DNAPL RECOVERY MONITORING PROGRAM (DRMP) REMEDIATION SYSTEM OPTIMIZATION INITIATIVE

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1.0 Introduction and Objectives

The focus of this document is on creosote, a dense non-aqueous phase liquid (DNAPL). At many wood treating sites, creosote DNAPL is found in the subsurface. Often, the DNAPL is found at residual saturation[1] and is immobile; at other sites, the DNAPL is found above residual saturation and is mobile. At sites where DNAPL is mobile, creosote DNAPL recovery via wells is often required. Therefore, this document also focuses on DNAPL recovery, specifically pumping creosote DNAPL.

The standard regulatory approach with regard to DNAPL presence is to recover DNAPL to the "maximum extent practicable" (MEP). MEP is often ill defined, yielding a performance-based remedy that has a poorly-defined endpoint strategy with uncertain objectives and measurement metrics. In addition, inadequate characterization[2] and monitoring of DNAPL distribution and characteristics often leads to ineffectively applied technologies to recover DNAPL and a limited ability to predict remedial performance and duration. This leads to delayed site closures and the potential over-allocation of limited resources with little or no reduction in risk.

It is unclear if DNAPL recovery will result in future changes in site-care requirements. This is because site remedial goals are usually risked based, and MEP remediation may have little impact on risk reduction. Recent reviews conclude that complete DNAPL mass removal is unlikely even where source zone remedial technologies in addition to pumping DNAPL are used (U.S. EPA, 2003 and NRC, 2005). Consequently, there is an apparent disconnect between the risk-based strategy used for soil and groundwater remediation and the MEP strategy used for remediation of DNAPL.

The objectives of this document, therefore, are: (1) to better define MEP, (2) to present methods to monitor the effectiveness of DNAPL recovery, and (3) to provide guidance on data collection that will aid in determining when it is appropriate to terminate DNAPL recovery. As part of this effort, a regulatory overview is provided, DNAPL recovery objectives are discussed, DNAPL properties and behavior (as they pertain to DNAPL recovery) are reviewed, and DNAPL recovery experience at Beazer sites is summarized. This is followed by guidance to meet the three objectives listed above.

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[1] The saturation (vol. of NAPL/vol. of voids) at which the NAPL becomes discontinuous and is immobilized by capillary forces under ambient groundwater flow conditions.

[2] Inadequate characterization may be unavoidable due to the nature of DNAPL making it difficult to locate in the subsurface.

2.0 Regulatory Overview

Two issues are addressed from a regulatory viewpoint. The first concerns the need for an interim action if DNAPL is discovering during the process of site characterization. The second is the definition of MEP.

2.1 Interim Remedial Measures

According to the State of Arkansas Department of Environmental Quality (ADEQ) (http://www.adeq.state.ar.us/rst/branch_technical/default.htm), until recently, the presence of NAPL caused an environmental emergency, requiring immediate attempts at recovery. Finding NAPL in a monitoring well carried a large psychological impact, and expedited recovery attempts made everyone involved feel that something worthwhile was being accomplished. Continuing, ADEQ states, unfortunately, it is impossible to correlate an observed thickness of product in a monitoring well with risk to human health and the environment. Further experience over the last decade has shown that even aggressive and effective product recovery does not significantly influence the environmental outcome for the release site, and as a result, interim (that is, before the release is fully investigated/assessed) product recovery as a risk management tool has been de-emphasized in Arkansas.

The de-emphasis on interim actions may be true in Arkansas, but this type of reaction to DNAPL presence continues in other states. As an example, for the Koppers portion of the Cabot Carbon/Koppers Superfund site in Gainesville, FL at a July 21, 2004 meeting to discuss characterization results that indicated creosote had impacted the Hawthorn Group, thought to be an effective confining bed, the reaction of the regulatory agencies was to request an interim remedial measure (IRM) be implemented immediately. Although there may be exceptions, characterization should be fairly complete prior to implementing a remedy. From a strictly technical viewpoint, IRMs only should be implemented if they result in an actual risk reduction or if they provide data that will be helpful to final remedy selection.

2.2 Maximum Extent Practicable

For product recovery (whether interim or final), many states use the MEP standard but define it differently. Examples of what MEP means by state are listed below.

GA	1/8 inch
IN	Extent of technology
IA	<0.1 gal/mo for 12 mos.
KS	Site priority; economical feasibility
MD	Sheen
MI	1/8 inch
MO	Sheen
NM	1/8 inch
SC	Less than 0.01 ft. for 6 mos.
UT	Any measurable amount
VT	Protection of receptors

VA	0.01 or less and protection of uncontaminated zones
WA	MCLs
WV	Sheen

The problems with the MEP approach and ways to resolve these problems for light non-aqueous phase liquids (LNAPLs) have been the subject of the Remediation Technologies Development Forum (RTDF) NAPL Cleanup Alliance (Alliance), which consists of public and private members and was established in 2001. A document resulting from the Alliance is A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL) (U.S. EPA, 2005). This document stresses the need to better understand NAPL distribution, NAPL mobility, and the potential recoverable amount of NAPL, such that proper decisions can be made with regard to NAPL management. The steps listed in this document include: (1) definition of endpoints, (2) development of contingency plans, and (3) implementation and monitoring performance of well-defined metrics. According to U.S. EPA (2005), goals should be reasonable, practical, and as specific as possible. In may be useful to develop goals based on the acronym SMART – Specific, Measurable, Achievable, Results-oriented, and Time-bound.

This approach also is beginning to be adopted by some states. For example, Texas has the Texas Risk Reduction Program (TRRP); TRRP-32 is a NAPL Recovery Guide that it is currently under development. When this Guide is available, it will take a risk-based approach to NAPL recovery.

3.0 DNAPL Recovery Objectives

When determining DNAPL recovery objectives, it is important to consider (1) overall project remedial objectives, (2) the net benefit, and (3) technical and financial feasibility of the technology. Prior to initiating DNAPL recovery, estimate the quantity of DNAPL in the subsurface and what percentage of this quantity is recoverable. This estimate, due to the nature of DNAPL will be uncertain. Communicate this information to regulators in order to set expectations. Define specific reasonable and practical endpoints for the recovery effort (e.g., when asymptotic recovery is reached). Develop a contingency plan which would be implemented if endpoints cannot be achieved.

