the-art line sampling and instrument devices/tools can be deployed on cone penetrometers and soil probing equipment (discussed in more detail below).

A cable (wire or fiber optic) runs from the probe through the center of the rod string to the data collection system in the vehicle. The type of cable used to transmit data will depend upon the type of sensor and contamination. In addition, the hollow stem of the drill string and a hole in the tip allow grouting of the hole as the drill string is removed.

A variety of tools can be deployed in conjunction with DPT probes. Generally, all of the cone penetrometer-based devices are capable of measuring standard stratigraphic parameters (e.g., tip stress, sleeve friction, pore water pressure). Depending on the contaminant and site-specific geology, more specialized parameters may also be measurable. Several DPT configurations are available; those potentially applicable to DNAPL investigations are outlined below.

Core sampling

These devices gather core samples, which are retrieved/extracted for analysis. Some devices allow for a single sample to be gathered at a desired depth (e.g., split spoon sampler), while others allow for multiple samples to be obtained at various depths. These samples are used to define the three-dimensional characteristics of the contaminant plume. Current research is developing a wireline system, which will allow samples to be retrieved while the CPT is deployed, rather than having to retrieve and deploy the entire sample rod/case.

Seismic

These devices are used to measure compression and shear waves. The waves are generated by an aboveground source and are detected by geophones located within the probe. The recorded data are used to generate a profile of seismic wave speeds, damping characteristics, and soil strength parameters.

Laser Induced Fluorescence

Laser induced fluorescence (LIF) is a site characterization technique for detecting petroleum products containing aromatic hydrocarbons in soil and can not be used to detect chlorinated solvents directly. The sensor, located within the probe, consists of a laser coupled with an optical detector to measure fluorescence via optical fibers. Ultraviolet or laser light passes through a sapphire window in the probe. As the light passes through the soil, it excites some of the chemical bonds that make up the organic contaminants, and a sensor in the probe detects the fluorescent response.

Although LIF has primarily been used to locate petroleum-related compounds, which are less dense than water (i.e., LNAPLs), several investigators have documented indirect location of DNAPL source zones by identifying commingled fluorophores (Kram, 1998). Fluorescence excitation and emission spectra are collected and analyzed. Although DNAPL themselves do not fluoresce at standard excitation wavelengths, organic matter or co-contaminants that do fluoresce can leach preferentially into DNAPL. Thus, the fluorescence is used to infer the presence of DNAPL.

Below is a list of devices that utilize this technology in different ways to identify specific contaminant properties along with the standard CPT parameters:

- Rapid Optical Screening Tool (ROST), a tunable laser system
- Site Characterization & Analysis Penetrometer System (SCAPS), which uses a pulsed nitrogen laser
- Raman system, which involves simultaneous measurement of multiple wavelengths

Electrical Resistivity/Domain Reflectometry

These devices take advantage of the relationship between the soil dielectric constant and moisture content. The soil moisture content is determined by measuring the frequency shift of a high frequency excitation signal as it passes through the soil. The frequency shift is referred to as the resistivity. This concept is being used to characterize contaminated sites by using the difference in electrical resistivity between contaminated and uncontaminated soils. There are a few devices that have been designed to facilitate this concept.

Vision Cone Penetrometer

The vision cone penetrometer (V-CPT) consists of an electronic cone penetrometer fitted with one or two miniature video cameras and a lighting system that allows the investigator to visually observe the soil as the push probe is advanced. The V-CPT system provides continuous recording of the soil stratigraphic column at very high resolution. The unit can detect anomalous clay lenses, fissures and sand seams and has the potential to detect DNAPL globules.

Membrane Interface Probe

The membrane interface probe (MIP) is a tool developed by Geoprobe® Systems for logging VOCs in subsurface soils. A thin film membrane is impregnated into a stainless steel screen on the face of the direct push probe and is heated to 100–120° C. The volatile contaminants diffuse across the permeable membrane into the carrier gas line. The carrier gas (typically nitrogen) transfers the contaminants to either a photoionization detector (PID) or flame ionization detector (FID) at the surface. The real-time log also provides a depth/speed graph, electrical log of the formation, and temperature log of the heated sensor.

Advantages of the Technology

- DPT is generally faster and more cost-effective than conventional drilling and sampling.
- DPT sensors allow detection *in situ*, minimizing sampling technique errors.
- A complete, real-time profile can be created from the ground surface to the depth of penetration, identifying important layers that may be missed in an interval sampling approach.
- DPT is a minimally invasive approach to site characterization, minimizing potential cross contamination in environmentally sensitive areas.
- Drilling waste is virtually eliminated, resulting in potentially significant hazardous waste disposal cost savings.
- Significant reduction of exposure to potentially hazardous material, providing increased worker safety.

Limits of the Technology

- Above ground conditions (e.g., extremely muddy conditions, uneven terrain) may prohibit the emplacement of DPT equipment.
- Site-specific subsurface conditions (e.g., bedrock, boulders, wet soils, clay-rich soils) may inhibit the sampling or deployment of certain DPT devices.

Regulatory Concerns

There should be no regulatory concerns with the application of the technology. The technology is used to provide high-resolution site characterization and DNAPL source delineation, not quantified concentration data. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

2.2.2 Ribbon NAPL Sampler

How the Technology Works

The Ribbon NAPL Sampler (RNS) is a continuous, direct sampling device that can provide detailed depth discrete mapping of NAPLs (liquid solvents and/or petroleum products) in a borehole. This NAPL characterization technique uses a flexible membrane system consisting of an impermeable liner and an exterior covering on the liner which reacts with pure product (e.g., NAPL and DNAPL) to form a bright red dye stain on a white background. The pressurized liner forces the reactive cover tightly against the borehole wall. The reactive ribbon is recovered from the hole by inverting/peeling the liner from the hole. In this manner, the reactive ribbon does not touch the hole wall anywhere else as it is removed. The reactive ribbon can then be examined for the presence and extent of layers, and even globules, of NAPL in the subsurface as indicated by brilliant red marks on the ribbon. RNS can

be deployed relatively inexpensively with direct push or traditional methods for mapping of NAPLs and DNAPLs in both the vadose and saturated zones to identify source regions.

Advantages of the Technology

- The technology's design eliminates the mixing of sampling zones.
- The technology can be deployed in almost all types of geology.
- Continuous, direct sampling of DNAPLs and LNAPLs.
- Immediate field results for NAPL location.
- Minimal waste generated.
- Easy and inexpensive.

Limits of the Technology

- Deployment maybe difficult if borehole contains large cobbles or if the hole has a tendency to collapse.
- Unlike some other colorimetric tests, there is no way to estimate concentrations based on color gradation. The test is simply positive or negative for the presence of NAPL.
- Membrane must be in contact with NAPL.
- Works for pure phase hydrophobic contaminants only.

Regulatory Concerns

Regulatory concerns are a function of where the technology will be used, the nature of contamination, and the intended application of the technology. Regulators may be concerned with cross-contamination of absorbent pads unless they have seen a demonstration of the technology and may have specific requirements pertaining to confirmatory samples, borehole installation, well/borehole permits, and borehole sealing.

Site(s) Where Implemented

The Ribbon NAPL Sampler has been successfully deployed in both the saturated and vadose zones at a number of sites. The sampler has been deployed to a maximum of 70 ft using CPT, with greater depths attainable. Deployment methods are being developed for thin-cased drilling methods and fractured rock.

I. McCormick and Baxter Superfund Site, CA

The U.S. Army Corps of Engineers (Corps) utilized the RNS at the McCormick and Baxter Superfund Site in California. Three ribbon systems were emplaced by a Corps cone penetrometer rig. The RNS provided valuable information for the McCormick and Baxter team regarding the NAPL conceptual site model. Data collected with the RNS indicated that NAPL was present as small discrete globules. The RNS data was generally in agreement with SCAPS LIF data collected in collocated holes.

Other sites where the technology has been implemented include

- DOE Savannah River Site, Aiken, SC
- DOE Paducah Gaseous Diffusion Plant, Paducah, KY
- Cape Canaveral Air Station, Launch Complex 34, FL

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2.3 *In Situ* Tracers

In situ tracer tests are used to locate residual NAPLs by measuring changes in the concentrations of specific chemicals called tracers, which are either injected into the subsurface or are naturally present in the geosystem. These chemical tracers are effected by the presence of NAPL in the subsurface, and the resulting concentration gradients can be correlated to zones of residual NAPL. This technology is primarily for quantifying residual NAPL. Free-phase NAPL removal is usually recommended prior to injecting tracers. This section describes three emerging *in situ* techniques that employ such chemical tracers.

Appropriate use of *in situ* tracers requires adequate knowledge of the geosystem and solute migration pathways prior to designing and initiating a test. It is important to be able to predict the behavior of injected tracer chemicals prior to the test so that the information obtained can be evaluated in the context of an existing conceptual model of the site. Thus, like the majority of characterization technologies discussed in this document, a good set of preliminary site characterization data is needed up front to make design level estimates of DNAPL volume and distribution.

2.3.1 Partitioning Interwell Tracer Test (PITT)

How the Technology Works

The Partitioning Interwell Tracer Test (PITT) was developed by Dr. Gary A. Pope at the University of Texas in the early 1990's. The technology was developed from a predecessor that had been used to measure residual oil saturation distributed in water-flooded oil well fields. Dr. Pope and colleagues modified the method to determine the residual oil saturation, swept pore volume, and the total volume of heterogeneously distributed DNAPL. Further application of PITT technology to the environmental field was developed in conjunction with Dr. Richard Jackson of Duke Engineering and Services.

The technology involves the injection of a suite of tracers into the zone of contamination. A portion of the suite is “nonreactive” while the other portion is “reactive.” The nonreactive or *conservative* tracers tend not to react with the NAPL and, therefore, travel unhindered through the zone of contamination. The reactive or *partitioning* tracers have an affinity for the NAPL and, therefore,

attenuate (become slowed or retarded) as they travel through the contamination zone. Due to the varying natures of the two types of tracers, the time it takes for each to appear at the monitoring or extraction well will differ. The type of tracer to be used will vary depending upon the specific contaminant and zone of contamination. In the unsaturated zone, the tracers employed are gases, whereas liquid tracers are used in the saturated zone (Meinardus et al., 1998). Long-chain alcohols and fluorocarbons have been shown to work favorably in the saturated zone (Jin et al., 1995). For the vadose zone, perfluorocarbons have accomplished the same favorable results (Whitley et al., 1997).

The technology is much like a large-scale application of chromatography. The measurements that are taken allow for the volume and percent saturation of the contaminant to be formulated. The amount by which the partitioning tracer is delayed is assumed to be proportional to the saturation of NAPL in the porous media (Payne et al., 1998). Simultaneously, the injection and monitoring of the tracers permit a retardation factor to be calculated, which is directly related to the *in situ* contaminant mass within the targeted zone. Thus, chromatographic separation (concentration as a function of travel time) of the tracers due to this partitioning is used to measure the volume of DNAPL in the interwell zone (Meinardus et al., 1998) and can be mathematically translated into contaminant mass estimates.

PITTs require establishing a forced gradient flow-field between the point of injection and extraction, where ground water serves as a carrier to transport tracers across the zone of investigation. Therefore, a Conservative Interwell Tracer Test (CITT) may be conducted prior to the PITT. CITTs provide empirical data for the PITT design, contribute to the understanding of the hydrogeologic system, and afford the opportunity to refine tracer test procedures (Meinardus et al., 1998).

PITT technology is a useful tool not only to quantify and locate residual DNAPL contamination, but also to assess other technologies. When coupled with an *in situ* flood or flush, a PITT test completed prior to and upon completion of a flood/flush can provide an estimate of the fraction of contaminant removed and the volume remaining.

Limits of the Technology

- Ability to extract and/or monitor tracers may be difficult due to complex geologic properties.
- Requires adequate understanding of geosystem prior to test.
- May require treatment of extracted tracer solution.
- High organic matter may impede travel of tracers, affecting the residence time and skewing the estimated retardation factor of the contaminant.
- Contaminants located in areas of low permeability may not be accurately measured.
- Not appropriate for quantifying free-phase DNAPL. Removal of free-phase DNAPL is usually recommended prior to injecting tracers.

