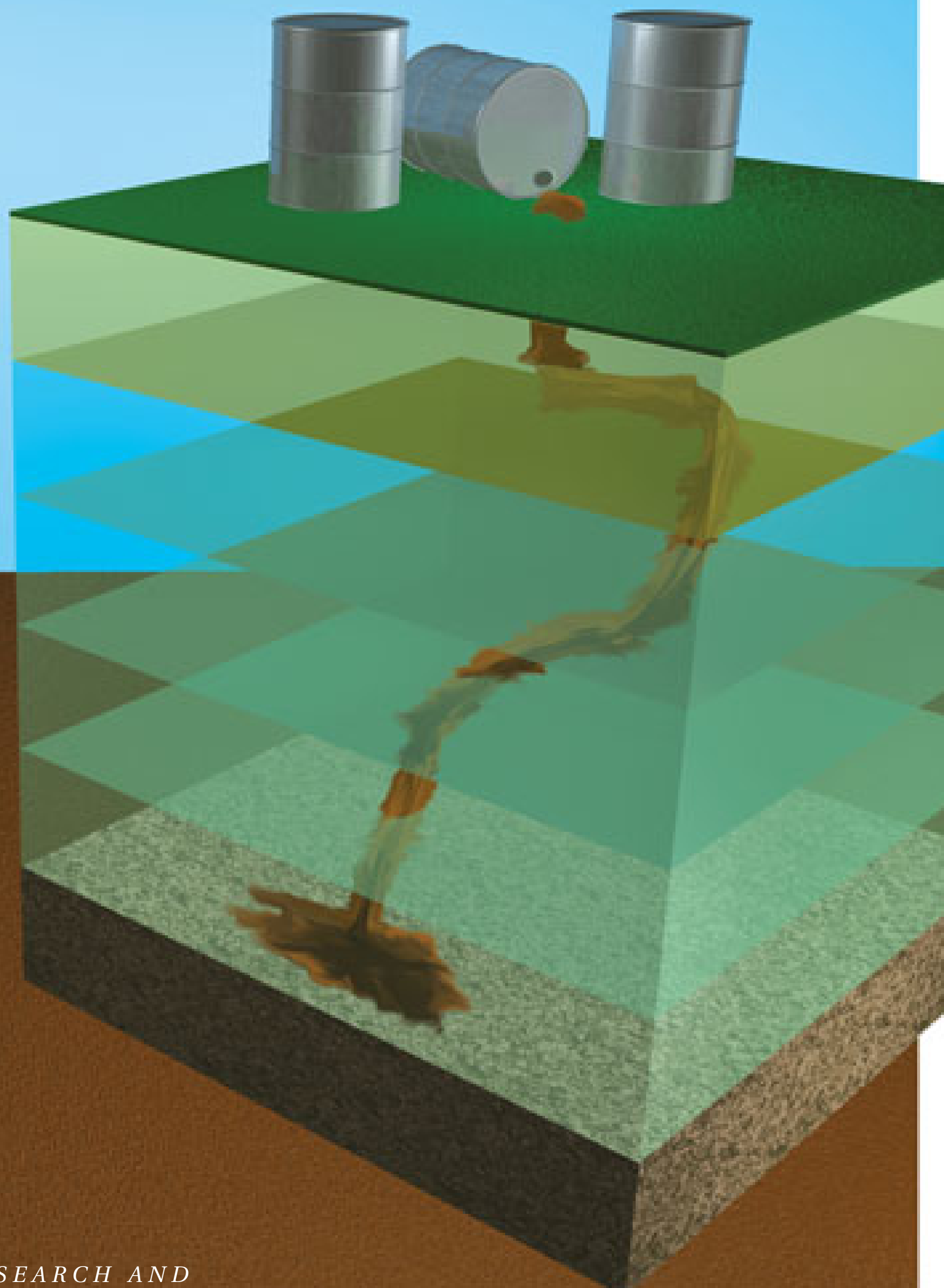
REMEDIATING



A workshop lists the challenges and research needs.

