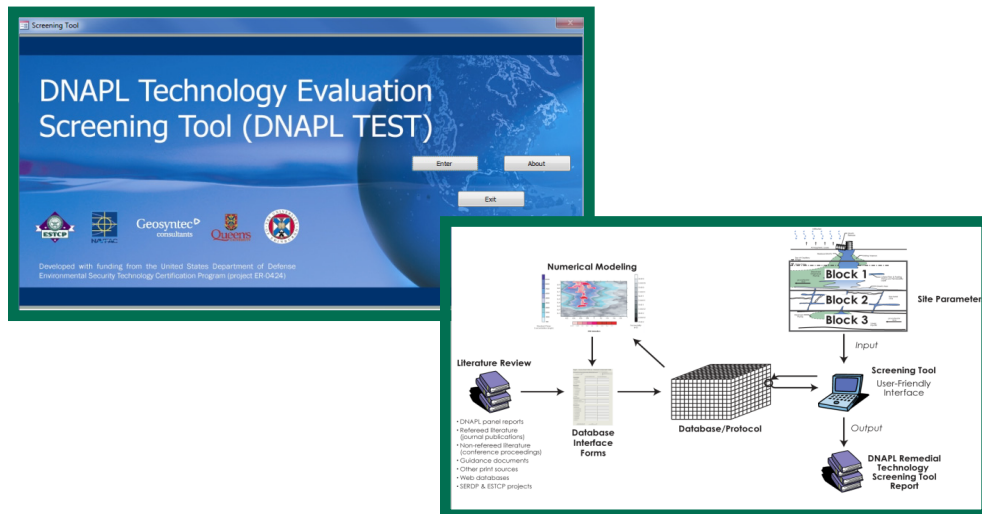


ESTCP Cost and Performance Report

(ER-200424)



Development of a Protocol and a Screening Tool for Selection of DNAPL Source Area Remediation

May 2012



ENVIRONMENTAL SECURITY
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ACRONYMS AND ABBREVIATIONS

1,1,1-TCA	1,1,1-trichloroethane
DNAPL	dense non-aqueous phase liquid
DNAPL TEST	DNAPL Technology Evaluation Screening Tool
DoD	Department of Defense
DQR	data quality rankings
EISB	enhanced in situ bioremediation
EPA SITE	Environmental Protection Agency Superfund Innovative Technology Evaluation
ERH	electrical resistive heating
ESTCP	Environmental Security Technology Certification Program
f_{oc}	fraction of organic carbon
HD	hydraulic displacement
IRP	Installation Restoration Program
ISCO	in situ chemical oxidation
m ³	cubic meter(s)
MCL	maximum contaminant level
MNA	monitored natural attenuation
NAPL	non-aqueous phase liquid
NAVFAC ESC	Naval Facilities Engineering Command – Engineering Service Center
O&M	operation and maintenance
P&T	pump and treat
PCE	tetrachloroethene
RAO	remedial action objective
RC	response complete
RPM	remedial program manager
RX	porous media
SEAR	surfactant enhanced aquifer remediation
TCE	trichloroethene
TCH	thermal conductive heating
VOC	volatile organic compound
ZVI	zero-valent iron

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no endorsement or recommendation is implied.*

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DISCLAIMER

Several remedial technologies are represented in dense non-aqueous phase liquid Technology Evaluation Screening Tool (DNAPL TEST). Naval Facilities Engineering Command – Engineering Service Center (NAVFAC ESC) does not endorse the use of any specific technology nor vendor. The information pertaining to the technologies performance was collected from various sources including conference proceedings, Environmental Security Technology Certification Program (ESTCP) reports, consultants’ reports, government documents, peer-reviewed journal articles, theses, and vendor publications. The source of the information is made available to the DNAPL TEST user in the citations. Additionally, numerical modeling of remediation technologies was completed to supplement available field and laboratory data, and to quantify other metrics difficult to quantify in a field setting. NAVFAC ESC does not necessarily endorse the use of any modeling or simulations software programs used in this exercise.