In many DNAPL recovery projects, the endpoint is not clear. As a result, there is continuing debate about when pumping can be stopped. Termination criteria should be established beforehand, and data should be evaluated continually during the project, to determine when these endpoints have been achieved. Measurable, technology-specific parameters should be used to gauge whether or not the current remedial phase is complete and whether the system is ready to be shut down or transitioned to a next phase. Termination criteria are typically based on numerical targets or endpoints to which operational monitoring data are compared.

There has been considerable experience pumping LNAPL, and recently, documents with an LNAPL and DNAPL remediation focus have been published. Therefore, as a first step in developing recovery objectives, a review of these documents is provide. The source remediation covered in these documents is more comprehensive than just pumping DNAPL. Therefore, the broader view of source remediation is included in this section.

3.1 Review of Objectives Proposed by Others

It is helpful to review what has been recommended for LNAPL recovery objectives (U.S. EPA, 2005) as it is closely related to DNAPL recovery; specific examples of LNAPL recovery endpoints include:

- Recovery rate for an LNAPL recovery system is reduced to an established value (e.g., three gallons per day);
- Specific COC in LNAPL is reduced to a target value at “x” monitoring locations over “y” period of time;
- Stability of the dissolved-phase plume is demonstrated based on a dissolved COC-concentration threshold at “x” monitoring locations over “y” period of time;
- LNAPL transmissivity is reduced to a certain value at “x” monitoring locations;
- LNAPL saturations at all points within the area of distribution have been reduced to levels below residual saturation, as measured by “a” method and cross-checked with “b” method;
- Groundwater samples from “xx” monitoring wells did not contain LNAPL-related organic constituents at concentrations above drinking-water maximum contaminant levels (MCLs) for four consecutive quarterly monitoring events;
- LNAPL chemistry has been changed so it no longer contains VOCs at measurable concentrations using analytical method “d” and vapor concentrations in the vadose zone measured by method “e” are below measurable levels;
- A containment system meeting “g, h, i” specifications has been installed and tested for integrity; and
- Final relative permeability value is attained.

Endpoints should be defined with specific considerations including (U.S. EPA, 2005):

- Type of measurement,
- Method for sample collection,
- Analytical method,
- Location of measurement, (including point of compliance),
- The timeframe for measurements,
- Number of measurements, and
- Data analysis, statistical evaluation, and data presentation.

DNAPL recovery objectives and monitoring strategies are discussed in NRC (2005) and ITRC (2004). These documents consider source zone remedies in addition to DNAPL pumping. There are three elements of a remedial objective for a site (NRC, 2005): (1) identifying the objective, (2) determining the appropriate metric(s) to measure achievement of the objective, and (3) determining the status of the objective. Communication of these three elements with stakeholders is important.

NRC (2005) lists four categories of objectives: (1) physical objective that relate to changes in site conditions, (2) risk-reduction objectives related to human health and the environment, (3) financial objectives related to life-cycle and other costs, and (4) schedule-driven objectives related to the time required to reach particular milestones (e.g., brownfield development). Physical objectives include (a) mass removal, (b) concentration reduction, (c) mass flux reduction, (d) reduction of source migration potential, (e) dissolved plume size reduction and/or stabilization, (f) changes in toxicity and/or mobility of residuals, and (g) elimination of barriers to subsequent remedial action (e.g., bioremediation). Contaminant mass flux reduction is an area of current research and has the potential of becoming a regulatory goal. The relationship between mass removal and mass flux reduction is discussed in Appendix A. Risk-reduction objectives include reducing the level of exposure and reducing chemical toxicity. Under financial objectives are reduction in life-cycle costs and reductions in remediation time and site uncertainties. Potential metrics for performance assessment of DNAPL zone treatment are provided below (ITRC, 2004).

Estimates of DNAPL Source Treatment Progress	**Estimates of DNAPL Source Mass Reduction**	**Estimates of DNAPL Source Treatment Impact**
Decrease in Soil Conc. – Measure constituents in soil cores	Mass Extracted – Ex situ measurement of waste streams (vapor, NAPL, groundwater)	Decrease in Toxicity – Constituent analysis (soil core, groundwater)
Decrease in Groundwater Conc. – Measure constituents in groundwater samples	Mass Destroyed In Situ – Indicators of breakdown products in groundwater	Decrease in Mobility – Determine NAPL saturation (soil cores, PITT)
Decrease in Soil Vapor Conc. – Measure constituents in soil vapor samples	Mass Remaining – Measure before/after masses (soil cores, PITT)	Decrease in Plume Loading – Measure mass flux (transect of wells and multi-level samplers, Tubingen integrated pumping tests, transect of borehole flux meters)

The existing framework for site cleanup objectives is generally driven by the two threshold criteria in the National Contingency Plan (NCP): (1) to be protective of human health and the environment and (2) to comply with Applicable or Relevant and Appropriate Requirements (ARARs). In practice, the criterion "protective of human health" has usually been embodied in quantitative risk assessment, specifically as having a calculated cancer risk between 10^{-6} and 10^{-4} and a Hazard Index < 1.0. "Protection of the environment" is less clearly defined, but follows a similar risk assessment approach (ecological risk assessment).

Meeting ARARs usually triggers drinking water Maximum Contaminant Levels (MCLs) for groundwater. At many sites, the two threshold criteria are used to apply source zone treatments (e.g., thermal treatment, use of surfactants) in addition to DNAPL pumping. However, according to the NRC (2005), even if removal of DNAPL is quite complete, attainment of MCLs throughout the source zone can almost never be expected immediately after source zone remediation. The NCP foresaw this possibility and allowed for ARAR waivers, defined in

CERCLA and the NCP, where "Compliance with the requirement is technically impracticable from an engineering perspective."

Consequently, there is a tension between those who push for maximum source mass removal and those who push for source zone management due to the technically impracticability of achieving MCLs. A sense for which side of this issue has support can be gleaned from the observation that between fiscal year (FY) 1989 and FY 02 (14 years), a total of 58 sites has receive technical impracticable (TI) waivers (Ken Lovelace, presentation at the NGWA Theis Conference, January 14-17, 2005). To add perspective, U.S. EPA analyses (U.S. EPA, 1993) suggest that DNAPL is present at approximately 60 percent of Superfund sites where organic chemicals have been detected (> 1000 sites); whereas only 58 TI waivers have been issued and some of these cover minimal items, such as moving the compliance point.