HANS F. STROO

MARVIN UNGER
THE RETEC GROUP, INC.

C. HERB WARD
RICE UNIVERSITY

MICHAEL C. KAVANAUGH
MALCOLM PIRNIE, INC.

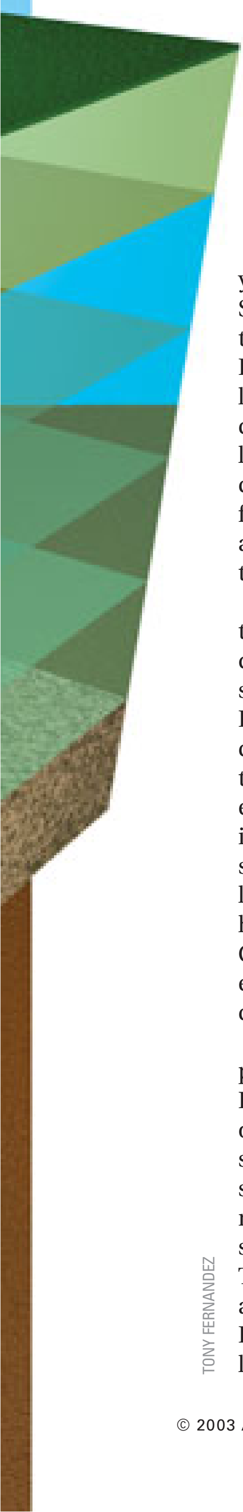
CATHERINE VOGEL

ANDREA LEESON

JEFFREY A. MARQUSEE

BRADLEY P. SMITH
STRATEGIC ENVIRONMENTAL RESEARCH AND DEVELOPMENT PROGRAM AND THE ENVIRONMENTAL SECURITY TECHNOLOGY CERTIFICATION PROGRAM

Chlorinated Solvent Source Zones



TONY FERNANDEZ

Chlorinated solvents are by far the most prevalent organic contaminants in groundwater. For example, chlorinated aliphatic hydrocarbons (CAHs), such as trichloroethylene and perchloroethylene, are found at approximately 80% of all Superfund sites with groundwater contamination and more than 3000 Department of Defense (DoD) sites in the United States (*1*). The life-cycle costs to clean up these sites are uncertain, but they are likely to require several billions of dollars on a national level. DoD alone could spend more than $100 million annually for hydraulic containment at these sites, such as using pump-and-treat technologies, and estimates of life-cycle costs exceed $2 billion.

CAHs are also among the most difficult contaminants to clean up, particularly when their dense nonaqueous-phase liquid (DNAPL) sources remain in the subsurface. Both the U.S. EPA and the National Academy of Sciences have concluded that DNAPL sources may be contained, but remediation to typical cleanup levels for most DNAPL sites is often "technically impracticable" (*2–4*). Other DNAPL sources, such as coal tar and creosote, pose similar problems. Although these other DNAPLs tend to have significantly different properties than the CAH ones—notably lower solubilities and higher boiling points—much of the following discussion is relevant to them as well.

Over the past 10–15 years, pump-and-treat processes have not fully remediated sites with DNAPL occurrences (*5*). However, recent tests of innovative source remediation technologies, such as surfactant or alcohol flooding and in situ thermal treatment, suggest significant mass removal and reductions in mass discharge from sources is possible at some DNAPL sites (*6–8*). These results have led to increasing regulatory and public pressure to remediate sources. However, source remediation can be extremely expensive in the short term, and we can rarely predict with confidence whether it will be effective. Innovative technologies have not been thoroughly evaluated, and therefore, research and development (R&D) is clearly needed in several areas to better understand whether and how to attempt source remediation. Prioritizing the most urgent research is essential, given limited funds and the large number of potential projects. This article summarizes the results of a workshop conducted by the Strategic Environmental Research and Development Program and the Environmental Security Technology Certification Program during August 6–8, 2001, to identify the highest R&D priorities.

