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Dense Non-Aqueous Phase Liquids (DNAPLs): Review of Emerging Characterization and Remediation Technologies (DNAPLs-1)

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.