Regulatory Concerns

The ability to hydraulically control and recover the tracers may be of concern to some regulators. Normally this will not be an issue as long as the tracers do not have toxic or hazardous properties. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Hill AFB, Operable Unit 2, UT

From 1967 to 1975, Hill AFB - Operable Unit 2 (OU2) was used to dispose of unknown quantities of chlorinated organic solvents from degreasing operations. These DNAPLs, primarily TCE, were placed into at least two unlined disposal trenches. These trenches were underlain by an alluvial sand aquifer, consisting of a heterogeneous mixture of sand and gravel, and is contained in a buried paleochannel eroded into thick clay deposits.

Before initiating the PITT, source water was injected while pumping at the extraction wells to establish a steady-state flow field. Once the partitioning coefficients were determined, partitioning tracer column studies were conducted with OU2 DNAPL and sediment. First, several partitioning tracer experiments were performed in the uncontaminated alluvium to determine if there was any retardation due to organic material in the sediment. Next, partitioning tracers were used to determine known residual DNAPL saturation in the contaminated sediment. Independent estimates of the amount of residual DNAPL present were also calculated using both a mass balance and a volume balance. The partitioning tracer estimates of residual DNAPL saturation coincided with volume and mass balance estimates.

All of the tracer curves acquired were analyzed using the method of temporal moments (Jin et al, 1995). The partition tracers were retarded with respect to the conservative tracer indicating that substantial quantities of DNAPL existed. The PITT estimated the residual DNAPL amount in the test area prior to remediation to be 346 gallons. The post-remediation PITTs indicated that the total amount of DNAPL recovered was 341 gallons. Based on the success of these PITTs, the U.S. Air Force will look to conduct additional large-scale PITTs to characterize the entire DNAPL zone at OU2.

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2.3.2 Radon-222

How the Technology Works

Radon-222 (^{222}Rn) is a naturally occurring, chemically inert radioactive gas resulting from the decay of Uranium-238 (^{238}U), which is present to some extent in any aquifer as a dissolved gas in the pore fluid. In the absence of NAPL, the ^{222}Rn concentration quickly reaches a site-specific equilibrium value. In the presence of NAPL, however, the ^{222}Rn concentration is greatly reduced due to preferential partitioning of ^{222}Rn into the NAPL phase. It follows that ^{222}Rn concentrations in regions containing NAPL are reduced in comparison with those data obtained from adjacent areas that do not contain NAPL.

A simple equilibrium model can be used to illustrate the partitioning process and the resulting ^{222}Rn deficit (Semprini et al., 1993):

$$\frac{C_{\text{NAPL}}}{C_{\text{bkgd}}} = \frac{1}{1 + S_{\text{NAPL}}(K - 1)}$$

- where
- C_{NAPL} = ^{222}Rn concentration in ground water from a NAPL contaminated region (pCi/L);
 - C_{bkgd} = ^{222}Rn concentration in ground water sampled from an adjacent NAPL free region (pCi/L);
 - S_{NAPL} = Residual volumetric NAPL saturation (L/L); and
 - K = NAPL:water ^{222}Rn partition coefficient ($[\text{pCi/L}_{\text{NAPL}}]/[\text{pCi/L}_{\text{Water}}]$).

This model predicts that as the residual NAPL saturation increases, the ^{222}Rn concentration within the NAPL-contaminated zone will decrease compared to ^{222}Rn levels in background samples. In addition to characterizing the presence of NAPL, the effect of remediation can be gauged by monitoring ^{222}Rn concentrations in the treatment region with increasing ^{222}Rn concentrations, providing a quantitative estimate of the NAPL removed during remediation.

Limits of the Technology

- Obtaining accurate measurements of ^{222}Rn concentrations in ground water requires specialized sampling and analytical procedures beyond the scope of most conventional ground water investigations.
- Obtaining a site-specific value of the NAPL:water ^{222}Rn partition coefficient is extremely difficult, resulting in a decrease in the accuracy of the model if a non site-specific values are used.
- Requires adequate understanding of geosystem and background ^{222}Rn concentrations prior to test.
- As with any new characterization technique, an extensive database with which to compare results does not exist.
- Radon concentrations must be fairly homogeneous throughout the contaminated area. In areas where there might be a highly variable quantity of radon, such as areas with radioactive waste or natural uranium deposits, the technology may not be as accurate.

Regulatory Concerns

It is not anticipated that there should be any regulatory concerns with the implementation of this technology. Since ^{222}Rn is already present in the subsurface, there will not be a need to inject any materials into the subsurface. As with any field-screening technology, state regulatory technical requirements may limit the acceptance of field data or require a percentage of confirmation laboratory data utilizing conventional sampling methods.

Site(s) Where Implemented

I. Building Complex 834, Lawrence Livermore National Laboratory, Site 300, Livermore, CA

This technology was developed through the successful implementation of several small-scale laboratory and column studies. To date this technology has been successfully applied at the field-scale at the Building 834 Complex, Lawrence Livermore National Laboratory Site 300. Past operations at this facility have led to the subsurface being heavily contaminated with various NAPLs, including PCE, TCE, BTEX, and diesel fuels.

At the Building 834 Complex, a 17-well survey was conducted. Monitoring of these wells revealed a variation greater than two orders of magnitude (a low of 8 pCi/L to +/- 1500 pCi/L). Lower ^{222}Rn concentrations were measured around a diesel fuel storage tank (an area where known leaks have occurred) and around a drainage ditch (an area known to have collected surface TCE spills). Monitoring results revealed a strong correlation between the 'presence of' and 'amount of' NAPL to the measured levels of ^{222}Rn , when compared to the ^{222}Rn background levels in noncontaminated areas.

Results from this experiment concluded that qualitative and quantitative measurements of present residual NAPL can be determined by ^{222}Rn deficits in pore fluids, within NAPL-contaminated areas. Therefore, by measuring ^{222}Rn concentrations in a number of wells, it may be possible to identify those locations where NAPL is likely present and to quantify the residual NAPL saturation in each of the locations. In addition, this method may be favorable because (1) injection of materials into the subsurface is not required, and (2) existing monitoring wells can be used to perform the needed (passive) sampling of ground water.

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2.3.3 Multiphase Multicomponent Equilibrium Partitioning Software for Soil Sample Analysis

Multiphase multicomponent equilibrium partitioning (MMEP) software for soil sample analysis distributes chemicals measured in a soil sample among known and potential phases to achieve equilibrium conditions. The important known and potential phases in a soil sample are soil, water, air, and NAPL. For site characterization purposes, a primary objective of these calculations is to

determine whether NAPL itself existed in a sample immediately prior to collection. The process of containerizing and preserving samples causes redistribution of organic compounds that generally work against the preservation of a NAPL phase within the sample. In addition, MMEP calculations are used to estimate the original *in situ* amount and composition of NAPL in a sample and the original *in situ* concentrations of NAPL components in each phase.

How the Technology Works

Chemical compounds partition between water, soil, air, and NAPL. The soil phase is typically considered to be the soil organic matter, which acts as an absorbent. The NAPL phase (if present) is composed entirely of the chemicals measured in the soil sample. Each chemical partitions between these phases until the chemical potential is equal in all phases.

MMEP calculations begin with the assumption that NAPL did not exist in the original *in situ* sample. Measured or estimated values for porosity, water content, phase densities, and/or soil organic matter content are used to define the relative *in situ* volumes and masses of the air, water, and natural soil organic phases. Chemicals are distributed among the phases according to well-established relationships, while the total mass of the chemicals is constrained by the total concentrations measured in the soil sample. If the initial iteration indicates that a chemical's aqueous concentration is greater than its effective aqueous solubility, then a NAPL phase is predicted for the sample. In this case, subsequent iterations converge to a solution that provides the saturation and composition of NAPL and the concentrations of NAPL components in the non-NAPL phases based on calculated effective aqueous solubilities and conservation of mass and volume for all phases and chemicals.

Calculating whether a NAPL phase originally existed in a soil sample is fairly simple when only one contaminant is involved (Feenstra et al., 1991). Estimating the amount of NAPL is not as straightforward, because the volume of NAPL requires iterative adjustments to the estimated volume of water or air content if the porosity is fixed. Calculations become even more complicated when two or more organic contaminants are detected in the sample, because the effective aqueous solubility for each NAPL component is proportional to the unknown mole fraction in the NAPL phase (analogous to Raoult's Law for gas mixtures). A soil sample analysis provides only the total concentrations of identifiable compounds among all phases. Additional difficulties arise for NAPL consisting of fuel, oil, or other hydrocarbon distillates. Many of the components of these NAPLs cannot be identified and quantified, requiring the adoption of simplifying assumptions such as grouping components based on equivalent carbon number (Park and San Juan, 2000).

The first published MMEP code for soil chemical analyses was SOILCALC (Mott 1995). This code distributes chemicals between soil, air, water, and NAPL phases and predicts NAPL composition. Special features of this code include a large hydrocarbon property database and the ability to calculate air-water partitioning as a function of temperature. Use of this code is restricted to samples that have small NAPL saturation or no NAPL, because there is no provision for NAPL to occupy any space. Thus, NAPL saturation is not calculated by this code.

The only known MMEP software codes capable of estimating both the saturation and composition of multicomponent NAPL in a soil sample are NAPLANAL and GWProt. NAPLANAL was developed by Duke Engineering & Services and is documented in Mariner et al. (1997). The NAPLANAL software package includes several chemical databases containing properties and

partition coefficients for a large number of organic compounds, including chlorinated solvents and other DNAPL components. These data can be modified by the user, and new compounds can be added. GWProt is a Microsoft Excel program designed for hydrocarbon NAPL (Park and San Juan, 2000). Its database consists of properties attributed to groups of hydrocarbons having similar equivalent carbon numbers.

Advantages of the Technology

MMEP calculations can be used to estimate *in situ* NAPL saturation (i.e., the volume of pore space occupied by NAPL), the *in situ* concentrations of each chemical in each phase, and the *in situ* NAPL composition. When NAPL saturation is estimated to be zero, MMEP software can be used to calculate a “dilution factor,” which describes how close the sample is to having a NAPL phase.

For overall site characterization, determining whether NAPL exists *in situ* helps investigators distinguish NAPL source zones from zones that may only be affected by the migration of vapor or aqueous plumes. In addition, estimates of the amount and composition of NAPL in soils are important for the design of remediation strategies and the assessment of remediation alternatives.

Limits of the Technology

The accuracy of the calculations depends highly on the accuracy of the input data. A sample’s chemical analysis can be compromised by improper sampling and preservation, failure to identify and quantify all organic contaminants, and incomplete extraction of contaminants. There has been much progress in recent years in establishing reliable methods to preserve volatile organic compounds in soil samples using methanol and/or special containers (Liikala et al., 1996; Hewitt, 1999).

The values of the physical properties of the soil sample and the chemical properties of the NAPL components also affect the results. Sensitivity analyses can be conducted by varying these properties and other input values over their likely ranges. Such sensitivity analyses can be easily performed using MMEP software.

Cost Considerations

SOILCALC, NAPLANAL, and GWProt can be obtained free of charge from the original authors. The NAPLANAL software package can be downloaded from www.napl.net/publications.html.

Regulatory Concerns

MMEP calculations typically must be performed by a computer, because they require iterative determination of a unique inverse solution to a set of nonlinear equations. However, the final calculations can be easily checked by simple hand calculations to ensure that all partitioning relationships are upheld, mass and volume are conserved, and effective aqueous solubilities are correctly calculated.

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3.0 EMERGING REMEDIATION TECHNOLOGIES

The use of any *in situ* technology involves the imposition of physical, chemical, and/or biological changes to the contaminated geosystem through

- injection of air, carrier gases, water, steam, or solutions;
- addition of heat in the form of electromagnetic radiation or electrical current; and/or
- injection of chemicals.

The following sections discuss various emerging *in situ* DNAPL remediation technologies. The purpose of this section is to provide the reviewer with sufficient baseline information about each technology to allow an initial screening of its strengths and weaknesses. It is not meant to be a definitive guide for technology selection. Reference citations are provided that should guide the reader to additional information concerning each technology.

Only technologies that are perceived as emerging, or innovative, and have been tested in the field with published data, are included in this report. In developing this list, the work group attempted to focus on systems that were purported to be effective in remediating DNAPL in either its free-phase and/or residual-phase state. There are a large number of proven treatment methods that address dissolved phase remediation (many of which are addressed in *Technologies for Dense Non-Aqueous Phase Liquids Source Zone Remediation* [Fountain, 1998]). These technologies will not be discussed here.