3.2 Relevant Objective for DNAPL Pumping

In this section, only objectives that apply to DNAPL pumping are discussed. These objectives include: (1) mass removal, (2) mass flux reduction, (3) reduction of source migration potential, and (4) dissolved plume size reduction and/or stabilization. Often these objectives are combined. For example, if there is a potential for creosote to continue to migrate, the objective may be to reduce the DNAPL migration potential by mass removal. Or the goal may be to reduce or stabilize the down-gradient dissolved plume[3] by reducing the mass flux emanating from the DNAPL source by conducting DNAPL mass removal. The common theme in these objectives is mass removal, which is the focus of this discussion.

Removal of DNAPL mass from a source zone is a common objective at creosote sites. Creosote DNAPL mass removal can be accomplished by pumping DNAPL from wells. If only DNAPL is pumped, the process is sometimes referred to as passive recovery. When both DNAPL and groundwater are pumped, the process is sometimes referred as active recovery. In either case, the goal is often expressed as MEP.

Example DNAPL Pumping Objective

A proposed plan for DNAPL recovery was provided for the Lowry Superfund Site near Denver, CO (see www.lowrylandfillinfo.com). As part of the waste-pit remedy, the plan calls for NAPL removal to achieve an end-point criterion of 0.5 foot remaining after remediation. The end-point criterion was established to attain remediation efficiency (not risk reduction or chemical concentration limits). The rationale behind the decision was that the waste pits are within a larger area of the landfill that is contained. In addition, previous attempts to remediate the waste pits using excavation and vapor/liquid removal combined with electrical heating did not remediate the waste pits satisfactorily.

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[3] If the remedial goal is only to ensure plume stability, and passive bioremediation is shown to be effectively limiting plume migration, then NAPL removal is irrelevant.

4.0 DNAPL Properties and Implications

The distribution, mobility (potential to migrate), recoverability, and characteristics of DNAPL are key factors that need to be addressed for DNAPL recovery decisions. The anticipated time to cleanup is another key issue. These are influenced by a number of factors that are discussed in this section. Determination of DNAPL distribution is a subset of site characterization, which is discussed in a number of publications (e.g., Cohen and Mercer, 1993; Pankow and Cherry, 1996; U.S. EPA, 2003; and NRC, 2005). Consequently, characterization of DNAPL distribution is not discussed in this document. Characterization, however, is an important step and findings from characterization greatly affect DNAPL removal decisions. Further, DNAPL characterization is usually complicated, expensive, and is not a straightforward process. For example, accurate estimates of residual and mobile DNAPL volumes are valuable information, but these estimates are very difficult to obtain and are uncertain.

If it is at residual saturation, DNAPL will be largely non-pumpable. If the creosote DNAPL is above residual saturation, then a portion of the DNAPL is pumpable. Pankow and Cherry (1996, p. 496) indicate that under the most favorable circumstances, free-product pumping removes a maximum of one-half or two-thirds of the DNAPL, leaving abundant DNAPL to serve as a long-term source. This is consistent with experience with petroleum recovery in oil fields. Levorsen (1967, p. 466) reports that the recoveries from oil pools are sometimes as much as 70 or 80 percent of the original oil in place, although for most such pools, recover is usually less than 60 percent.

Creosote in the subsurface is acted upon by three forces: (1) gravitational forces (pressure due to gravity), (2) capillary forces (capillary pressure) and (3) hydraulic force (also known as viscous force or hydrodynamic pressure). In general, capillary forces tend to trap creosote while gravitational and hydraulic forces tend to mobilize creosote. Creosote will be mobilized when the vector sum of the gravitational and hydraulic forces exceed capillary forces.

Creosote trapping due to capillary forces occurs in two ways: (1) creosote is trapped within the pores at residual saturation and (2) creosote is trapped as pools (above residual saturation) on top of less permeable layers (due to insufficient DNAPL entry pressure to displace water in a fine-grained, low-permeability layer). Consequently, once the surface source is eliminated, creosote will migrate until a flow equilibrium is reached whereby the mobile creosote is trapped by capillary forces at residual saturation within pores and/or as pools on top of stratigraphic traps (low-permeability, capillary pressure barriers).

The volume of DNAPL that is mobile and can be recovered depends of several factors, including (1) residual saturation trapped by capillary forces, (2) heterogeneity of the soil, (3) mobility of the DNAPL and (4) site-specific DNAPL properties. DNAPL properties that affect mobility are discussed below.

4.1 DNAPL Properties

DNAPL properties impact DNAPL recovery and need to be determined prior to any DNAPL recovery operation. At a minimum, DNAPL density and viscosity need to be determined, and, if possible, interfacial tension and wettability should be determined. Each of these properties is discussed below.

Density (or specific gravity) of DNAPL creates a tendency for DNAPLs to migrate downward through the saturated zone. Specific gravity is the density of a substance divided by the density of water. Because water has a density of 1 g/cm^3, specific gravity is the same as density without units. The density for creosote ranges from about 1.03 to 1.10 g/cm^3, which is slightly denser than water. Because the density is close to that of water, creosote does not experience as large a gravitational driving force for vertical migration as other DNAPLs such as chlorinated solvents.

DNAPL **viscosity** also affects migration. Kinematic viscosity [usually provided in centistokes (cSt) where 1 cSt = 1 centipoise cm^3/gm] is the absolute viscosity divided by the fluid density. Viscosity is a measure of the fluid's internal friction. The absolute viscosity for creosote generally ranges from approximately 6 to 26 centipoise (cp), which is thicker than water that has an absolute viscosity of 1.14 cp at 15° C. Creosote generally has higher viscosity than other DNAPLs such as chlorinated solvents, and migrates more slowly under similar hydraulic gradients.

The **interfacial tension** (IFT) refers to the tensile force that exists in the interface separating two immiscible fluids (e.g., creosote and water). It is provided in dynes/cm or N/m [where 1 N/m = 1000 dynes/cm]. The IFT for creosote generally ranges from approximately 17 to 23 dynes/cm. In a review of data from 21 field sites, Kueper (2002) observed a range in IFT of 5 to 30 dynes/cm. The IFT values for creosote at the fall in the middle of this range. Lower values of IFT tend to decrease the spread of a DNAPL perpendicular to its primary migration direction and decrease the force needed for DNAPL to displace water from saturated media.

Wettability refers to the preferential spreading of one fluid over a solid surface in a two-fluid system. It depends on the fluid's interfacial tension. The fluid drawn into the pore is the wetting fluid, whereas, the fluid repelled by capillary forces is the non-wetting fluid (small contact angles increase the DNAPL entry pressure). Consequently, the wetting fluid will occupy smaller pores and smaller portions of larger pores (thin films), and the non-wetting fluid will occupy the larger pores, especially within the middle or larger portion of the pore (ganglia). Creosote distribution at the pore scale is controlled primarily by its wettability (Powers et al., 1996).