Nature of the problem

Interest in a more aggressive strategy for source removal has increased since the mid-1990s. Innovative technologies, such as in situ oxidation, various in situ thermal technologies, surfactant and cosolvent flushing, and bioremediation, were developed and marketed to overcome the perceived technical impracticability of source treatment. However, evaluating these technologies for specific site applications has proven difficult. The initial capital costs can be very high, and the long-term efficacy and economic return are difficult to predict (*9*). Moreover, DNAPL source zones are often very difficult to locate and characterize in the field, which complicates any assessment. In addition, aggressive treatments can cause pronounced changes in the distribution and the physical and chemical nature of the remaining DNAPL. For example, a DNAPL can be forced into less permeable zones or into previously uncontaminated areas. Table 1 demonstrates that controlled field tests performed on innovative source treatment technologies yield mixed results. Losses of greater than 90% of the source DNAPL have been measured at some sites, but 50–70% is more typical. As a result, there is considerable uncertainty regarding the efficacy of

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these technologies in terms of mass removal, mass loading to dissolved plumes, risk reduction, lowering the ultimate cleanup costs, or speeding up site restoration (*4, 10*). A broader issue is whether any of these technologies should be used at a specific site, and if so, what is an appropriate measure of success (*11*).

we cannot currently predict the impacts of mass depletion on contaminant mass discharge (*22, 23*). Simply measuring discharge from sources involves significant uncertainty (*24*). Another remedial goal may be reducing the lifetime of the contamination, but again, limited data exist on the long-term impacts.

TABLE 1

Field demonstrations of DNAPL treatment technologies

Different technologies provide various results for cleaning up dense nonaqueous-phase liquids (DNAPLs) in the field.

Technology	Location	Percent mass loss	Reference	Notes
Surfactant flushing	Dover Air Force Base, Del.	61	(*20*)	Contained test cell
Surfactant flushing	Camp Lejeune, N.C.	>90[a]	(*39*)	Little removal from lower-permeability areas
Surfactant flushing	Hill Air Force Base, Utah	≤98	(*6*)	Homogeneous sands
Cosolvent flushing	Dover Air Force Base, Del.	64[b]	(*38*)	Contained test cell
Cosolvent flushing	Jacksonville, Fla.	62–65	(*8*)	92% reduction in groundwater concentrations
In situ air sparging	Dover AFB, Del.	59	(*20*)	Contained test cell
In situ oxidation	Cape Canaveral, Fla.	62–84	(*40*)	Migration of DNAPL outside treatment area
Six-phase heating	Cape Canaveral, Fla.	90	(*40*)	Possible migration through lower confining layer

[a] Removal occurred primarily from the most permeable zone (5×10^{-4} cm/s), with little removal from lower zone (1×10^{-4} cm/s), which emphasizes difficulties in even slightly heterogeneous subsurface materials.

[b] Test was not operated to attain maximum possible removal in order to evaluate subsequent biodegradation using residual cosolvent as the carbon source.

Our ability to locate and characterize DNAPL sources significantly affects the decision of whether to attempt source-zone remediation. Even minor heterogeneities can lead to extremely complex migration pathways and localized entrapment (*12, 13*). CAHs can also diffuse into and out of the surrounding matrix, greatly reducing access to a possible long-term source of dissolved contaminants (*14*). As a result, finding and quantifying the source area and then delivering remedial agents can be extremely challenging. This difficulty has contributed to the apparent failure of many of the DNAPL source removal technologies to achieve cleanup goals (*10, 15–17*).

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Even when sources can be located and accessed, the ability of source removal technologies to improve groundwater quality and reduce overall plume management costs is controversial (*18–21*). Modeling and limited data suggest that even removing more than 90% of the source will not reduce concentrations in groundwater (*18*). However, Figure 1 demonstrates that if treatment generally removes the most accessible DNAPL located in the more permeable areas in heterogeneous environments, then the mass discharge from sources can be greatly reduced by even limited mass removal.