3.1 *In Situ* Flushing

How the Technology Works

An *in situ* flushing system involves the design and installation of a system of injection and extraction wells capable of hydraulically sweeping the entire volume of aquifer that is contaminated with DNAPL (Figure 1). A fluid, having properties specific to the DNAPL and geosystem under consideration, is injected into the vadose zone and/or saturated zone and thoroughly swept through the DNAPL zone. The injected solution reacts with the contaminants by lowering the interfacial tension between the DNAPL and aqueous phase and alters other physical properties, enhancing DNAPL solubility or mobility as it is flushed through the zone of contamination. A mixture of the injected fluid and contaminant, the *elutriate*, along with ground water, is then captured through extraction wells. Once brought to the surface, the ground water and elutriate are treated and either reinjected into the geosystem or discharged. Recovered DNAPL and other waste residuals are treated and/or disposed.

The injected solution consists of one or more reagents, which are soluble or miscible in the aqueous

phase. The use of specific reagents will vary depending upon contaminant characteristics and site conditions. The physical and/or chemical properties of the contaminant (e.g., density, viscosity, interfacial tension with water) are the primary factors that dictate the choice of reagent(s). Site conditions (e.g., heterogeneity of the soil, hydraulic properties of the system, ground water geochemistry, and soil mineralogy) also affect the choice of reagents as well as their properties in the injectate solution and the means by which the solution is flushed through the target DNAPL zone. The two classes of reagents addressed in this document are the two most common: co-solvent and surfactant.

Surfactants (surface active agents) are chemical compounds whose molecular structure (hydrophilic head and oleophilic tail) enables them to alter the properties of organic-water interfaces. In a DNAPL-contaminated aquifer, this property of surfactants effects free-phase mobilization of residual DNAPL or dramatically increases the solubility and mass transfer rate of organic molecules from the DNAPL into the mobile flushing solution. Thus, there are two primary ways in which surfactants can be utilized for DNAPL removal: solubilizing surfactant flood and mobilizing surfactant flood.

A *solubilizing surfactant flood* involves the injection of surfactants into the subsurface as an aqueous solution, where the solution is flushed through the zones containing DNAPL. The purpose of this flood is to increase the total aqueous solubility of the contaminant. Upon contact with the DNAPL, the surfactants bring about a two to three order of magnitude or greater increase in the total aqueous solubility of the DNAPL components. The second type of flush is a *mobilizing surfactant flood*. In a mobilizing surfactant flood, surfactants are likewise injected in an aqueous solution, but the objective is to lower the DNAPL-water interfacial tension to the point that physical mobilization of the DNAPL takes place. The “oil bank” is then displaced by the continuing flushing and is withdrawn by the extraction wells. The degree of solubilization versus mobilization occurring in a surfactant flood can be controlled through appropriate surfactant selection and the use of other chemicals such as a co-solvent, electrolyte, and polymer in a formulation that is determined based on bench-scale testing of phase behavior. In both the case of the solubilizing surfactant flood and the mobilizing surfactant flood, surfactant flooding is followed by water flooding to remove injected chemicals and solubilized or mobilized DNAPL contaminant.

Co-solvents (most commonly alcohols such as ethanol, methanol, and isopropanol) are similar to surfactants in that they alter the properties of solution interfaces and are often combined with surfactants to improve flood performance. Because of their miscibility, alcohols can be effective in lowering the interfacial tension between water and the contaminant and effectively increasing its aqueous solubility. This is due to the tendency of some alcohols to partition significantly into the DNAPL phase; therefore, the density of the DNAPL can be manipulated *in situ* through appropriate alcohol selection.

The effect with which and the rate at which the alcohol interacts with the contaminant is dependent upon the co-solvent concentration applied and the characteristics of the contaminant and/or site conditions. Alcohol injected at a low concentration (1–5% by volume) requires many pore volumes of fluid injection to remediate significant amounts of the contaminant (Technology Practices Manual for Surfactants and Cosolvents, 1997). Flushing with these levels of alcohol is considered a “co-solvent” flood. This is because the primary compounds of this system are water and the contaminant. Injection of alcohol at a higher concentration (70–95%) is termed an alcohol flood, since alcohol and

the contaminant are the primary elements within the system (Technology Practices Manual for Surfactants and Co-solvents, 1997). Due to the increased concentrations, fewer pore volumes of injectate fluid are needed to mobilize the contaminant, as compared to a co-solvent flood. Additionally, as is the case for surfactants, the physical and chemical properties of the DNAPL also influence how readily the alcohol increases the aqueous solubility of the contaminant and decreases the interfacial tension. The site geology also affects the flood performance, independent of the alcohol concentration. These factors must be accounted for in flood design using data from laboratory testing of soil and DNAPL samples and matching the proper alcohol to the DNAPL prior to implementing the technology.

Because a selected alcohol is not as effective as a carefully selected surfactant at dissolving DNAPL, an alcohol flood may require many more pore volumes of flushing solution than a surfactant flood to achieve the desired performance objective. Furthermore, for DNAPLs exhibiting higher molecular weight, viscosity, and compositional complexity, the low molecular weight alcohols are less effective at DNAPL dissolution, while the higher weight or more complex alcohols are immiscible and much less soluble in water. Therefore, the range of DNAPL types that can be flushed with co-solvent alcohols alone is relatively limited, mostly restricted to the lighter chlorinated ethanes and ethenes. Like surfactant flushing, co-solvent flushing is usually followed by water flooding to remove injected chemicals and solubilized or mobilized DNAPL.

Advantages of the Technology

- This is a mature technology, supported by decades of research and field tests. Additionally, environmental applications have become more numerous in recent years.
- Field performance has been quantitatively assessed using several methods for a large number of sites.
- The technology has been shown to be effective for several DNAPL types, including spent degreasing solvents (TCE and TCA), dry cleaning solvents (PCE), and heavy fuel oils. Laboratory work has also demonstrated applicability for coal tar/creosote and PCB-containing mineral oils.
- Design of *in situ* flushing can benefit from the use of existing and EPA-approved quantitative process design simulators.
- *In situ* flushing is in an advanced state of development where costs are being optimized by practitioners through automated systems, a consistent design and implementation approach, and optimization of project schedules and reagent use. For large projects with economy of scale, unit costs approaching \$100 per cubic yard of DNAPL-contaminated aquifer or lower can be expected.

Limits of the Technology

- *In situ* soil flushing works best and is most cost-effective at sites with soil having moderate to high permeability.
- Heterogeneous geosystems having significant permeability contrasts may impede injected solutions from significantly contacting DNAPL present in lower permeability zones.
- Soils exhibiting high native fractions of organic carbon can impede the effectiveness of the technology by adsorbing and retarding the movement of the chemical reagents.
- Flushing fluids must be designed that do not contain additives, which may themselves create new ground water contamination.
- In depth site characterization of ground water flow is required to design an effective well system.

In addition, hydraulic containment must be factored into the design to ensure that the contamination does not spread and that extraction wells collect the targeted fluids.

- *In situ* soil flushing is tailored to treat specific contaminants and may not be effective for all classes of contaminants at a site.
- Because alcohols do not strip easily (due to their miscibility), separating the alcohols from the elutriate for purposes of reuse/reinjection is often infeasible or cost-prohibitive. In addition, surfactant microemulsions can be difficult to separate and/or cause foaming in some systems.

Regulatory Concerns

There are a variety of regulatory concerns that may be associated with the implementation of this technology. One such concern is recovery of the injected chemical solutions and mobilized DNAPL, which, once mobilized, may migrate (if not contained and recovered) to contaminate surrounding areas. Tracer tests, as well as limited field testing using surfactants, can be conducted to ensure recovery is feasible. Another concern is toxicity of injected chemicals (some surfactants as well as high levels of alcohol are toxic to microorganisms) and their impact on residual concentrations remaining in the aquifer following flooding activities. These factors must be considered, especially if this technology is going to be coupled with bioremediation. Handling of chemicals may also be of concern, since high concentrations of alcohol can be flammable and explosive. Concentrated alcohols should be handled with care to avoid personal injury and damage to the environment during transportation, handling, and injection. Additionally, reinjection/reuse of the reagents will more than likely be of concern. If the ground water and/or elutriate is going to be recycled, the required solution may be to meet water quality standards before being reinjected (this may vary from site to site and/or agency to agency).

Site(s) Where Implemented

The technology has been demonstrated at various sites, including Hill AFB OU-2 (Utah), Pearl Harbor Naval Base (Hawaii), Sage's Dry Cleaner Site (Florida), and Camp Lejeune (North Carolina), which is summarized below.

I. Camp Lejeune, Site 88, NC

A demonstration of surfactant-enhanced aquifer remediation (SEAR) was conducted for rapid source-zone remediation of a DNAPL site at Marine Corps Base, Camp Lejeune, NC. The specific location is known as Site 88, the location of the central dry cleaning facility for the base. Separate phase PCE is present at Site 88 in a shallow, surficial aquifer that is bounded below by a clay aquitard at about 20 feet below ground surface. The shallow aquifer is characterized as a relatively low-permeability formation composed of fine to very-fine sand, with a fining downward sequence in the bottom two feet of the aquifer. The bottom fine-grained zone, referred to as the basal silt layer, grades to a silt then clayey silt before contacting the aquitard. Permeability decreases downward through the basal silt layer as a function of decreasing grain size with depth. The test zone for the SEAR demonstration was 20 ft by 30 ft, and the pore volume treated was approximately 5000 gallons. The surfactant flood utilized a custom surfactant, which was developed for the dual objectives of high PCE solubilization and desirable effluent treatment properties (for surfactant recovery and reuse). Five pore volumes of surfactant solution were injected into the test zone, and 76 gallons of PCE were removed. A partitioning tracer test (PITT) was conducted before the SEAR, and 60 soil core samples were analyzed after the SEAR to

evaluate the performance of the surfactant flood. A total of 29 ± 7 gallons of DNAPL is estimated to remain in the test zone following the surfactant flood, which is distributed between the upper zone (fine sand sediments) and the lower zone (basal silt layer). Post-SEAR data were further analyzed by subdividing the test zone into the upper and lower zones. The results indicate that approximately 5 gallons of DNAPL remain in the upper zone (equivalent to 92–96% removal from the upper zone), and approximately 24 gallons of DNAPL is estimated to remain in the lower zone, which was relatively unaffected by the surfactant flood. The inability to effectively remediate the lower zone was due to decreasing permeability in the basal silt layer. (Hydraulic conductivity (K) in the upper zone is estimated to be on the order of about 1×10^{-4} to 5×10^{-4} cm/sec, whereas K in the basal silt is estimated to be as low as about 1×10^{-5} to 1×10^{-4} cm/sec, decreasing with depth to the aquitard.)

Prior to the surfactant flood, the highest DNAPL saturations occurred in the upper zone (i.e., more permeable zone), which was the primary source of the dissolved PCE plume at Site 88. Post-SEAR DNAPL conditions indicate that >92% of the source was removed from the upper zone and that the remainder is relatively isolated in the lower zone (i.e., low-permeability zone). The transport of dissolved PCE from DNAPL in the lower zone to the upper zone will be primarily limited to diffusion. Therefore, the source of the dissolved PCE plume transport is believed to be greatly reduced compared to pre-SEAR conditions.

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3.2 Dynamic Underground Stripping

How the Technology Works

Thermal techniques used for recovery of liquids from the subsurface are not new. Petroleum industry literature has documented a large amount of research and application of thermal processes to enhance oil recovery. However, the use of thermal techniques to enhance *in situ* recovery of DNAPLs is relatively new, having only been applied for *in situ* environmental remediation since the mid 1980's.

The process of heating the subsurface by injecting steam, also known as Dynamic Underground Stripping (DUS), enhances the SVE process by increasing vapor pressure and volatilization rates of volatile and semi-volatile compounds. Reduction of viscosity and residual saturation of semi-volatile and nonvolatile compounds result from soil heating and cause greater mobility and greater removal efficiency of DNAPLs. Recovery of viscous contaminants, such as coal tar and creosote, has recently been shown to consist of several component mechanisms: mobilization and recovery of buoyant separate-phase material, volatilization of semi-volatile fractions, *in situ* hydrous pyrolysis oxidation of dissolved phase contaminants, and enhanced aerobic and thermophilic biodegradation.