Depending on the fluids and the media, NAPL can be the wetting fluid, the non-wetting fluid or be mixed wetting. However, according to U.S. EPA (2005, p. 22), "In the saturated zone, water is typically the wetting-fluid (i.e., it forms a continuous layer on, or preferentially wets, the particles) and LNAPL is the non-wetting fluid (i.e., it resides inside the pore spaces and is surrounded by a film of water). In the unsaturated zone, where there is an air phase in addition to the water and LNAPL, the air is the non-wetting fluid, the water is still typically the wetting fluid, and the LNAPL resides between the two other fluids." U.S. EPA (2005) further state, "If LNAPL is not continuous from one pore to the next, then LNAPL will not flow from one pore to the next: it will be immobile, which is referred to as the LNAPL residual saturation." Although this recent (March 2005) U.S. EPA document focuses on LNAPL, the same general conditions apply to DNAPL. For example, another recent publication, NRC (2005, p. 50) indicates, "For many natural minerals, including quartz and carbonates, water is more strongly attracted to the mineral surface than are common DNAPL constituents. Thus, in such media, water generally is the wetting phase, distributing itself along the solid surfaces and in small-aperture pore regions and fractures."

Zheng et al. (2001) performed wettability work with quartz material. This work showed that the wettability of creosote can be a function of pH, where quartz is predicted to be DNAPL-wetting below pH 5 and water-wetting at higher pH values. There are other factors that can change creosote wettability: (1) weathering that results in compositional changes in the DNAPL over time (loss of more soluble components and/or incorporation of organic material from the soil) and (2) sorption on the solid surfaces (Powers et al., 1996; Harrold et al., 2003). For these changes to occur requires DNAPL contact in the subsurface over time. These changes in composition and sorption can alter the wettability. Finally, another weathering or aging impact on creosote is that a semi-gelatinous interfacial film or skin can develop at the interface between water and creosote (Nelson et al., 1996). This skin apparently is the result of weak bonds between water molecules and creosote constituents (Powers et al., 1996). The significance of this skin on creosote migration is unclear.

The affect of changes in wetting behavior due to the residence time of DNAPL in the porous media is discussed by Harrold et al. (2001). For a first-time spill, the advancing contact angle of the DNAPL should be low (water-wet). The receding contact angle of the spill tail can be larger. In the case of repeated spills, preferential pathways are created by the previous invasion. In this case, the resulting established fluid saturation and potential changes in wettability influence subsequent DNAPL migration.

The implications of water-wet versus DNAPL-wet conditions are illustrated in Hugaboom and Powers (2002). Following creosote recovery using waterflooding in laboratory columns, for a DNAPL-wet system, remaining DNAPL saturations ranged from 38 % to 47 %. Significantly lower final DNAPL saturation was achieved for water-wetting systems (15 % to 30 %). Therefore, for a DNAPL-wet system, less creosote is likely to pool, but more creosote will be trapped at the larger residual saturation. The opposite occurs for a water-wet system.

5.0 DNAPL Recovery Experience at Beazer Sites

Sites where Beazer has conducted DNAPL removal pilot tests or are currently removing DNAPL include: (1) Carbondale, IL, (2) Charleston, SC, (3) Follansbee, WV, (4) Hocomonco Pond, Westborough, MA, (5) Montgomery, AL, (6) Nashua, NH, (7) North Little Rock, AR, (8) Reed City, MI, (9) Salisbury, MD, (10) Seaboard Site, Kearny NJ, (11) South Cavalcade, TX, (12) Texarkana, TX, (13) Youngstown, OH, and (14) Gainesville, FL. Recovery of creosote ranges from approximately 100 gallons per year (gpy) to approximately 5,000 gpy.

Based on this experience, pilot testing is recommended to evaluate the effectiveness of DNAPL recovery prior to committing to a full-scale operation. As discussed earlier, the success of DNAPL recovery depends on many site-specific factors requiring pilot testing. In general, large-diameter wells are preferred where in-well DNAPL separation can be achieved. In addition, it is desirable to re-circulate groundwater, where possible, to increase hydraulic gradients and enhance DNAPL recovery. Monitoring generally includes DNAPL and groundwater levels and DNAPL and groundwater recovery.

6.0 DNAPL Recovery Guidance

DNAPL recovery can include the following: (1) pumping groundwater to mobilize creosote at residual saturation (immobile creosote under ambient conditions), (2) active recovery where groundwater and mobile creosote are pumped, and (3) passive recovery where only mobile DNAPL is pumped. Each of these types of DNAPL recovery efforts is discussed with regard to the objectives of this report: (1) to better define MEP, (2) to present methods to monitor the effectiveness of DNAPL recovery, and (3) to provide guidance on data collection that will aid in determining when it is appropriate to terminate DNAPL recovery.

6.1 Mobilization of Residual Creosote

A fluid in porous media can only migrate if it has continuity. If it breaks apart forming ganglia and blobs that are disconnected, creosote is not mobile; that is, it is trapped by capillary forces at ambient flow conditions. Flow conditions can change that mobilize residual creosote. Examples of changes in flow conditions include:

(1) Drilling a well that changes the hydraulics immediately adjacent to the well. This can result in creosote accumulating in the well, but once bail, the creosote will not return if at residual saturation.
(2) Lowering the water table causing a zone that was saturated to become unsaturated (part of the vadose zone). Cohen and Mercer (1993) compiled residual saturation data that show residual DNAPL saturation below the water table (saturated zone) is greater than residual DNAPL saturation above the water table (vadose zone). Consequently, lowering the water table will reduce creosote residual saturation, causing some creosote to be mobilized. This mobilized creosote will likely migrate downward due to gravity drainage.
(3) Changing the hydraulic gradient adjacent to a well by pumping groundwater. Residual DNAPL can be mobilized (blob mobilization) by increasing hydraulic gradients sufficiently to overcome capillary forces that are trapping the creosote (Wilson and Conrad, 1984).

The focus in this section is on increasing hydraulic gradients via pumping to mobilize residual saturation. This is referred to as **hydraulic gradient-enhanced DNAPL recovery**. In general, hydraulic gradient-enhanced DNAPL recovery is not very effective and is only used under unique circumstances, where there may be non-technical remedial drivers.