How to measure success is a key issue. Reducing contaminant mass discharge may be one goal, but

Because long-term performance data will not be available for several years, modeling is essential. The current models for predicting DNAPL migration and remediation impacts are not sufficiently robust or require site data that are extremely difficult to obtain. Current numerical models are complex and require computing power, user training, and long processing times (*25, 26*). Remediation technologies can drastically affect the DNAPL distribution, but in ways that are not fully understood (*8, 15, 27*).

Beyond these scientific uncertainties, economics and regulatory issues can impact R&D needs. For example, the economic feasibility of source removal can be difficult to establish, particularly when using net present value (NPV) assessments. DNAPL sources and their associated dissolved plumes can exist for hundreds of years, which means reducing containment times by factors of 2–10 may have little impact on the NPV of site management (*28*) or on the long-term stewardship costs of sites that cannot be cleaned up for unrestricted use.

Source removal may have more impact on the mass discharge from the source than on the maximum concentrations in the down-gradient dissolved plume (*28*), but it is unclear whether this would be an acceptable remediation goal from a regulatory point of view. People living on or near such sites generally favor source removal to whatever extent feasible, even if potable water levels are unattainable. However, the responsible parties often resist such expenditures, particularly because most DNAPL sites have containment systems already in place, and there is little certainty that the site management costs will decrease after source removal. Finally, uncertainties persist regarding the impacts of residual contamination in groundwater on natural resource damage claims, which could drive more aggressive source zone remediation.

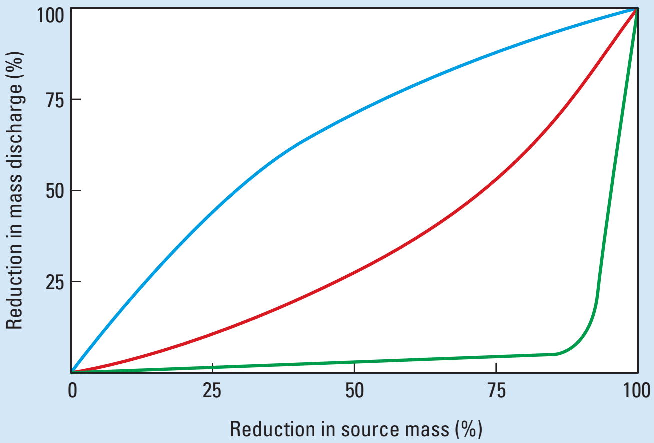
Most agree that source removal alone will not result in closure, but it is a first step in a treatment process. Moreover, if a decision for no or only partial source removal is implemented, it is not clear that policies will be developed to allow and even encourage use of passive follow-on technologies that are less costly than, for example, continuing pump and treat. In addition, the impacts of source removal technologies on these more passive ones, such as natural attenuation and permeable reactive barriers, need to be better understood.

The workshop panel listed at the end of this article identified high- and moderate-priority R&D needs for science and technology, which are listed in the box on the next page. The following high-priority needs pertain to three focus areas: site characterization and monitoring, performance assessment and risk analysis, and remediation technology development.

FIGURE 1

Relating DNAPL source to mass discharge

Modeling and limited data suggest that even removing more than 90% of the dense nonaqueous-phase liquid (DNAPL) source will not reduce concentrations in groundwater. However, this figure shows that if treatment removes the most accessible DNAPL, the mass discharge from sources in heterogeneous environments can be greatly reduced by even limited mass removal. The green line shows the theoretical relationship in a homogeneous aquifer with little reduction in source mass; the red line is extrapolated from data from a field demonstration at Dover Air Force Base in Dover, Del.; and the blue line shows the theoretical relationship in a highly heterogeneous aquifer with most of the DNAPL located in the higher permeability zones.



Source: Data for green line are from Ref. *18*, red line from Ref. *38*, and blue line from Ref. *20*.