The vapor pressure of volatile contaminants is a key determining factor for the use of soil vapor extraction as an appropriate remediation strategy. Typically, a value of 1 mm Hg is used as the

minimum for application of soil vapor extraction at ambient temperatures (approximately 60° F). Semi-volatile and nonvolatile materials have vapor pressures considerably lower than 1 mm Hg at ambient temperatures and, therefore, SVE has not been successful at remediating these materials. However, vapor pressure increases substantially as temperature increases. The increasing vapor pressure results in increased volatilization to the point that semi-volatile materials, such as diesel fuel, are almost entirely volatilized at soil temperatures that can be attained by steam injection. SVE systems can then remove the released vapors for treatment at the surface using conventional technologies such as thermal oxidation, catalytic oxidation, or carbon adsorption.

The mobility of semi-volatile and nonvolatile hydrocarbons is greatly affected by the viscosity and residual saturation of materials. The viscosity of hydrocarbons varies greatly in response to temperature. In addition, materials with high viscosity, such as the heavier fuel oils, have correspondingly high residual saturation concentrations in soils. These highly viscous materials do not readily migrate through the soil and are adsorbed to the soil at high residual saturation concentrations. When thermal energy is applied to the soil, the increasing temperatures cause the viscosity and the residual saturation to decrease markedly. In the case of No. 5 fuel oil, as the soil temperature approaches 212° F, the viscosity and residual saturation of the No. 5 oil are similar to those of diesel fuel at ambient conditions, meaning it will migrate readily through the soil and can be easily extracted by conventional extraction techniques.

Hydrous pyrolysis oxidation (HPO) is a process that destroys organic contaminants *in situ*. HPO destroys DNAPLs and dissolved contaminants in place by hydrothermal oxidation. The technique involves injection of steam and oxygen into a contaminated subsurface unit, creating a heated oxygenated zone that oxidizes and degrades the contaminants.

The delivery concept for HPO utilizes steam injection to provide heat to the subsurface. When the steam injection is periodically halted, the steam condenses at the perimeter of the heated zone. Unheated, contaminated ground water flows toward the heated periphery of the treatment zone. This unheated, contaminated ground water mixes with the steam condensate, heated ground water, and oxygen, often introduced with a stream of air, and any dissolved contaminants are oxidized. The unheated ground water return process of steam condensation avoids many of the mixing problems encountered in other *in situ* oxidation schemes that result in contaminant displacement without a return process to mix the oxidizing reagent and the contaminant. In addition, the oxidation of contaminants at steam temperatures is extremely rapid (less than one week for TCE and two weeks for naphthalene) if sufficient oxygen is present. Because the subsurface is heated during the process, HPO takes advantage of the large increase in mass transfer rates, such as increased diffusion out of silty sediments, making contaminants more available for destruction.

During thermal-enhanced remediation processes, biodegradation continues to be a viable mass removal mechanism. Despite the perception that biologic communities are adversely impacted by thermal processes, aerobic, anaerobic, and thermophilic bacteria continue to degrade hydrocarbons while thermal techniques are employed. In zones where soil temperatures do not reach steam temperature (around the perimeter of the heated zone, beneath the ground water surface), both aerobic and anaerobic biodegradation is significantly enhanced. Biodegradation in the vadose zone very rapidly becomes totally aerobic as the oxygen content of the soil increases due to migration of air due to soil vapor extraction operations. In many instances, facultative biologic communities remain dominantly anaerobic below the ground water surface, where soil vapor extraction is less effective. In both cases, biodegradation rates increase substantially as the soil temperature rises into the 100 to 120° F range. As soil temperatures continue to rise, thermophilic bacteria colonies show significant increases in activity. These colonies degrade a significant amount of contaminant mass when the soil temperatures are near steam temperature.

Advantages of the Technology

- The process can be applied to a wide range of contaminants, both chlorinated and nonchlorinated.
- The technology is a “brute force” mass removal tool that can remove free product utilizing steam pressure fronts to push mobilized product to collection wells prior to polishing with other technologies.
- The technology can volatilize semi-volatile contaminants in both the vadose and saturated zones for collection by standard SVE methods.
- Mobilization of nonvolatile, viscous contaminants can be readily accomplished throughout the subsurface.
- Volatilization and mobilization have been accomplished throughout the vadose zone and in the saturated zone to depths of 200 ft.
- The HPO component of steam injection can be applied along with enhanced bioremediation to degrade contaminants *in situ*.
- Many volatile chlorinated solvents achieve buoyancy when heated to 160° F and become LNAPL in the heated zone, which can be recovered by conventional means used, for example, with gasoline product recovery systems.

Limits of the Technology

- High capital costs tend to limit the applicability to large, highly contaminated sites.
- High injection pressures could result in soil fracturing in shallow applications (<30 ft).
- Not effective in low permeability zones without enhancement to improve secondary porosity and fluid transfer properties of the clay.
- If not controlled, downward infiltration of steam condensate may impact uncontaminated aquifers.

Regulatory Concerns

Regulatory concerns can be separated into three issues: the potential for release of hazardous vapors to the atmosphere, the potential for mobilization of DNAPLs downward into the aquifer due to decreased viscosity, and physical hazards associated with high pressure steam.

The potential release of hazardous vapors to the atmosphere is greater at a site where thermal technologies are being used than at a conventional site due to the generation of contaminant-laden steam, which may be under considerable pressure. Additional demonstration of capture by the SVE

and gas pressure monitoring may be necessary at such a site, and more frequent and widespread air monitoring may be required compared with conventional extraction sites. The additional costs associated with this monitoring may be offset by the much shorter remediation times.

The potential for the mobilization of DNAPL downward into previously uncontaminated zones may be a concern. In addition to a demonstration of hydraulic capture, a detailed investigation of the capacity of the underlying aquitard to stop downward migration may be required. Consideration should be given to the effects high temperature and steam may have on the ability of the aquitard to prevent downward migration of DNAPL.

Physical safety will also be more of an issue than at other remedial sites. Hazards associated with on-site steam generation and handling will require the erection of barriers around the site. Project personnel responsible for boiler operation and site safety must be fully trained in all aspects of steam generation.

Cost Considerations

Thermal techniques have been shown to effectively remove semi-volatile and nonvolatile contaminants, including DNAPLs, from the subsurface at rates that are orders of magnitude greater than conventional approaches. For example, creosote has been removed and/or degraded at rates as high as 7000 lbs/day. At three sites along the West Coast, contaminant masses of 35,000 to more than 100,000 gallons have been removed and degraded in 18 months or less. Costs for these removal actions are in the \$50 to \$100 per cubic yard treated range.

Steam injection is an aggressive removal approach, entailing a high-capital expenditure accompanied by a significantly shortened operational period resulting in reduced labor and analytical costs. Cost for large-scale applications, such as the Visalia Superfund Site described below, can approach \$60 per cubic yard treated.

Site(s) Where Implemented

I. Southern California Edison Poleyard Superfund Site, Visalia, CA

Southern California Edison implemented Dynamic Underground Stripping (DUS) at its Visalia, California poleyard beginning in May 15, 1997, which has resulted in the removal of more than 150,000 gallons or 1.2 million pounds of creosote from subsurface soils and ground water. Alluvial soil consisting of silty sands and clay layers underlay the site. Depth to ground water at the site is approximately 70 ft, with contamination characterized to a maximum depth of 130 ft. Prior to steam injection, the existing water treatment plant removed about one pound per day of creosote. Steam injection wells, which were located at multiple levels surrounding and below the source area of approximately 2 acres, accelerated the average removal rates approximately 1200 times. Maximum removal rates were as high as 12,000 pounds per day. Approximately 50% of the creosote has been removed as free product, with an almost equal percentage of creosote removed as vapor phase, aqueous phase, and carbon dioxide (HPO). Polish steam injection continues at the poleyard, and current removal rates have declined to less than 50 gallons per day. Respirometry data from soil gas suggested that significant destruction was attributable to thermophyllic bacteria activity, although further microbial study would be necessary to confirm this. HPO was also credited with destruction of pentachlorophenol present in ground water,

which had been used subsequent to creosote to treat utility poles at this location.

As of the date of publication, aqueous-phase organics, (primarily pentachlorophenol) are still at concentrations that exceed the remediation standards as set forth in the RAP/ROD. Steam injection and pump-and-treat containment will continue until sufficient data analysis can predict when concentrations of the COCs will decay below remediation standards. It is predicted that pump and treat will continue after steam injection cessation to maintain containment as decay is monitored.

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II. Puget Sound Naval Shipyard, Bremerton, WA

A technology demonstration steam injection program for recovering heavy oils and fuels was implemented at a one-acre former underground storage tank site at the Puget Sound Naval Shipyard. A subsurface investigation, including soil and free product sampling, vertical induction profiling, and ground water pump testing was conducted to further characterize the extent of subsurface impacts and develop specific design criteria. Soil samples collected during the investigation were used to perform a steam injection bench-scale test and bioremediation treatability study. Due to the high viscosity of No. 6 fuel oil, a steam injection remediation system using an innovative soil heating and product recovery process was designed and implemented.

The site's soils (sand and gravel glacial till deposits) and the depth of ground water (100 ft bgs) required that an injection and extraction system be installed in a multilevel configuration. Shallow, medium, and deep levels were defined for the implementation of a steam injection system, augmented by total fluids and vapor pumping. Eight nested steam injection points and three liquid/vapor extraction points were installed to depths of 50, 80 and 110 ft. An oil-water separator and dissolved air floatation system treated recovered product. To control steam front migration and recover diesel, a soil vapor extraction system with a regenerative thermal oxidizer for off-gas treatment was employed.

During the first nine months of operation, the system reduced the mass in place by 35,000 equivalent gallons of No. 6 fuel oil and diesel. The majority of the mass reduction was accomplished by separate phase liquid recovery. Anaerobic biodegradation was the next most successful mechanism, followed by vapor extraction of volatilized diesel fuel and aerobic biodegradation. This mass represents approximately 58 percent of the estimate in the treatment area. Additional mass has been recovered beyond the nine-month technology demonstration period. The implementation of the technology during the demonstration period was accomplished for a cost of approximately \$61 per cubic yard treated or \$7 per pound of contaminant removed.

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3.3 Six-Phase Heating™

How the Technology Works

Six-Phase Heating™ (SPH) is an *in situ* thermal remediation technology developed at DOE's Pacific Northwest National Laboratory that uses electrical resistive heating in conjunction with conventional extraction technologies to remediate soil and ground water. The method heats the vadose zone or aquifer in a more uniform manner than other technologies using resistance heating. Standard three-phase alternating current (AC) is converted to six-phase AC and connected to a hexagonal-shaped array of electrodes emplaced in vertical well bores. A seventh neutral electrode is placed at the center of the array, normally in combination with an extraction well for soil vapor and/or water. An additional remedial process associated with SPH, which involves the *in situ* destruction of organic compounds by the development of a low temperature plasma, has been demonstrated in bench-scale tests but has not yet been field tested. This process, referred to as *in situ* corona, has been shown to occur when high voltage is applied to soil that has been dried using the six phase technology.

The physical process of resistive heating is focused on units within the soil column that have high porosity and low permeability characteristics (silts and clays), which have historically been the least affected by conventional extraction technologies (such as pump and treat and soil vapor extraction). Heating of the NAPL raises the vapor pressure, thereby increasing volatility, decreasing viscosity of the remaining NAPL, and increasing its mobility. Steam is generated *in situ*, which becomes heavily laden with NAPL and then is drawn to the soil vapor extraction well and treated by carbon adsorption or other conventional destruction technologies at the surface. Field tests in the vadose zone have reported that *in situ* steam generation and subsequent drying of the vadose zone also improve the permeability of the clay-rich zones, although the mechanism is not clearly understood. Treatment times vary from several weeks to several months, depending on conditions at individual sites. Heating the soil may also enhance the biological activity in the soil column, increasing the effectiveness of bioremediation.

Limits of the Technology

- SPH appears to be a versatile technology, which shows promise in clay-rich portions of the vadose zone and aquifer. The technology also appears viable but has not yet been field tested, in fractured bedrock settings.
- The treatment area of a single array is limited by the current density and size of electrodes (typically 30 to 40 feet), but recent technological improvements have increased the array diameter in some applications to as much as 60 ft. Depths are limited by the drilling technology rather than by the heating technology.
- The vadose zone and the aquifer can be heated simultaneously, although the thickness of the zone is limited by the electrical power available. Power costs in some parts of the country may limit the utility of this technology, although this may be more than offset by the more rapid remediation

achieved using SPH compared to conventional technologies without thermal enhancement.