<u>Maximum Extent Practicable.</u> The MEP concept generally does not apply to the situation where the DNAPL is immobile and will not flow to a well under ambient conditions.

<u>Effectiveness Monitoring.</u> To determine if hydraulic gradient-enhanced is effective, the following data should be collected and regularly reviewed:

- Water-table elevations (monitoring wells),
- DNAPL thickness and extracted volumes (pumped well),
- Groundwater extraction rates (pumped well), and
- Extracted DNAPL/water ratios for various pumping rates (pumped well).

The schedule for monitoring the above parameters depends on site-specific conditions.

Pumping Termination Guidance. This method of creosote removal is not very effective, generally requiring many gallons of groundwater to be pumped and treated in order to recover very few gallons of creosote. In addition, this method likely will only remove a small portion of creosote trapped at residual saturation, leaving behind most of the creosote that was there prior to pumping.

Example. As an example, a well was pumped in the Surficial Aquifer at the Cabot Carbon/Koppers Superfund Site as part of a pilot study. The Surficial Aquifer is about 30 feet thick (saturated thickness of 20 feet) and consists of silty sand with a hydraulic conductivity of about 17 ft/day. The well did not contain creosote prior to pumping but was located in the process area where creosote releases were likely. The well was pumped at rates ranging from 0.5 to 2.5 gallons per minute (gpm). At a pumping rate of 0.5 gpm, the resulting hydraulic gradient was insufficient to mobilize creosote. At a pumping rate of 2.5 gpm, the aquifer could not maintain the rate causing the pump to stop, and again creosote was not mobilized. By varying the pumping rate and monitoring the volume of creosote and groundwater extracted, it was determined that the pumping rate with the highest DNAPL yield was between 1.5 and 2.0 gpm. The radius-of-influence for the combined pumping rates was estimated to be between 15 and 40 feet.

After pumping for over 158 days, an estimated 335,169 gallons of groundwater were extracted and 89.95 gallons of DNAPL were recovered. The groundwater to DNAPL extracted ratio was 0.000268 (0.03%). That is, for every 1 gallon of DNAPL recovered, approximately 3,726 gallons of groundwater needed to be extracted and treated. This DNAPL recovery rate is relatively low as compared to other DNAPL recovery programs conducted by Beazer, but is consistent with local hydrogeological and residual DNAPL conditions in the Surficial Aquifer. Typically, more effective and efficient DNAPL recovery programs operate at approximately 1 to 3% DNAPL recovery (DNAPL to groundwater extraction ratio), but involve active recovery, discussed below. At this site, an updated Feasibility Study (FS) is being prepared and the results of this pilot study will be use in that FS.

6.2 Active Recovery

Active recovery involves pumping both groundwater and mobile creosote (above residual saturation) that likely is pooled. Researchers who model DNAPL refer to the DNAPL architecture[4], which refers to the DNAPL distribution in the subsurface. DNAPL architecture often is use to distinguish ganglia versus pooled DNAPL, where ganglia is considered immobile (residual saturation) and pooled is mobile (above residual saturation). Active recovery is an attempt to remove pooled creosote. When pumping both creosote and water, large-diameter

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[4] Although a popular modeling concept, DNAPL architecture is very difficult to determine in the field.

wells with in-well DNAPL separation and recirculation of the co-produced groundwater are the preferred approach.

Maximum Extent Practicable. As indicated earlier in this document, MEP can be tied to several specific remedial goals. For example, if the goal is plume containment and DNAPL recovery is being performed in support of that goal, then depending on site conditions (e.g., immobile DNAPL and a naturally attenuating dissolved plume that is stable), then it can be argued that DNAPL recovery is unnecessary. Another goal may be to remove DNAPL in order to stabilize the DNAPL pool. In this case, MEP will be tied to DNAPL pool mobility and a demonstration that the pool is stable. A DNAPL immobility demonstration may be difficult leading to continued DNAPL recovery. In many cases, however, MEP is only tied to mass removal. In this case, as long as any amount of DNAPL can be recovered, regulators may require continued pumping, no matter what technical arguments are made.

Effectiveness Monitoring. As indicated above, remedial goals will differ by site, and monitoring needs to be tailored to the remedial goals. At a minimum, monitoring should include both water and DNAPL recovered over time. With time, water production may greatly exceed DNAPL production (i.e., the water/DNAPL pumping ratio may increase over time). The requirement to pump and treat many gallons of water for minimal DNAPL recovery is an indication that the DNAPL recovery effectiveness is declining. Typically, more effective and efficient DNAPL recovery programs operate at approximately 1 to 3% DNAPL recovery (DNAPL to groundwater extraction ratio). One should also monitor DNAPL and groundwater levels.

If the remediation goal is to stabilize the DNAPL pool, an understanding of the site stratigraphy is necessary, especially identifying low permeability layers on which DNAPL might pool and stratagraphic traps (e.g., troughs or bowls on top of the low permeability layer). It will also be necessary to define the vertical and lateral extent of mobile (or potentially mobile) DNAPL. One commonly accepted method to determine the presence of potentially mobile DNAPL in the subsurface is the observation of DNAPL accumulation in wells. That is, if DNAPL can flow into a well for a prolonged period after its installation, it is an indication that the DNAPL may be potentially mobile and/or pooled. The absence of DNAPL in wells is indicative of the absence of mobile pools of DNAPL, and that DNAPL is trapped at residual saturation. Monitoring DNAPL in wells over time should help establish whether the pooled DNAPL is stable or not. This information can be used to help determine the need for continued DNAPL recovery.

Pumping Termination Guidance. If possible, it may be desirable to perform passive recovery (see section 6.3) only so that groundwater does not have to be treated or re-injected (if that option is available). Consequently, declines in the DNAPL to groundwater extraction ratios may be used to justify a conversion to passive recovery or DNAPL extraction termination.

The risks associated with pumping termination need to be fully explained. This not only includes risks to human health, but also includes risks to the environment. For example, assuming that all mobile/potentially mobile creosote can be removed from the subsurface, a large volume of creosote at residual saturation will remain. This residual creosote provides a continuing source to a dissolved plume, whether or not mobile/potentially mobile creosote is removed. Therefore, the only risk that is mitigated by removal of mobile/potentially mobile creosote is the risk associated with potential DNAPL migration. If one can show that the DNAPL pool is stable, then no risk reduction is achieve by DNAPL removal.