Site characterization and monitoring

Source zone delineation and characterization. Locating and delineating DNAPLs are difficult because of their complex spatial distributions as they migrate through the subsurface. Geophysical methods have not proven useful for locating DNAPLs at meaningful resolutions (*29*), despite advances in this area, such as partitioning interwell tracer tests (*30*) and natural radon abundance (*31*). Source delineation still typically relies on point-scale techniques, such as wells or borings that are often costly and subject to error. Variable-scale source delineation techniques, which are designed to integrate information needed for identifying source zones on the order of a few meters to tens of meters, could save considerable time and money.

Even when sources are delineated, it is necessary to characterize their important physical and chemical attributes, which include both the macroscale and local distributions of NAPL in the subsurface, as well as its chemical composition. Without understanding the distribution of NAPL within the subsurface and within zones of differing permeabilities, we cannot accurately estimate the total mass or volume present, or evaluate whether groundwater or treatment reagents have access to the contaminants. Although difficult to analyze in situ, meaningful risk assessment and remedial design require knowing the NAPL's chemical composition. Analytical tools or protocols to directly measure DNAPL composition would be extremely useful.

Interactions at NAPL interfaces. The biological, physical, and chemical interactions that occur at the interface between NAPLs and the aqueous phase are poorly understood. However, these interactions can significantly impact source zone treatment effectiveness. For example, in theory, NAPL contaminant degradation reactions that occur in the aqueous phase can dramatically enhance interphase mass transfer. Such reactions can reduce the thickness of the boundary layer and increase the concentration gradient across it, thereby increasing dissolution rates by factors of 10 or more (*32*).

The actual enhancement may differ from reported theoretical calculations. Dissolution may decrease over time because interfacial resistance develops as films form because of reaction products from oxidation or microbial reactions. Alternatively, treatment rates may even be increased further, for example, by using reagents that preferentially partition to the NAPL–water interface. To optimize the treatment's effectiveness, research is needed on the fundamental processes controlling interactions at the interface between NAPLs and the aqueous phase, including the effects of NAPL morphology and composition, aqueous-phase water chemistry and microbiology, and flow regime characteristics.

Managing uncertainty in risk assessment and remediation. The extent and distribution of contaminants and the hydraulic, chemical, and biological processes that control their migration and persistence in the subsurface are extremely difficult to quantify and assess. Furthermore, the significant heterogeneity of most subsurface environments dictates that critical site parameters—such as hydraulic conductivity, groundwater velocity, microbial activity, contaminant concentration, and sorption/desorption rates—can vary over orders of magnitude within relatively short

spatial distances. As a result, predictions or decisions based on this knowledge are very uncertain. In addition, the mathematical models for such predictions are generally based on small, well-characterized systems, but are likely to have severe limitations when applied to larger, highly variable field sites.

Unfortunately, the level of uncertainty inherent in parameter estimation and model predictions is generally not recognized or expressed in these models. However, meaningful risk assessment and cost–benefit analyses are not possible without an understanding of uncertainty. Evaluating the uncertainty in model predictions is particularly essential in assessing risks associated with monitored natural attenuation and post-treatment source zone mass flux reduction.

Research and development needs for DNAPLs

The workshop members ranked the following areas for dealing with dense nonaqueous-phase liquids (DNAPLs).

High priority

Assessment of source zone treatment technologies
Benefits of partial mass removal from sources
Physical/chemical/biological interactions at NAPL interfaces
Source zone delineation and characterization
Diagnostic tools to measure remediation performance
Quantifying uncertainty in DNAPL characterization
Cost-effective assessment tools and methodologies
Source zone bioremediation and bioaugmentation
Sustainability of monitored natural attenuation
Assessment of thermal treatment

Moderate priority

Consistent methods for remediation technology cost comparisons
Transport and remediation of fractured media and karst aquifers
Improved prediction of the risks to indoor air from soil vapors
Decision trees for source delineation and remediation
Surface water discharge and engineered wetlands
Scale-up issues (pilot-to-field-scale transfer)

Thus, tools and methodologies must be developed to both quantify and reduce the uncertainty of parameter estimation and model prediction. Such tool improvements could include better in situ characterization techniques for hydraulic, chemical, and biological processes/properties; statistical protocols for parameter estimation from sparse and variable quality data; methods for scaling up from field to lab; methods/models for assessing remedial performance uncertainty; or remedial designs/technologies that are relatively insensitive to spatial variability in subsurface properties. Developing these modeling protocols/tools will also help determine the need for additional site characterization work and formulate optimal site characterization plans to reduce the uncertainty in model predictions. Research is also needed to demonstrate and validate parameter estimation methods, remedial performance simulators, and uncertainty modeling tools at the field scale using real site data.