Regulatory Concerns

Regulatory concerns can be separated into three issues: the potential for release of hazardous vapors to the atmosphere, the potential for mobilization of DNAPLs downward into the aquifer due to decreased viscosity, and physical hazards associated with high voltage and high temperatures.

The potential release of hazardous vapors to the atmosphere is greater at a SPH site than at a conventional site due to the generation of contaminant-laden steam, which may be under considerable pressure. Additional demonstration of capture by the SVE and gas pressure monitoring may be necessary at a six phase site, and more frequent and widespread air monitoring may be required compared with conventional extraction sites. The additional costs associated with this monitoring may be offset by the much shorter remediation times.

The potential for the mobilization of DNAPL downward into previously uncontaminated zones may be an issue. In addition to a demonstration of hydraulic capture, a detailed investigation of the capacity of the underlying aquitard to stop downward migration may be required. Consideration should be given to the effects high temperature and steam may have on the ability of the aquitard to prevent downward migration of DNAPL.

Physical safety will also be more of an issue than at other remedial sites. High voltage hazards will require the erection of barriers around the site and a very thorough investigation of buried objects to ensure that conductive metal objects and closed containers such as pipes and tanks, which may present an explosive hazard, are not present.

Site(s) Where Implemented

I. Savannah River Site, M Area Process Sewer/Integrated Demonstration Site, Aiken, SC

Pilot-scale and full-scale remediation of the vadose zone and aquifer using SPH technology were performed at the Savannah River M Area Process Sewer/ Integrated Demonstration Site over 17-days in 1993. High concentrations of PCE (4,529 $\mu\text{g}/\text{kg}$) were 99.7% removed from a 10-ft-thick clay layer at a depth of 40 ft bgs. Estimated remedial cost was \$88 per cubic yard, assuming the entire site had been remediated.

Point of Contact:

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II. Former Electronics Manufacturing Site, Skokie, IL

Aquifer testing of SPH remedial technology was performed at a former electronics manufacturing site in Skokie, IL. The site contained free-phase TCE, TCA and cis-DCE pooled on a dense clay till aquitard at the base of a fine grained sand aquifer. Depth to water was seven ft and depth to the base of the aquifer was 18 ft. The remediation occurred between June 1998 and May 1999 and resulted in an estimated greater than 99% removal of contaminants at a cost of \$32 per cubic

yard. The site is being evaluated for closure.

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3.4 *In Situ* Chemical Oxidation

Chemical oxidation processes involve oxidation-reduction (redox) reactions, which are essentially an exchange of electrons between chemical species. This exchange of electrons affects the oxidation state (valence) of the chemical species involved. The carbon bonds are broken as a result and the organic compounds are either completely destroyed or converted to smaller and typically less hazardous compounds. Recent advances in the development of this technology include systems that effectively deliver and distribute reagents into soil and ground water so that *in situ* chemical oxidation (ISCO) is possible.

ISCO technology is nonselective with regard to target compounds and has been shown to be effective on halogenated and nonhalogenated volatiles and semivolatiles, polychlorinated biphenyls (PCBs), pesticides, and cyanides. However, the rate of reaction is highly variable, depending on the compound being treated. Many of the most common contaminants, such as halogenated hydrocarbons, saturated aliphatic hydrocarbons, and benzene, have a relatively low rate of reactivity.

Remediation success using ISCO is heavily dependent on the ability to deliver the oxidant to the contaminated area. As is the case with *in situ* thermal and soil flushing technologies, low soil permeability and heterogeneity can be problematic for ISCO systems. Potential delivery methods include soil mixing, direct injection, and oxidant recirculation. Additional research is needed to determine delivery system configurations and dosing rates to achieve remedial action objectives.

The primary costs associated with implementing an ISCO system (apart from site characterization costs) include delivery system design and installation costs, mass of DNAPL to treat, and the quantity of reagent needed for complete oxidation. (MSE, 1998). In general, the operation and maintenance (O&M) costs associated with ISCO are expected to be significantly less than O&M costs for traditional remediation technologies such as pump and treat, due to reduced treatment times and equipment requirements. To reduce the cost and potential adverse side effects of deploying the technology, a computer code (ISCO3D) was developed by Duke Engineering & Services to simulate the coupled processes of NAPL dissolution, chemical reactions, and solute mass transport in the *in-situ* chemical oxidization system. ISCO3D fills the gap between the laboratory studies necessary for design and field operations by providing a numerical model capable of simulating the oxidation processes efficiently and robustly.

Three of the most common *in situ* chemical oxidation technologies are discussed in the following subsections: potassium permanganate (KMnO_4), hydrogen peroxide (H_2O_2), and ozone (O_3).

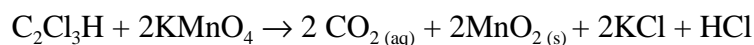
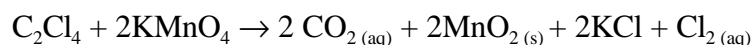
3.4.1 Potassium Permanganate/ KMnO_4

How the Technology Works

Chemical oxidation using potassium permanganate has been used for decades for drinking water treatment and municipal and industrial wastewater treatment. *In situ* chemical oxidation using potassium permanganate is an emerging technique for remediating sites with contaminated soil and/or ground water, including those sites containing DNAPLs.

Potassium permanganate (KMnO_4) can oxidize a wide range of inorganic and organic compounds. Chlorinated solvents, polynuclear aromatic hydrocarbons (PAHs), phenolics (including creosols), and cyanides are potential candidates for oxidation with KMnO_4 . This discussion will focus on chlorinated solvents since these compounds are often associated with DNAPL sites. Organic compounds that contain carbon-carbon double bonds (alkenes) are more readily oxidized by KMnO_4 than compounds having single carbon-carbon bonds (alkanes). Thus, KMnO_4 should be more effective at remediating DNAPLs consisting of TCE or PCE rather than 1,1,1-trichloroethane (TCA).

The oxidation of PCE (C_2Cl_4) and TCE ($\text{C}_2\text{Cl}_3\text{H}$) by KMnO_4 is governed by the following reactions:



The by-products (HCl, Cl_2 , etc.) that are released into the subsurface are generally not considered to be harmful in the environment. However, it is important to understand the fate of the primary by-products in order to minimize adverse impacts to the treatment zone [LeChance, et. al., 1998]:

- CO_2 – carbon dioxide will combine with water to form the carbonate series and lower the pH of the ground water. If the reaction rate exceeds the carrying capacity of the water, a separate vapor phase will form within the soil matrix. This will result in a decrease in the relative permeability with respect to water of the matrix. Thus, formation of CO_2 vapors within the soil pores could adversely impact the ability to inject KMnO_4 solution into the saturated zone.
- Cl_2 – chlorine gas is highly reactive, and it will readily combine with water to form hypochlorous acid (HOCl) and hypochlorite (OCl⁻). These two compounds are also very strong oxidants, and they will be readily reduced by available organic matter within the soil matrix.
- HCl – hydrochloric acid will be neutralized by carbonate soils (provided that the soils have enough buffer capacity to complete this reaction).
- MnO_2 – manganese dioxide will precipitate out, coating soil grains. The buildup of manganese dioxide, and other manganese oxides that may be formed, may reduce soil matrix permeability over time, further hindering delivery of oxidant to contaminated zones.

Chemical oxidation occurs at both the soil interface and free-phase interface (for NAPL situations) and within the interstitial ground water (for dissolved compounds). Environmental parameters that influence the rate and degree of permanganate oxidations include pH, temperature, contact (or reaction) time, and oxidant concentration. Meyers (1998) notes that compounds with a carbon-carbon double bond are typically quite readily oxidized by KMnO_4 under mild conditions (pH 4–8, ambient temperature).

Since KMnO_4 is insoluble in organic compounds such as TCE and PCE, the oxidation rate is

dependent on the rate of NAPL dissolution and mass transfer to the aqueous phase. The interphase mass transfer rate can be improved by chemical gradients created during treatment, especially if high aqueous concentrations of KMnO_4 are used (see Figure 2 in LaChance et al., 1998).

Advantages of the Technology

- KMnO_4 can completely oxidize certain chlorinated hydrocarbons *in situ*, including those commonly found at DNAPL sites (e.g., TCE, PCE) without the production of toxic daughter products.
- Recent pilot and field demonstrations suggest that KMnO_4 can be used to treat DNAPL sources within both the saturated and unsaturated zones.
- Rapid reaction times and high destruction efficiencies can be achieved with KMnO_4 , leading to significant concentration reductions at source areas and reduced remediation costs over the life of the project.
- Since unreacted KMnO_4 in solution is relatively stable, it can diffuse into media with low permeabilities (e.g., silt and clay) over time, further enhancing oxidant delivery to hard-to-treat contaminated zones.
- KMnO_4 is easily handled in the solid form and, given its high solubility in water, is easily mixed and injected into the subsurface.
- The design, construction, and operation of chemical delivery systems are relatively straightforward.
- The contaminants are treated *in situ* and are converted to innocuous and/or natural occurring compounds (e.g., H_2O , CO_2 , and halides).
- By acting/reacting upon the contaminant in place, the reagent will not cause vertical movement of the contaminant, which is often a concern with other remediation technologies.
- By increasing dissolved oxygen (DO) levels throughout the treatment area, this process aids in bioremediation or aerobic microbial consumption of contaminants.

Limits of the Technology

- This treatment process, while fast acting, does require sufficient time to allow the redox reaction to go to completion; otherwise, residual compounds may remain in the contaminant stream.
- Hazardous intermediate compounds may be formed due to incomplete oxidation caused by insufficient quantity of either oxidant or catalyst, the presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagents, and/or inadequate mixing or contact time between contaminant and oxidizing agent.
- Large amounts of reagents are required for treatment of DNAPLs.
- Lack of proper site characterization and/or monitoring of technology operations may result in adverse effects, such as development of explosive forces due to excess buildup of pressure (below the ground surface) or permeability reduction from by-product formation.
- KMnO_4 dosing needs to be regulated to reduce the potential to overproduce CO_2 and MnO_2 by-products, as these can further hinder the delivery of oxidants to contaminated zones.

Regulatory Concerns

The primary regulatory concern associated with this remedial technology may be the injection of chemicals and/or untreated ground water into the subsurface, particularly if a ground water recirculation scheme is used to deliver the oxidant to ground water. Other regulatory concerns could be the ability to effectively monitor the treatment performance given the difficulty in locating and

sampling DNAPL source areas, the potential to push contamination further into the aquifer as the solution is injected, the potential for the formation and mobilization of colloids due to the breakdown of natural organic matter, and the potential formation of toxic intermediate products if insufficient oxidation occurs.

Site(s) Where Implemented

In general, when compared to ISCO with hydrogen peroxide, there are few sites where KMnO_4 has been used to oxidize contaminants *in situ* and even fewer sites that evaluated its use for DNAPL treatment. The following sections contain summaries of two projects, conducted at Department of Energy (DOE) and Department of Defense (DoD) sites, which have evaluated the effectiveness of ISCO using KMnO_4 to treat DNAPL source areas.

I. DOE Portsmouth Gaseous Diffusion Plant, Area X-701B, Piketon, OH

In situ chemical oxidation through recirculation (ISCOR) was field tested at the X-701B area of the Portsmouth Gaseous Diffusion Plant (PGDP) in Piketon, Ohio. The test site encompasses an area on the PGDP facility that used to contain an unlined pond (reportedly used from 1954 to 1988 to treat metal bearing wastewaters, solvent solutions, and acidic wastewater).

Initial remedial technologies employed at the site included draining the pond of free liquids and removing contaminated sludge and underlying soils. Monitoring well sampling, however, indicated that high concentrations of TCE remained in the saturated zone of the underlying Gallia aquifer (characterized as a fine-grained silty-sand matrix interspersed with gravelly lenses, approximately 3 to 7 ft thick with a permeability in the range of 1×10^{-3} cm/s).

The treatment process involved the installation of two 200 ft-long horizontal wells, approximately 35 ft bgs, oriented perpendicular to the predominant ground water flow direction. Water was then extracted from a downgradient well, treated with crystalline KMnO_4 (mixed to a 2.5 to 4.0 percent by weight aqueous solution of KMnO_4), and re-injected into an upgradient well.