Example. Consider the Hocomonco Pond Site, Westborough, MA as an example. The primary groundwater-bearing unit is a heterogeneous glacial drift that is between 30 to more than 100 ft thick. Below this unit is confining materials of dense glacial till, saprolite and bedrock. Because of DNAPL at depth issues, a technical impracticability (TI) waiver was issued in September 1997. Within the TI waiver area are two primary DNAPL entry locations – the Kettle Pond Area and the former lagoon area. DNAPL migrated to the base of the glacial drift and moved laterally on the glacial till and is generally contained in a stratigraphic trough. DNAPL is found between about 50 to 170 ft beneath the Kettle Pond Area and is less than 25 ft deep below the former lagoon area. Up to 14 wells contained DNAPL within the TI zone. As part of the TI waiver, plume containment (including DNAPL recovery) is one of the remediation goals. DNAPL recovery needs to continue until it “is no longer effective”.

DNAPL recovery began in March 1995 with 4 wells. Two wells were used for active recovery at a total groundwater pumping rate of about 15 gpm; the other two wells were used for passive recovery, extracting only DNAPL. Pumped groundwater was treated on-site at a treatment plant. By May 2003, 52,377 gallons of DNAPL had been removed. With time, the DNAPL to groundwater extraction ratio declined in the two active recovery wells. This decline in recovery efficiency along with a desire to develop the property, which would require removal of the treatment plant, lead to a cessation of groundwater pumping in May 2003. This was followed by passive recovery only and monitoring. By incorporating more wells in the passive recovery effort, monthly DNAPL recovery totals under passive recovery were similar to the monthly totals that were achieved under active recovery.

6.3 Passive Recovery

Passive recovery involves pumping only mobile creosote (above residual saturation) that likely is pooled. Like active recovery, passive recovery is an attempt to remove pooled creosote. It is likely that pumped creosote that is removed from the ground will be replaced by groundwater. It should be noted that viscous fingering occurs when a less viscous fluid (e.g., water) displaces a more viscous fluid (e.g., creosote). The interface between creosote and groundwater is unstable and over time forms a growing pattern of fingers of groundwater invading the creosote. This will eventually lead to groundwater breakthrough at recovery wells. It is well known in the petroleum industry that when water breakthrough occurs, water production will increase and oil production will decrease. Thus, the phenomenon of viscous fingering and water breakthrough needs to be considered in designing a passive recovery system (including well locations and extraction rates).

Maximum Extent Practicable. See the discussion under active recovery.

Effectiveness Monitoring. See the discussion under active recovery. DNAPL recovery rates over time need to be monitored. Also, any DNAPL in nearby wells needs to be monitored to see how DNAPL thicknesses are responding to pumping. Water levels need to be monitored as increases/decreases in water levels may have an impact on DNAPL thicknesses in wells.

Pumping Termination Guidance. Termination criteria provided by some states are listed in Section 2.2. Another criterion that may be use is when mass removal is reaching an asymptote (that is, the volume DNAPL removed over a given period decreases over time and approaches a constant value). Regulators will likely require that this constant value be fairly low, on the order of a few gallons a week or less.

7.0 Conclusions and Recommendations

When communicating with regulators on DNAPL recovery issues, it is important to provide estimates of the DNAPL in place and the percentage of that DNAPL that can be recovered. Due to residual saturation alone, as much as 30% of the DNAPL will be left behind following a well designed DNAPL recovery program. This needs to be considered when defining MEP; that is, all DNAPL can not be removed, so leaving some product in wells likely will not change site-care or site risk. In addition, MEP will depend on the goal of the DNAPL recovery program. If the goal is to achieve a stable DNAPL plume or dissolved plume, then MEP has a different meaning than a goal of mass removal. It is important, therefore, to educate stakeholders and define remedial goals and MEP early in the feasibility study discussion. Despite experience at numerous DNAPL sites showing that cleanup is not likely, some level of effort likely will be required to demonstrate that total mass removal is not possible. Even with this early discussion with regulators, it may be difficult to alter a MEP definition that is tied to mass removal.

Effectiveness of DNAPL recovery depends on the goals and the system design. Effectiveness is defined differently for different types of recovery. Hydraulic gradient-enhanced DNAPL recovery is not very effective. Active DNAPL recovery depends on the ratio of DNAPL to groundwater extracted, where 1 to 3% is considered effective. For passive DNAPL recovery, where only DNAPL is removed, effectiveness relates to managing groundwater breakthrough.

Performance monitoring generally involves monitoring DNAPL and groundwater extraction and DNAPL and groundwater levels. These data can be used to optimize DNAPL recovery and to determine when to terminated DNAPL recovery. Termination of DNAPL recovery depends on goals that were negotiated at the beginning of the recovery process.

References

Cohen, R.M. and J.W. Mercer, 1993. DNAPL Site Evaluation, C.K. Smoley (CRC Press), Boca Raton, FL.

Harrold, G., D.C. Gooddy, S. Reid, D.N. Lerner and S.A. Leharne, 2003. Changes in Interfacial Tension of Chlorinated Solvents following Flow through U.K. Soils and Shallow Aquifer Material, Environ. Sci. Technol., vol. 37, no. 9, pp. 1919-1925.

Hugaboom, D.A. and S.E. Powers, 2002. Recovery of Coal Tar and Creosote from Porous Media: The Influence of Wettability, GWM&R, vol. 22, no. 4, pp. 83-90.

Interstate Technology & Regulatory Council (ITRC), 2004. Strategies for Monitoring the Performance of DNAPL Source Zone Remedies (August).

Kueper, B.H., 2002. Presentation at the Massachusetts Licensed Site Professional Association Workshop (June), Marlboro, MA.

Levorsen, A.I. (revised and edited by F.A.F Berry), 1967. Geology of Petroleum, W.H. Freeman and Company, San Francisco, CA.

National Research Council (NRC), 2005. Contaminants in the Subsurface – Source Zone Assessment and Remediation, The National Academies Press, Washington, D.C.

Nelson, E.C., S. Ghoshal, J.C. Edwards, G.X. Marsh, and R.L. Luthy, 1996. Chemical Characterization of Coal Tar-Water Interfacial Films, Environ. Sci. Technol., vol. 30, no. 3, pp. 1014-1023.

Pankow, J.F. and J. A. Cherry, 1996. Dense Chlorinated Solvents and other DNAPLs in Groundwater, Waterloo Press, Portland, OR.

Powers, S.E., W.H. Anckner, and T.F. Seacord, 1996. Wettability of NAPL-Contaminated Sands, J. Envir. Eng., vol. 122, no. 10, pp. 889-896.