Performance assessment and risk analysis

Benefits of partial source removal. Complete DNAPL mass removal from the source zone below the water table is technically infeasible in most geologic settings because sources are difficult to locate and may be in pools or lower permeability regions (*27*). This incomplete removal may decrease the total mass discharge from the source after treatment. In some cases, treatment can temporarily increase discharge by increasing the NAPL/aqueous interfacial area, whereas in other cases, treatment may have little effect on discharge. For example, at some sites, matrix diffusion dominates the mass discharge (*8, 14*) and makes it very difficult to remove the NAPL.

Unfortunately, few data are available on the magnitude or the variability of mass discharge rates, particularly at sites undergoing source treatment. Research is needed to develop methods to measure mass discharge rates accurately (*7*), to expand predictive models of treatment effects, and to obtain quantitative field data on mass discharge before and after source treatment.

Assessment of in situ thermal treatment. The specific source treatment technology most in need of research is in situ thermal treatment, because of its potential efficacy and the large uncertainties regarding its implementation. Thermal treatment could remove much of the source, even in low-permeability areas, but it is expensive and there are few independent (nonvendor) evaluations of its performance. Several apparently successful demonstrations have been performed, however. For example, EPA lists 58 field sites in its database, many with impressive results (*33*).

Quantitative field demonstrations are needed. In particular, how well thermal treatment overcomes difficulties presented by large permeability contrasts in situ, which can lead to thermal conduction into the low-permeability zones, needs to be evaluated in field-scale performance demonstrations. To complete these field evaluations successfully, a reliable sampling methodology needs to be established. In addition, research is needed on the performance of thermal treatment at relatively low temperatures because limited data suggest effective treatment can occur at temperatures much lower than those typically used. (Typical temperatures are near 100 °C.) Finally, the possibility of NAPL condensation at the edge of the heated zone needs to be carefully evaluated.

Diagnostic tools to evaluate remediation performance. Existing and developing remediation technologies need to be evaluated in a consistent and meaningful manner, both at the pilot and field scales. Such evaluations can help practitioners obtain optimal performance from existing technologies and ensure that new technologies are assessed fairly. For several remediation technologies, this evaluation may require developing new diagnostic tools, as well as technical guidance on using them. In situ air sparging is a good example (*34*). This research effort has helped the technology evolve from a "hit or miss" approach to a more robust remediation tool.

The first step is to identify which technologies need additional tools; in situ bioremediation and in situ thermal treatment were identified as the most critical needs at this time. Examples of diagnostic tools include push–pull tests to measure rates of biodegradation in situ, tracer tests to measure contaminant transport rates, groundwater velocity probes, and gene probes that can evaluate the presence of DNA from specific degrader organisms. The second step involves developing a conceptual framework for using existing and newer diagnostic tools to evaluate specific remediation technologies.

Effects of treatment amendments. In situ treatment can cause important changes in subsurface conditions, such as alterations in the site's physical, chemical, and microbiological parameters that impact flow and transport processes; changes in NAPL distribution and composition due to solubilization and mobilization; and geochemical and microbial perturbations. For example, adding chemical oxidants can produce gases or precipitates that may reduce permeability or limit delivery and mixing of the reagents. Surfactants can mobilize NAPL constituents or possibly enhance subsequent biodegradation. We currently do not understand these complex effects sufficiently to provide guidance for remedial project managers to adequately predict or monitor these potential side effects.