Treatment effectiveness was monitored by evaluating concentrations of TCE, K^+ , MnO_4^- , Cl^- , and other water chemistry parameters. Before treatment, TCE concentrations in ground water were approximately 164 mg/L. At the end of the treatment, TCE concentrations had decreased to 94 mg/L. A total of 10,740 kg of permanganate was injected for 32 days through the horizontal well. In addition, a total of 1,960 kg of permanganate was delivered for 8 days by a vertical well located at the center of the treatment zone. Levels continued to drop, with TCE concentrations falling to about 28 mg/L two weeks after treatment had ceased. Some rebound in TCE concentrations was observed several months after flushing had ceased, however.

In addition, the ISCO3D program was tested at the DOE's PGDP facility during the field ISCO demonstration. The simulations showed that the basic characteristics of the experiment were reproduced by the ISCO3D code. The injected permanganate front shows a pattern of preferential flow near the two ends of the horizontal wells. The field observations and computer simulation indicate that TCE concentration was significantly reduced where the permanganate was delivered as compared with the initial TCE distribution in the aquifer. After 7 days, the contour line of 0.005 mg/L TCE (drinking water standard) was located near the horizontal injection well. The 0.005 mg/L TCE contour line expanded outward during the entire 32-day permanganate injection

period.

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II. U.S. Army CRREL Site, Hanover, NH

A pilot-scale ISCO demonstration project using KMnO_4 was implemented in the winter of 1997 at the U.S. Army Cold Regions Research and Engineering Laboratory (CRREL) in Hanover, New Hampshire.

The demonstration was performed in an area of the site where a 3,000 gallon release of TCE had occurred from an aboveground storage tank in 1970. The site is underlain by 65 meters of unconsolidated glaciofluvial and glaciolacustrine deposits. The depth to the water table is approximately 40 meters bgs. The upper 16 meters of unconsolidated deposits consist of interbedded fine sand and silt (sand layers) with discrete layers of dense and cohesive silt (silt layers) that range in thickness between 0.5 to 50 cm. The moisture content of the sand and silt layers ranged between 10 and 20 percent, and 20 to 30 percent, respectively. Free-phase TCE (DNAPL) is present in the unsaturated zone within dense silt layers between 6 and 8 meters bgs. TCE concentrations in this zone varied between 10 to 60,000 mg/kg.

An evaluation of remedial technologies determined that technologies based on flushing the subsurface with fluids (e.g., air or water) to remove contaminants would be ineffective due to capillary effects and mass transfer limitations.

The treatment process entailed installing a 15-cm piezometer to the desired treatment depth. A solution of KMnO_4 was then delivered over a 21-day period. During this time period, treatment was evaluated by collecting pore-water samples from three *in situ* ground water samplers (e.g., lysimeter blocks) placed near the injection well. These samples were compared to the TCE and chloride concentration levels taken both before and during the injection of the oxidant.

The contaminant reduction data were inconclusive due to the heterogeneous nature of the site and the small sample volumes. Contaminant reduction, however, is inferred by the increase of chloride concentrations in pore-water that was observed during treatment and the decrease that was observed after KMnO_4 injection ceased (McKay, 1999).

Full-scale operations of ISCO with KMnO_4 are slated to begin at two locations on the site in

August 1999 and are expected to continue for approximately two years.

Point of Contact:

Daniel McKay

U.S. Army Cold Regions Research and Engineering Laboratory

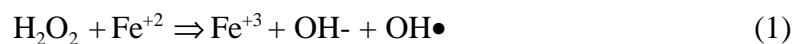
Hanover, NH

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3.4.2 Hydrogen Peroxide/H₂O₂

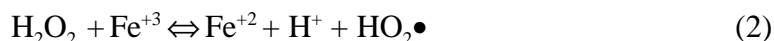
How the Technology Works

Hydrogen peroxide is an effective oxidizing agent. However, to achieve the desired contaminant reductions in a reasonable time, a transition-metals catalyst is required. Iron is most commonly used, and, when mixed with hydrogen peroxide, the catalyst is known as Fenton's Reagent. The chemistry of Fenton's Reagent (1) is well documented for producing hydroxyl radicals by the reaction of hydrogen peroxide and ferrous iron (Fe⁺²). The hydroxyl radicals (OH•) serve as very powerful, effective, and nonspecific oxidizing agents, second only to fluorine in oxidizing power.



The iron can be applied either as iron oxides within the soil or separately as a solubilized iron salt. With DNAPLs, oxidation occurs within the soil interface. When organic contaminants become desorbed from the soil, or otherwise enter the aqueous phase, oxidation occurs within the interstitial ground water. In a manner similar to photolysis using ultraviolet light, highly reactive, short-lived hydroxyl radicals are generated which can degrade even recalcitrant organics.

When iron is the catalyst, during the optimum reaction sequence, ferrous iron (Fe⁺²) is converted to ferric iron (Fe⁺³). Under properly controlled and buffered conditions, ferric iron can be regenerated back to ferrous iron by a subsequent reaction with another molecule of hydrogen peroxide (2).



Many reactions occur during the oxidation of a contaminant; but as shown by reaction (3), a contaminant (RHX), hydrogen peroxide, and ferric iron (as a catalyst) are consumed to produce carbon dioxide and water. RHX represents a halogenated organic compound, and X represents a halide.



Recent advances in the development of chemical oxidation include technologies that serve to deliver and distribute reagents into soil and ground water. This technology development allows for remediation of chlorinated solvents to occur *in situ*. With DNAPLs, oxidation occurs at the soil-ground water interface. Organic contaminants become desorbed from the soil, entering the interstitial ground water. Therefore, a patented injection process is often used to inject the hydrogen peroxide, catalyst, and buffering solution (if needed) into the ground water zone where DNAPL contamination is located. The end products of this *in situ* process are carbon dioxide, water, and chloride ions, all

of which are relatively harmless.

Soil decontamination with H_2O_2 has been demonstrated on the following kinds of organics:

- Chlorinated solvents (TCE, PCE)
- Munitions (TNT, RDX)
- Pesticides (chlorophenoxy, atrazine, pendimethalin)
- Petroleum residues (BTEX, PAH, TPH, MTBE, diesel fuel)
- Wood preservatives (PCP, creosote)
- Miscellaneous compounds such as PCBs and phenolics

Advantages of the Technology

- Under ideal conditions, H_2O_2 can completely oxidize certain chlorinated hydrocarbons *in situ*, including those commonly found at DNAPL sites (e.g., TCE, PCE), without the production of toxic daughter products.
- H_2O_2 can be used to treat DNAPL sources within both the saturated and unsaturated zones.
- Rapid reaction times and high destruction efficiencies can be achieved with H_2O_2 , leading to significant concentration reductions at source areas and reduced remediation costs over the life of the project.
- The design, construction, and operation of chemical delivery systems is relatively straightforward.
- Since H_2O_2 degrades rapidly in the environment, excess oxidant in the subsurface does not represent an environmental impact.
- The contaminants are treated *in situ* and are converted to innocuous and/or natural occurring compounds (e.g., H_2O , CO_2 , and halides).
- By acting/reacting upon the contaminant in place, the reagent will not cause vertical movement of the contaminant, which is often a concern with other remediation technologies.
- By increasing dissolved oxygen (DO) levels throughout the treatment area, this process aids in bioremediation or aerobic microbial consumption of contaminants.

Limits of the Technology

- This treatment process, while fast acting, does require sufficient time to allow the redox reaction to go to completion; otherwise, residual compounds may remain in the contaminant stream.
- Hazardous intermediate compounds may be formed due to incomplete oxidation caused by insufficient quantity of either oxidant or catalyst, the presence of interfering compounds (natural organic-rich media, iron and/or manganese) that consume the reagents, and/or inadequate mixing or contact time between contaminant and oxidizing agent.
- Large amounts of reagents are required for treatment of DNAPLs.
- Lack of proper site characterization and/or monitoring of technology operations may result in adverse effects, such as development of explosive forces due to excess buildup of pressure (below the ground surface).

Regulatory Concerns

In some states, variances have been granted from rules that prohibit ‘zones of discharge’ for discharges through remediation wells. Typically these variances are contingent on the following:

- A corrective action plan must be approved by the state agency.

- The discharge must be through an underground injection control well that meets all the applicable construction, operating, and monitoring requirements of the state agency.
- The zone of discharge must be acceptable to the state agency, typically a ten foot radius from the point of injection but always within the contamination plume.
- The rate and volume of reagent injection must not cause undesirable migration of either the reagents or of contaminants already present in the aquifer.
- The corrective action plan must address ground water monitoring requirements associated with the use of the technology based on site-specific hydrogeology and conditions.

Site(s) Where Implemented

I. Anniston Army Depot, Anniston, AL

Full-scale soil remediation using *in situ* chemical oxidation for removal of DNAPLs was begun in 1997 at Anniston Army Depot, Anniston, Alabama. The site consists of three industrial waste lagoons backfilled with clay in 1978. It is approximately 2 acres in size with over 43,125 cubic yards of contaminated soil containing TCE, DCE, methylene chloride, and benzene, toluene, ethylbenzene, and xylene (BTEX). TCE accounts for approximately 85% of the 72,000 lbs of volatile organic contamination. The majority of contaminants were found at depths of 8 ft and greater. The highest concentrations of TCE occur at depths between 8 and 10 ft (maximum 20,100 mg/kg). The water table fluctuates from 25–30 ft below the surface.

Three different sized injector wells were installed to target three distinct depth intervals. Single shallow injectors screened from 8–14 ft were installed in areas where contamination was shallower than 15 ft. Single intermediate injectors were installed where contamination was found from 15–20 ft, and paired shallow and deep injectors screened from 20–26 ft were installed in areas where contamination was found at both deep and shallow depths. In addition, 25 deep ground water injector wells were used for monitoring, and a vent flow balance system was installed to aid in maintaining an effective radial dispersion of catalyst and peroxide.

The Geo-Cleanse patented injection process was employed to deliver peroxide and trace quantities of ferrous sulfate and acid (to control pH) into the contaminated soil. Chemical oxidation of the soil took place over a 120-day period during which 109,000 gallons of 50% H₂O₂ were injected through a total of 255 injectors. Post-treatment sampling began while the full-scale treatment was still in progress. In cases where contaminant concentrations remained above EPA's Soil Screening Levels (SSLs), the location was re-treated for polishing treatment (U.S. EPA, 1998).

The total cost to complete this project is estimated to be \$5.7M. This full-scale treatment was initiated in July 1997. For those areas where sampling and polishing have been completed, results indicate that this process was effective in reducing contaminant concentrations in clays to below SSLs. Soil concentrations of up to 1,760 mg/kg of TCE have been reduced to below detection. Additional polishing treatment may still be warranted, depending upon the results of final sampling in the remaining blocks. Operating data indicate no adverse migration of organics to surrounding soils or ground water.

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II. Westinghouse Savannah River Site, Aiken, SC

DOE's Savannah River Site is located in Aiken, South Carolina. Three and a half million lbs of solvents, primarily PCE and TCE, were discharged to the soils and ground water in the A/M Area from 1958 until 1985. This area was once a fuel and target fabrication facility where uranium, lithium, aluminum and other materials were processed into fuel elements and targets for use in nuclear production reactors.

The selected test site is in a bowl-shaped surface depression, is 50 x 50 feet, and is adjacent to a seepage basin. It is within a suspected subsurface trough, along which DNAPL is migrating. Soil concentrations of PCE in the test area ranged from 10 to 150 mg/kg. Highest concentrations were found in a zone at approximately 140 feet below ground surface (bgs). The average PCE concentrations in ground water were 119 mg/l.

The 1997 demonstration of *in situ* chemical oxidation was conducted in three phases: pre-test characterization, technology test, and post-test characterization. Pre- and post-test characterization consisted of collecting continuous soil cores from which soil samples were taken and analyzed by GC headspace method to measure PCE and TCE concentrations. Rotasonic drilling was used to collect soil cores and to install all wells for the test. By comparing post-test data to pre-test characterization data, the destruction efficiency of the treatment technology was determined. The technology utilized was the patented Geo-Cleanse injection process, whereby H₂O₂ and a catalyst (ferrous sulfate) were injected. This treatment (injection) was conducted over a 6-day period.