U.S. EPA, 1993. Guidance for Evaluating the Technical Impracticability of Groundwater Restoration. OSWER Directive 9234.2-25. Office of Solid Waste and Emergency Response, Washington, D.C.

U.S. EPA, 2003. The DNAPL Remediation Challenge: Is There a Case for Source Depletion?, EPA/600/R-03/143 (December).

U.S. EPA, 2005. A Decision-Making Framework for Cleanup of Sites Impacted with Light Non-Aqueous Phase Liquids (LNAPL), EPA 542-R-04-011 (March).

Wilson, J.L. and S.H. Conrad, 1984. Is physical displacement of residual hydrocarbons a realistic possibility in aquifer restoration? Proceeding of the NWWA/API Conference on Petroleum

Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Restoration, National Water Well Association-American Petroleum Institute, Houston, Texas, pp. 274-298.

Zheng, J., S.H. Behrens, M. Borkovec and S.E. Powers, 2001. Predicting the Wettability of Quartz Surfaces exposed to Dense Nonaqueous Phase Liquids, Environ. Sci. Technol., vol. 23, no. 11, pp. 2207-2213.

APPENDIX A
Partial DNAPL Mass Removal

Introduction

In the past 10 to 15 years, innovative in-situ technologies have been proposed for removal and/or destruction of contaminant mass in DNAPL source zones. These technologies can be characterized broadly as (1) thermal technologies, (2) flushing technologies using surfactants or cosolvents, (3) chemical oxidation or reduction technologies, and (4) biological technologies. Technologies in categories (1) and (2) require injection and withdrawal wells, whereas the technologies in categories (3) and (4) generally require only injection of the treatment fluids/constituents. Although these technologies remove/destroy mass, to date, there are no known applications of these technologies where 100 % of the DNAPL mass has been removed/destroyed. Many applications to date have been pilot studies, and mass removal claims are difficult to verify, causing the percentage of mass removed by the technology to be uncertain. Therefore, given the high costs associated with these DNAPL source remediation technologies, the benefits of partial source removal should be determined prior to attempting DNAPL source remediation.

Remediation of a DNAPL source requires specific knowledge of the total source location. Although advances have been made in tools used to characterize DNAPL sites, DNAPL delineation is still very challenging. Therefore, one factor that leads to partial DNAPL mass removal/destruction is the failure to accurately locate all of the DNAPL. In addition, most source remediation technologies are still being developed, have limited full-scale field application, and require further research (SERDP, 2002). Furthermore, there are few, if any, DNAPL sites where source remediation has been applied, MCLs have been met, and site closure was achieved. At sites where partial DNAPL mass has been removed/destroyed, there is little or no documentation of impacts to the down-gradient dissolve plume. Because of the risk of failure to achieve compliance with stringent groundwater cleanup goals, combined with uncertainties in predicting costs, performance, and the likely benefits of partial source depletion, there has been a reluctance to undertake aggressive and costly source depletion technologies. At the majority of DNAPL sites, containment of the source zone and/or management of the plume for cost-effective risk/liability reduction and regulatory compliance have been the strategy of choice. Regulatory pressures are now challenging the containment strategy.

Pros and Cons of Partial DNAPL Mass Removal

The potential benefits of DNAPL source depletion have been the subject of an on-going debate in the remediation field. In order to remediate a DNAPL source, it needs to be located and characterized. When characterizing a DNAPL source, there are risks associated with mobilization and cross contamination. Once located, DNAPL remediation is often a costly activity. Therefore, it is important that the pros and cons of partial DNAPL removal be evaluated for each site. A common way to evaluate partial mass removal is in terms of risk management benefits (e.g., are risks associated with the site reduced?) and the potential for reducing the total life-cycle cost to achieve site closure (e.g., are future site care requirements reduced?). Risk reduction (or increases) can include traditional human and ecological risks, risks to remediation workers, and risks associated with DNAPL mobilization. Traditional risk assessments are site specific and no general comments are made here. If pooled DNAPL can be located and not mobilized by the characterization effort, then partial removal of the DNAPL (e.g., via pumping free-phase DNAPL) to reduce DNAPL mobility and mitigate potential further spread of the source is a benefit. The magnitude of this benefit depends on the amount of pooled DNAPL mass, local stratigraphy, and DNAPL properties, such as density and viscosity. On the other hand, if the DNAPL is at residual saturation, it is already immobile; thus, additional mass reduction in the case of DNAPL at residual saturation does not provide a benefit in terms of reducing DNAPL mobility, and source remediation potentially could mobilize the residual DNAPL.

Source depletion provides a potential benefit in reducing the longevity of the source and associated plume. This potential benefit is common to all source depletion strategies, but is difficult to predict and quantify. This is because the mass remaining, its distribution after source depletion, system hydrodynamics, and chemical reactions are difficult to quantify at many sites. This makes predicting future behavior highly uncertain. It also may be the case that the reduction in longevity is inconsequential to subsequent site care. That is, site (source and plume) management may still be required for a long period of time even after partial DNAPL mass removal.

Depleting the DNAPL source zone may result in near-term reduction in contaminant mass discharge rate (i.e., mass of contaminant per unit time) leaving the source area. Containing the DNAPL source will achieve the same benefit. The mass discharge rate is defined as the mass of contaminant per unit time migrating across a hypothetical vertical cross section (a “control” plane) in the aquifer down gradient of the source zone, and perpendicular to the direction of groundwater flow. Reduction of the mass discharge rate leaving the source zone also may result in near-term plume attenuation, eliminating the need for active plume control measures. Unfortunately, it is not possible to predict what the mass discharge rate leaving the source zone will be after source depletion or what its impact will be on the dissolved plume. It also is uncertain what impact aggressive source remediation will have on biodegradation. Post-remedial monitoring is required, and may indicate the need for continued plume control measures or additional source remediation (i.e., future site care requirements may not change following source remediation).

There are at least four issues with using reduction in mass flux as a potential benefit of partial source remediation. First, there are few, if any, field studies where mass flux reduction has been shown (measured) to occur following partial removal. Second, measurement of mass flux in the field is uncertain and difficult. Third, the hope is that the reduced mass flux will be naturally attenuated (more effectively than prior to partial mass removal), but there is no guarantee that this will occur and natural attenuation is highly site specific. Finally, regulators measure remedial success or compliance by looking at concentrations, not mass flux, to determine if MCLs are met at a compliance point.