Questions that need to be addressed, in separate research projects or as part of other pilot tests or technology demonstrations, include biological diversity before and after remediation; residual materials remaining in the subsurface after treatment, and how they continue to react both biologically and chemically in the system; effects of treatment on the flow field; nature and risks of any byproducts produced as a result of treatment; and time needed for the system to return to a point of no environmental concern.

Remediation technology development

Source zone bioremediation and bioaugmentation. In situ bioremediation may be an economical and effective technology for source zone treatment (*32, 35*). However, to use this technology with confidence, we need a better understanding of the interrelated dissolution and degradation processes, as well as the appropriate uses of bioaugmentation. Careful long-term experiments under field conditions, with appropriate controls, are essential for demonstrating this technology. Mass balances to fully understand the effects on mass reduction, enhanced dissolution, and overall biodegradation will be difficult to perform. More mechanistic research is also needed to better understand the interrelated dissolution and degradation processes. Without a more thorough understanding of these complex interrelated phenomena, any predictions regarding the economic or environmental benefits of this approach will be suspect.

In some cases, bioaugmentation with organisms capable of completing all of the steps required for reductive dechlorination may be necessary (*36*). For example, metabolites such as *cis*-dichloroethene frequently accumulate. In some cases, adding appropriate organisms can relieve this accumulation. However, drastic source remediation technologies, such as in situ thermal treatment, may kill off the appropriate organisms, so that bioaugmentation may be needed after this first phase of treatment.

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We do not understand when bioaugmentation will be needed, or what conditions guarantee success. Little is known regarding the distribution of microorganisms from delivery points, so the factors influencing survival and effectiveness of the added organisms need study. Research is needed for various field conditions, and particularly in high-sulfate environments, because the possible inhibition of dechlorination in sulfate-reducing environments is controversial (*37*). Molecular or other tools are needed for the cost-effective monitoring of the fate and distribution of the introduced microbes. We also need to explore alternative delivery systems and quantitative models to predict subsurface transport of the organisms.

Plan for the future

R&D is needed on several fronts if we are to reduce the uncertainty and waste of resources. The following general recommendations summarize the consensus research needs developed at the workshop.

Develop better performance assessment tools. We need to understand how well available technologies work, especially under different site conditions, and how they can be optimized. Diagnostic tools to evaluate performance and guidance for using these tools will also be needed.

Develop tools to measure mass and mass discharge rates. To measure the impacts of source treatment or to understand the real risks posed by a residual source, accurate estimates of the total mass and the mass discharge before and after treatment are essential. The current state of the science is not adequate, and the development of better methods to measure source mass and mass discharge is one of the highest priorities for future work.

Focus on existing remedial technologies. More efficient use of existing technologies will be more valuable than developing still newer technologies. State-of-the-art technology assessments are needed, particularly for source zone treatment technologies. The source zone treatment technologies most in need of careful R&D efforts are in situ thermal treatment and in situ bioremediation.

The research needed will be technically difficult, and in some cases, costly and time-consuming. But considering the extent of the problems and the potential costs, the research is essential if we are to manage DNAPL-impacted sites efficiently.

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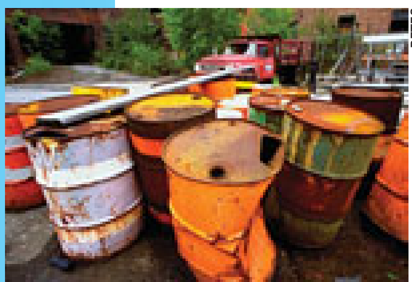

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Hans F. Stroo is a senior scientist and Marvin Unger is a program manager with the The RETEC Group, Inc., in Canada. C. Herb Ward is the Foyt Family Chair of Engineering at Rice University. Michael C. Kavanaugh is vice president and natural science technology leader at Malcolm Pirnie, Inc. Catherine Vogel, Andrea Leeson, Jeffrey A. Marqusee, and Bradley P. Smith manage the Strategic Environmental Research and Development Program and the Environmental Security Technology Certification Program for the U.S. Department of Defense. Contact Stroo at hstroo@retec.com or 541-482-1404.