Success of this demonstration was based on destruction of DNAPL in the treatment zone. The best measure of destruction is based on measurement of DNAPL globules in the sediment before and after the treatment process. Results of pre- and post-test characterization indicated a significant decrease in DNAPL concentration after the technology test. The estimated pre-test mass of DNAPL in the treatment zone was 600 lbs, and the estimated post-test mass of DNAPL was 40 lbs. This reduction is a destruction rate of approximately 90 percent for the treatment zone. Total destruction of all DNAPL was not achieved and can be attributed to the process not contacting all DNAPL globules in the fine-grained sediments. Injected hydrogen peroxide takes the path of least resistance through areas of higher permeability, which in this case is through sandy regions of the treatment zone.

On a unit cost basis, this technology becomes cost competitive with pump and treat using air stripping (\$87/lb, SRS costs) for a DNAPL pool of approximately 9,500 lbs. at a depth of 155 ft bgs. Depth is a major contributor to the overall costs when this technology is employed. For a DNAPL pool of volume V, as depth to the DNAPL pool increases, the costs for remediation will increase. Thus, both size of the DNAPL pool and depth to the DNAPL pool must be considered in determining when this technology becomes cost competitive with the chosen baseline technology.

Other factors (advantages) contributing to the decision to use this technology include duration of treatment and end products of treatment. Treatment time ranges from days to weeks. Factors affecting the duration of the treatment include other compounds that may be oxidized under similar conditions, geochemical makeup of the treatment zone, and tightness of the treatment zone (i.e., access to DNAPL). End products of *in situ* oxidation are very attractive. No waste is generated from the treatment process, and no material is brought to the surface. End products of this process are carbon dioxide, water, and chloride ions. All of these compounds are considered harmless materials.

Additional questions raised during the demonstration concerned effects of the treatment on the geochemistry and microbiology in the target zone. Work, which began in 1998 and has recently been completed, will attempt to answer these questions.

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3.4.3 Ozone/O₃

How the Technology Works

Ozone is an allotrope of oxygen that contains three oxygen molecules (O₃) rather than the more common oxygen gas, which consists of two oxygen molecules (O₂). Ozone is unstable in nature and, because of this, serves as an aggressive oxidizing agent (oxidation potential of 2.1 volts). However, due to its short half-life (30 seconds in distilled water at 20 degrees Celsius), ozone must be produced on site, which is typically done by passing dewatered air between oppositely charged plates or through charged tubes. In addition, on-site production eliminates storage and handling problems associated with other oxidants.

An air sparging system is typically used to deliver ozone to the subsurface. Once below the surface, ozone serves to oxidize organic contaminants in two ways: by direct oxidation with ozone or by the generation of free radical intermediates, such as hydroxyls. The hydroxyl radicals are nonselective oxidizers that rapidly attack organic contaminants (typically in less than 10 seconds) and break down their carbon-carbon bonds.

Ozonation may also assist bioremediation by breaking down complex compounds into simpler compounds, which are more easily degraded. When ozone decomposes, a source of oxygen is provided to the microbial community, aiding bioremediation. Ozone is also a sterilizing agent in high concentrations or through long residence times, so the ozone must be carefully controlled if bioremediation is to be encouraged. Amendments, such as hydrogen peroxide, can also be used with ozone to generate free radicals.

Advantages of the Technology

Ozone can be used for the treatment of ground water contaminated with a wide variety of organic compounds, including those typically resistant to oxidation using conventional technologies. It is effective on

- aromatic hydrocarbons,
- pesticides,
- chlorinated solvents, and
- ordnance compounds (e.g., explosives).

The technology is particularly effective for use at facilities using, storing, and/or disposing of chlorinated or nonchlorinated solvents and/or pesticides; and at military facilities where ordnance compounds have been manufactured, used, stored, or disposed.

Limits of the Technology

- Susceptible to interference from free radical scavengers such as acids.
- Requires the aqueous stream be treated to be relatively free of metal ions and insoluble oil or greases to minimize the potential for fouling of the equipment.

Regulatory Concerns

Pilot testing may be required by state agencies prior to full-scale implementation of air sparging. Also, the air sparging system should be designed to prevent or minimize the migration of contaminants away from the plume or source area.

Site(s) Where Implemented

I. Nellis Air Force Base, NV

A Remedial Investigation at Nellis Air Force Base identified a plume of TCE-impacted ground water at site ST-44. Site ST-44 occupies a 900 ft by 1,200 ft area, along the flight line encompassing Buildings 269, 270, 271, and 277 (Flight Line Fire Station), as well as the adjacent paved areas. Under the Installation Restoration Program (IRP), a pilot test was conducted to determine the feasibility of using *in situ* ozone sparging to reduce TCE contamination at ST-44.

ERM Program Management Company (ERM PC) and K-V Associates, Inc. (KVA) conducted the pilot test. The ozone sparging system consisted of three sparge wells, which were located based upon review of available site information regarding TCE-impacted ground water plume location, site geology, and previous KVA experience. Each sparge well consisted of a double-screened well with KVA Spargepoints both within the well and at the bottom of the boring. The C-Sparge™ system is designed to introduce fine bubbles of ozonated air below and into the plume of TCE-impacted ground water. Within the central part of the well, a submersible pump circulates the water to displace the vertically moving bubbles sideways, increasing dispersion and contact to maximize TCE degradation.

Based on pre-pilot testing, the radius of influence (ROI) was estimated at approximately 30 to 40 ft. The air/ozone mixture was set and maintained at 2.5 ppm ozone concentration for a total loading of 60 grams ozone per day from each master unit. A 20 cfm vapor control system was installed with each master unit at the request of the Nevada Department of Environmental Protection to account for any VOCs exiting in the offgas from the sparge well.

The testing saw many difficulties with the pilot system due to low permeability of soils. In addition, there were problems with the electrical supply and with the well packer assemblies,

resulting in blowouts under system pressures and dead heading of pumps. The pilot test results showed varying amounts of TCE reductions in wells and spargers; however, rebound in TCE levels was seen in 4 out of 5 wells and 1 out of 3 spargers.

The ground water ROI may be greater than the sparging ROI. Based on current testing in Europe, it is believed that the ROI can be increased 100 ft or greater using double-screened recirculation wells, larger pumps, and pressure relief between layers to encourage contact and recirculation.

Recommended changes to further the application of the C-Sparger™ system at Site ST-44 are

- a recirculation pump with even higher discharge pressure;
- a more permanent, dedicated electrical supply;
- secure enclosures to prevent tampering;
- a contract for weekly or routine maintenance to ensure that the system operates at peak performance;
- periodic use of recording piezometers and ground water flow meters to verify proper circulation; and
- install recirculation wells in selected locations.

3.4.4 Safety Considerations

When an ISCO technology is employed, the volatility of some contaminants may be sensitive to temperature, and there could be a significant change in both the concentration and distribution of flammable vapors and/or toxic nonflammable vapors. This dynamic environment is less predictable than most other cleanup situations where less powerful remediation methods are unable to drive the cleanup by greatly changing a site's established phase equilibrium of contaminants. Therefore, both precautionary and preventative measures are appropriate.

If the contaminants include petroleum or flammable solvents, potential fire and explosion hazards need to be considered, so that appropriate equipment and operating procedures can be specified for their prevention. These hazards may include

- the potential for subsurface migration of vapors, either through pathways in the aquifer and soil itself or via underground conduits such as sewer lines, utilities, storm drains, etc., and the destination of those pathways should migration occur;
- the presence of free product in the subsurface, either in underground utilities or in the form of non-aqueous phase liquids, which could be volatilized by the heat of an exothermic chemical reaction in concentrations that exceed the lower explosive level;
- the presence of underground petroleum or flammable liquid storage tanks and dispenser pipelines near the source of heat generated by chemical oxidation reactions; and
- possible ignition sources (electrical equipment, devices and switches, vehicle exhaust sparks, mechanical sources of sparks, etc.) at potential vapor migration pathway destinations.

Measures that may need to be taken to mitigate these hazards include

- monitoring of vapor concentrations, for comparison with lower explosive levels, at the site and/or in conduits and other potential pathways and buildings during operation of the chemical oxidation system;
- identifying the chemical reactants involved and determining the amount of heat liberated by their

reaction;

- monitoring of aquifer and/or vadose temperature during treatment;
- determining the maximum temperature that may be tolerated before it is necessary to shut down operation;
- controlling the reactant concentrations and/or quantities as a means of controlling temperature;
- using a vacuum extraction system to collect vapors at sites where significant amounts of volatilization are expected to occur; and
- removing flammable contents from tanks and dispenser pipelines and replacing with inert gases, such as nitrogen or carbon dioxide.

If the only contaminants are chlorinated hydrocarbons, the risk of a fire is reduced since those compounds are not flammable. However, caution should be exercised to prevent the release or migration of quantities and concentrations of chlorinated vapors that may be harmful from a toxicological or environmental standpoint.

4.0 STAKEHOLDER CONCERNS

Involvement of stakeholder and tribal representatives (as applicable) at every stage of the evaluation and selection of treatment systems and vendors will lead to better, more defensible selections and expedite cleanup of contaminated sites. The responsible parties' objective should be to integrate stakeholder involvement into all of its processes.

This section contains a brief outline of generic stakeholder concerns for the deployment of any remediation technology and is based on the November 1996 Revised Predecisional Draft *Tribal and Stakeholders Principles for use in Evaluating Technology Systems for Mixed Low Level Waste Treatment* developed jointly by the U.S. Department of Energy and the Tribal and Stakeholder Working Group. A more detailed summary of this report is included in Appendix B.

4.1 The Six Principles

There are six principles for governing the selection and implementation of any remediation technology from a stakeholder perspective:

1. Minimize effluents.
2. Minimize effects on human health and the environment.
3. Minimize waste generation.
4. Address social, cultural, and spiritual considerations.
5. Provide adequate and understandable information.
6. Incorporate tribal and stakeholder involvement into the responsible parties' procurement process and the performance evaluation of contractors on stakeholder participation.

These principles are applicable to evaluation and selection of remediation and waste treatment systems. They augment conventional technical criteria by introducing additional considerations that technical staffs, possibly assisted by technically trained tribal and stakeholder representatives, should address to make such systems more acceptable to the general public.

The principles are qualitative in nature and provide no quantitative limits that can be used to delineate between acceptable and unacceptable systems. They should be considered goals for which technical staffs should strive to enhance public acceptance.

Uncertainties regarding public acceptance of remediation and waste treatment systems will always exist. These uncertainties can be reduced by timely and meaningful involvement of tribal and stakeholder representatives from the beginning of technology development processes. Doing so will promote early identification of significant issues, joint resolution of these issues, and “real-time” concurrence about public acceptance of the proposed treatment system. Finding ways to identify appropriate representatives and keep them informed are recommended.

4.2 Specific Comments on DNAPLs and Remediation Technologies

Comments on both the issue of DNAPL contamination and the different technologies that might be used for site characterization and remediation were solicited from members of the Center for Public Environmental Oversight (CPEO) via their military site listserver (cpeo-military@igc.org). This e-mail forum has an active membership of stakeholders, responsible parties, state and federal regulators, and technical and public-participation consultants. Specific case-studies are described in Appendix B.

Alcohol or Co-solvent Flushing and Surfactant Flushing

Benefits

- *Ex situ* treatment is perceived as effective and controllable, with the contaminated soil treated and the extracted contamination and spent alcohol, co-solvent, and surfactant collected and disposed of in a safe manner.

Problems

- If the stratigraphy does not contain a solid, thick clay layer underlying the contaminated soil, flushing may transport the chlorinated organics directly to the ground water with resultant contamination of the aquifer.
- If there is a clay layer with sufficient integrity, great pains must be taken to construct multiple (possibly redundant) extraction wells in both the vertical and horizontal planes on the periphery of the contaminated soil to ensure that all introduced flushing agents and chlorinated organics in solution will be recovered. One outcome could be the rapid transport of the contaminants to the top of the clay; and, depending on the conditions there, the contaminants might be difficult to collect. The cost of multiple extraction wells may deter responsible parties from installing a sufficient number to ensure the system works properly.
- Lack of knowledge of the physical or chemical effects that alcohol, co-solvent, or surfactants will have on the chlorinated solvents.

In Situ Oxidation

Benefits

- Potassium permanganate and other chemical oxidants can attack the DNAPL directly. These technologies appear to be quite effective as they completely destroy most DNAPL compounds.

Problems

- As with any potential treatment of a DNAPL source, the treatment zone around the source needs to be monitored and effectively isolated from the rest of the aquifer to avoid pushing the contamination to previously unimpacted areas.