Because there has been little or no experience in the field where mass flux changes have been measured following partial DNAPL mass removal, most of the experience in this area has been gained from theoretical studies. Recent theoretical analyses (Sale and McWhorter, 2001; Falta,

2001) suggest that depletion of DNAPL mass located in unconsolidated geologic media can result in a reduction of the contaminant mass flux (in units of mass per unit area per time) at the down-gradient control planes. The changes in the spatial distribution of the local contaminant fluxes and the magnitude of the resulting mass discharge (that is, local fluxes integrated over the entire control plane) are complexly related to the amount of mass removed, the hydrologic heterogeneity, the initial DNAPL architecture, the correlation between hydraulic conductivity and the DNAPL saturation at the local scale, as well as complex contaminant partitioning and reactions. Therefore, these modeling results provide insights into contaminant behavior but are unlikely to yield prediction of site-specific results.

A key question is how much mass needs to be removed before a meaningful reduction in mass flux is achieved. Sale and McWhorter (2001) show that for a homogeneous media, "removal of the vast majority of the DNAPL will likely be necessary to achieve significant near-term improvements in groundwater quality." Falta (2001) considered heterogeneous media and his simulation results suggest that for a given reduction in DNAPL mass, the largest discharge rate reduction is achieved for the case of negative correlation between hydraulic conductivity and DNAPL saturation. That is, if most of the DNAPL mass is located in the low permeable media, removal of the relatively small fraction of DNAPL mass resident in the permeable media provides a relatively large reduction in contaminant flux. For the positive correlation case, a larger fractional mass reduction is required to achieve the same level of flux reduction. For example, Falta (2001) shows that for the negative-correlation case, 50 % DNAPL mass reduction leads to an approximate 80 % mass flux reduction, whereas for the positive-correlation case, 50 % DNAPL mass reduction only produces a 20 % mass flux reduction. For 90 % DNAPL mass reduction, the negative-correlation case produces approximately 95 % mass flux reduction; but for the positive-correlation case, the mass flux is reduced by about 80 %. More recently, Reynolds and Kueper (2002) considered the extreme heterogeneous case of fractured media, and obtained results that were different from those of Falta. In this case, chemicals that diffuse into the matrix caused dissolved phase contamination to exist in the system for more than 1000 years after the DNAPL was completely removed from the fracture. These results illustrate the complex nature of the problem, the uncertainties in making predictions, and the need for model verification.

While modeling provides insights into DNAPL fate, determination of positive or negative correlation is difficult to assess in a complicated hydrological setting and depends upon the release history, stratigraphy, and chemical composition of the DNAPL. Experimental approaches to measuring contaminant mass fluxes (local) and mass discharge rates (spatially integrated) have been proposed recently (Hatfield et al., 2001; Ptak and Teutsch, 2000; and Bockelmann et al., 2001), and field-scale evaluation of these techniques is the subject of on-going studies. Thus, these techniques are relatively new and have not been tested in a variety of hydrogeologic settings, raising questions concerning the accuracy of the techniques, analysis of results, and their cost.

Source depletion coupled with natural degradation processes is an area of current research. It is uncertain what impact aggressive source remediation will have on the local microbial population. As pointed out above, it also is uncertain what amount of mass reduction will be necessary to achieve a meaningful reduction in mass flux. It also is unclear what percentage of mass flux reduction will lead to satisfactory natural attenuation. Finally, even with a meaningful mass reduction, appropriate site conditions are required to achieve complete degradation. Thus, even after source remediation some form of active remediation (e.g., pump and treat or bioaugmentation) may be necessary for a long period of time (i.e., site care requirements may not change following source remediation).

Unfortunately, at the present time, the cost of source removal technologies is high and uncertain, and the performance of source removal technologies and the behavior of down-gradient dissolved plume following partial mass removal are uncertain. Also, the source removal technologies are not sufficiently mature at this time to permit sufficiently accurate comparisons on the basis of life-cycle costs. As a consequence, uncertainties regarding the effectiveness and overall cost of any particular source removal technology inhibit more widespread application of source depletion technologies. The potential benefits of source depletion are mainly conceptual in nature and conversion of these potential benefits into tangible and quantifiable factors is still primarily theoretical. In practice, the biggest hurdle in evaluating the benefits of source depletion has been the lack of a documented, scientifically defensible experience.

Summary

In summary, full-scale field applications of DNAPL source remediation technologies are very limited, and to date, there are no known DNAPL sites that have been remediated and closed. Consequently, the primary achievement of DNAPL source remediation is partial mass removal. The benefits of partial DNAPL mass removal on improving groundwater quality are uncertain and are based largely on theoretical calculations that have not been field verified. Uncertainties associated with DNAPL mass reduction include (1) locating and characterizing DNAPL sources, (2) estimating the amount of mass reduction that will be achieved, (3) estimating the impact to mass flux originating from the DNAPL source, (4) measuring the mass flux, and (5) estimating the impacts to the down-gradient dissolved plume. Because of the cost of DNAPL source zone remediation, it is important to evaluate the potential benefits of partial DNAPL mass removal on a site-by-site basis.

References

Bockelmann, A., T. Ptak, and G. Teutsch, 2001. An analytical quantification of mass fluxes and natural attenuation rate constants at a former gasworks site, *J. Contaminant Hydrology*, 53, 429-453.

Hatfield, K., M.D. Annable, S. Kuhn, P.S. Rao, and T. Campbell, 2001. A new method for quantifying contaminant flux at hazardous waste sites, GQ2001 Conference, Sheffield, UK.

Ptak, T., and G. Teutsch, 2000. Development and application of an integral investigation method for the characterization of groundwater contamination, Proceedings of the Seventh International FZK/TNO Conference on Contaminated Soil, 18-22 September, 2000, Leipzig, Germany.

Falta, R., 2001. EPA DNAPL Source Remediation Workshop Presentation, Dallas, TX, October.

Reynolds, D.A. and B.H. Kueper, 2002. Numerical Examination of the Factors Controlling DNAPL Migration Through a Single Fracture, *Ground Water*, vol. 40, no. 4, pp. 368-377.

Sale, T.C. and D.B. McWhorter, 2001. Steady state mass transfer from single-component dense nonaqueous phase liquids in uniform flow fields, *Water Resources Research*, vol. 37, no. 2, pp. 393-404.

SERDP, 2002. Final Report – SERDP/ESTCP Expert Panel Workshop on Research and Development Needs for Cleanup