Steam Injection

Benefits

- *Ex situ* treatment is perceived as effective and controllable, with the contaminated soil treated and the extracted contamination collected and disposed of in a safe manner.

Problems

- If the stratigraphy does not contain a solid, thick clay layer underlying the contaminated soil, steam injection may transport the chlorinated organics directly to the ground water with resultant significant contamination of the aquifer.
- If there is a clay layer with sufficient integrity, great pains must be taken to construct multiple (possibly redundant) extraction wells in both the vertical and horizontal planes on the periphery of the contaminated soil to ensure that all chlorinated organics in solution will be brought to the surface. One outcome could be the rapid transport of the contaminants to the top of clay; and

depending on the conditions there, the contaminants might be difficult to collect. The cost of multiple extraction wells may deter responsible parties from installing a sufficient number to ensure the system works properly.

- Lack of knowledge of the physical or chemical effects that steam injection will have on the chlorinated solvents.

5.0 CONCLUSIONS

This document provides an overview of emerging dense non-aqueous phase liquids (DNAPLs) characterization and remediation technologies so that regulators and technology end users, faced with DNAPL problems of their own, can become familiar with recent developments in this relatively new and expanding field. The technologies included in our review are, for the most part, not mature and therefore, limited data from actual field investigations or remedial operations are available.

The most common DNAPLs found at hazardous waste sites are chlorinated solvents, such as TCE and PCE. Millions of dollars a year are spent investigating and remediating such sites since, even in the low ppb range of concentrations, these compounds can pose significant threats to public health and the environment. Because most chlorinated solvents are hydrophobic and tend to adsorb to soil, they are difficult to recover using conventional pump and treat or flushing technologies. In addition, DNAPLs tend to migrate along subsurface channels or fissures, accumulating as pools above impermeable layers or forming fingers or ganglia of residual DNAPL, making them difficult to delineate using conventional investigatory methods.

Several innovative techniques for characterizing the subsurface distribution of DNAPLs are available, overcoming the limitations and cost of traditional drilling programs. Noninvasive geophysical technologies that were addressed include ground penetrating radar, cross-well radar, electrical resistance tomography, and high resolution seismic reflection, all of which produce computer-generated images of subsurface conditions to estimate the likely distribution of DNAPLs and guide confirmatory sampling. Chemical tracers are also being used to identify residual DNAPL zones based on their affinity for a particular contaminant and the measured change in tracer concentration between wells. The Partitioning Interwell Tracer Test (PITT) is a particularly promising technology employing a combination of conservative and partitioning tracers. Recent advances in cone penetrometer and sensor technology have enabled DNAPL sites to be characterized using vehicle-mounted probes. Probes are available for directly measuring contaminant concentrations *in situ*, in addition to measuring standard stratigraphic data, to provide flexible, real-time analysis. The probes can also be reconfigured to expedite the collection of soil, ground water, and soil gas samples for field laboratory analysis.

The emerging DNAPL remedial technologies reviewed in this document are *in situ* flushing, *in situ* chemical oxidation (ISCO), six-phase heating, and steam injection. *In situ* flushing involves injection of alcohols or surfactants to mobilize residual DNAPL and facilitate contaminant extraction by pumping. ISCO is a technology for destroying subsurface contaminants by sweeping the zones of contamination with an oxidizing agent, such as hydrogen peroxide, potassium permanganate, or ozone. The objective of six-phase heating and steam injection is to thermally enhance the extraction of contaminated vapors by increasing the rate of volatilization from the heated soil and enhance the

recovery of separate-phase DNAPL by lowering the fluid viscosity.

ITRC's DNAPLs Work Team believes the technologies covered in this overview document have significant potential to meet the challenges presented by DNAPL-contaminated sites. As these emerging technologies mature and more complete cost and performance data becomes available, ITRC will continue to promote their deployment nationwide by producing one or more guidance documents or case studies. These will help improve market conditions for DNAPL remediation technologies by providing a degree of consistency and predictability in technical requirements from state to state. Such ITRC guidance can also provide a common framework for state regulatory acceptance of these technologies.

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APPENDIX A

Acronyms

Acronyms

²²² Rn	Radon 222
²³⁸ U	Uranium 238
3D	3-dimensional format
AC	alternate current
AFB	Air Force Base
AFCEE	Air Force Center for Environmental Excellence
ARA	Applied Research Associates
ASTM	American Society for Testing Materials
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, xylene
cfm	cubic feet per minute
CITT	conservative interwell tracer test
CPEO	Center for Public Environmental Oversight
CPT	cone penetration test
CRREL	Cold Regions Research and Engineering Laboratory
DCE	dichloroethylene or dichloroethene
DNAPLs	dense non-aqueous phase liquids
DO	dissolved oxygen
DoD	Department of Defense
DOE	Department of Energy
EIT	electrical impedance tomography
EM	electromagnetic
EMR	electromagnetic resistivity survey
EOL	electromagnetic offset logging
ERT	electrical resistance tomography
Fe ⁺²	ferrous iron, Iron II
ft	feet or foot
GC	gas chromatograph
GPR	ground penetrating radar
H ₂ O ₂	hydrogen peroxide
Hg	Mercury
HPO	hydrous pyrolysis/oxidation
IRP	Installation Restoration Program
ISCO	<i>in situ</i> chemical oxidation
ISCOR	<i>in situ</i> chemical oxidation with recirculation
ITRC	Interstate Technology and Regulatory Cooperation
KMnO ₄	potassium permanganate
mm	millimeter
MSDS	Material Safety Data Sheet
MSL	mean sea level
MTBE	methyl tertiary butyl ether
NAPL	non-aqueous phase liquid
O&M	operation and maintenance

Acronyms (continued)

OH•	hydroxyl radical
OST	Office of Science and Technology
OU	operable unit
PAH	polynuclear aromatic hydrocarbon
PCBs	polychlorinated biphenyls
PCE	tetrachlorethylene <i>or</i> perchloroethene
PCP	pentachlorophenol
PID	photoionization detector
PITT	partitioning interwell tracer test
ppm	parts per million
PVC	polyvinyl chloride
RDX	royal demolition explosive or cyclonite
RHX	halogenated organic compound
RNS	Ribbon NAPL Sampler
ROI	radius of influence
ROST	Rapid Optical Screening Tool
SCAPS	Site Characterization & Analysis Penetrometer System
SEAR	Surfactant-Enhanced Aquifer Remediation
SPH	Six-Phase Heating
SRS	source removal system
SSLs	soil screening levels
SVE	soil vapor extraction
SwRI	Southwestern Research Institute
TCA	trichloroethane
TCE	trichloroethene or trichloroethylene
TNT	trinitrotoluene
TOC	total organic carbon
TPH	total petroleum hydrocarbon
TSWG	Tribal and Stakeholder Working Group
VIP	vertical induction profiling
VOA	volatile organic analysis or analyte

APPENDIX B

Summary of Tribal and Stakeholder Principles

Summary of Tribal and Stakeholder Principles

The principles summarized below are excerpted from the November 1996 Revised Predecisional Draft *Tribal and Stakeholders Principles for use in Evaluating Technology Systems for Mixed Low Level Waste Treatment* and were developed jointly by the U.S. Department of Energy Office of Science and Technology (OST, EM-50) and Tribal and Stakeholder Working Group (TSWG) Mixed Low Level Waste Treatment Systems Studies. The principles, although developed specifically for mixed low level waste treatment systems, are generic and can be applied to a broad range of systems studies in planning future research and development. These principles are intended to be used concurrently with the technical criteria to study and evaluate a broad scope of treatment systems.

Following the summarization of the tribal and stakeholder principles, specific comments and criticisms of technologies proposed for remediation of DNAPLs are documented. Additional principles that can be derived from these comments are then summarized.

Objective

Involvement of stakeholder and tribal representatives (as applicable) at every stage of the evaluation and selection of treatment systems and vendors will lead to better, more defensible selections and expedite clean up of the contaminated sites. The responsible parties' objective should be to integrate stakeholder involvement into all of its processes.

The Six Principles

1. Minimize effluents.
2. Minimize effects on human health and the environment.
3. Minimize waste generation.
4. Address social, cultural, and spiritual considerations.
5. Provide adequate and understandable information.
6. Incorporate tribal and stakeholder involvement into the responsible parties' procurement process and the performance evaluation of contractors on stakeholder participation.

General System Concepts

The following concepts are explained in the context of tribal and stakeholder viewpoints. These general concepts apply to one or more principles.

- Minimization – viewed as a two-part process: (1) Avoid adverse conditions (effluents, effects, waste generation, etc.), if practicable; and (2) When avoidance is not practicable, reduce remaining adverse conditions to their lowest practicable levels.
- Reliance on Regulatory Standards – mere conformance with these standards may provide less-than-adequate human health and environmental protection, and does not mean that a proposed system will gain widespread public acceptance. The regulatory standards represent minimum protective values. Actual exposures and releases should be reduced to their lowest possible levels. Monitoring requirements should be identified and included in Total Life Cycle Costs.
- System Selections – those system elements and design that best comply with the six principles will be most satisfactory to stakeholders. These include appropriate choices of (1) equipment, technologies and processes; (2) system design configurations; (3)

construction and process materials; (4) operating practices (construction, operations, transportation, storage/disposal, facility closure and environmental restoration); and (5) continuous monitoring of effluents.

- Procurement Process – stakeholder and tribal representatives should be involved in procurements, the selection process, and the performance evaluation of agencies and contractors.

Principles and Subprinciples

1. Minimize effluents.

- Minimize airborne and wastewater effluents that can carry hazardous materials or substances capable of causing adverse human health and environmental consequences.

2. Minimize effects on human health and the environment.

- Minimize worker exposures now and in the future.
- Minimize the potential for release of hazardous and radioactive materials from final storage/disposal products.
- Minimize the potential for accidents and incidents in the system.

3. Minimize waste generation.

- Minimize creation of new hazardous materials by treatments.
- Minimize the volume of final waste forms for storage/disposal.

4. Address social, cultural, and spiritual considerations.

- Minimize land use for storage/disposal.
- Minimize transportation from one site to another.
- Reflect special considerations for specific sites.
- Waste should be disposed in a retrievable manner.
- Respect cultural values.
- Minimize noise.
- Protect local vistas.
- Costs of complying with intergovernmental agreements should be included in Total Life Cycle Costs.

5. Provide adequate and understandable information.

- Provide technology screening and down-selection and system description and cost information, including details of the process and how unsuccessful systems could become viable.
- Provide information about systems' hazards and risk and the safety features provided to avoid or reduce these hazards and risks.
- Describe the processes that govern the conduct of the study:
 - ▶ Treatment study decision-making,
 - ▶ Federal agency or responsible party decision-making,
 - ▶ Tribal and stakeholder involvement,
 - ▶ Planned documentation and outcomes, and
 - ▶ Likely pollutants in gas or water effluents.
- Provide system and technology information within the framework of Tribal and Stakeholder Principles and Technical Criteria.

- Integrate or “bridge” thermal, nonthermal, and other applicable treatment systems studies for overall systems comparisons.
- Focus on existing stored waste and then add projected impact of future waste generation.
- Keep the tribal and stakeholder representatives involved and informed throughout the evolution of systems studies.
- Provide information on qualitative and quantitative analysis and monitoring of hazardous and radioactive components in effluents.
- Independent advisory resources should be made available to review the information and respond to those supplying the information.

6. Incorporate tribal and stakeholder involvement into the responsible parties’ procurement process and evaluate contractors on their stakeholder participation.

Application of Principles and Stakeholder Involvement

These principles are applicable to evaluation and selection of remediation and waste treatment systems. They augment conventional technical criteria by introducing additional considerations that technical staffs, possibly assisted by technically trained tribal and stakeholder representatives, should address in order to make such systems more acceptable to the general public.

The principles are qualitative in nature and provide no quantitative limits that can be used to delineate between acceptable and unacceptable systems. They should be considered goals toward which technical staffs should strive to enhance public acceptance.

Uncertainties regarding public acceptance of remediation and waste treatment systems will always exist. These uncertainties can be reduced by timely and meaningful involvement of tribal and stakeholder representatives from the beginning of technology development processes. Doing so will promote early identification of significant issues, joint resolution of these issues, and “real time” concurrence about public acceptance of the proposed treatment system. Means to identify appropriate representatives and keep them informed are recommended.

APPENDIX C

**ITRC Contacts, ITRC Fact Sheet, ITRC Product List, and
Document Evaluation Survey**

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