The data quality rankings (DQRs) in the DNAPL TEST are provided to the user as a means to express the completeness of the data set from the various literature sources. However, a high DQR should not be misconstrued as an endorsement to a specific journal, conference, website, or vendor publication.

Furthermore, the user of the DNAPL TEST software should be aware that results of the analysis do not constitute a prediction of how a technology will perform under the specified conditions. At the heart of the DNAPL TEST are the results of 200+ case studies, including over 80 modeling simulations. However, past performance and modeling simulations do not guarantee future performance. DNAPL architecture, the site’s biogeochemical conditions and geology/hydrogeology will determine technology performance. DNAPL TEST is to be used only as a guide for technology selection and cannot replace appropriate site-specific evaluations based on engineering judgment. ESTCP, NAVFAC ESC, Geosyntec Consultants, Queen’s University, and the University of Edinburgh are not liable for misuse of the information contained in, or output by, the DNAPL TEST software. Moreover, NAVFAC ESC does not endorse Geosyntec Consultants, Queen’s University, the University of Edinburgh, nor any of the participating entities in this effort.

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1.0 EXECUTIVE SUMMARY

1.1 OBJECTIVES

Multiple technologies have been developed and applied over the past few decades for remediation of chlorinated solvents in the subsurface. The remediation of solvents in the form of dense non-aqueous phase liquids (DNAPLs) is particularly challenging. Factors such as geology, geochemistry, hydrogeology, the composition and distribution of the DNAPL, as well as the presence and absence of other contaminants, play a role in technology selection and performance. To date, despite a multitude of reviews on several individual technologies, no comprehensive studies have been completed that illustrate which technologies generally work best under specific site conditions and desired remedial outcomes or goals.

The primary objective of the project was to develop a user-friendly screening tool that can be utilized by decision makers during the remedial technology selection or evaluation process to:

- Evaluate potential technology performance at a particular site
- Evaluate potential technology performance in different geological strata at a complex site
- Aid in the selection of feasible technologies for a particular site based on desired performance metrics
- Reduce the uncertainty of estimating and predicting remedial outcomes and implementation costs at DNAPL source zone sites.

1.2 TECHNOLOGY DESCRIPTION

The main goal of the Environmental Security Technology Certification Program (ESTCP) project ER-200424 was to assist environmental remediation practitioners in evaluating and selecting appropriate remedial technologies (given particular site conditions and performance goals). More importantly, given that the U.S. Department of Defense (DoD) is moving rapidly towards achieving Response Complete (RC) at 95% of Installation Restoration Program (IRP) sites by 2021, the information and screening tool developed as part of this project can be utilized to evaluate existing remedial systems. For those sites where remedies are not meeting established remedial action objectives (RAO), the screening tool can assist in determining whether there is a realistic expectation of meeting the RAOs for a given site and technology. The screening tool also can provide an assessment of alternative technologies to consider that may offer a higher likelihood of success.

The DNAPL Technology Evaluation Screening Tool (DNAPL TEST) was developed using data from published literature cases and modeling simulations that were used to supplement existing data. Hence, the basis of the screening tool is a database of information derived from case studies of field implementation of various remedial technologies, supported by numerical modeling of targeted technologies to address data gaps, and laboratory studies to provide information on fundamental processes impacting technology performance.

1.3 RESULTS

Observations on technology performance can be made based on the modeling results and field case study data collection completed to date. Some of these are summarized below:

- **Reductions in Groundwater Concentrations:** None of the site characteristic or technology implementation parameters that were evaluated as part of the statistical analysis were found to have a statistical correlation with reductions in groundwater concentrations; however, there does appear to be a relationship between the amount of DNAPL mass removed from the subsurface during treatment and reduction in groundwater concentration. This relationship appears to be independent of treatment technology.
- **DNAPL Mass Removal:** Near complete mass removal has been achieved with all technologies with the exception of hydraulic displacement (sometimes referred to as waterflooding). In field studies, the highest DNAPL mass removal was observed in thermal treatment case studies (94% to 96%) and the median mass removed for anaerobic enhanced in situ bioremediation (EISB), in situ chemical oxidation (ISCO), surfactant enhanced aquifer remediation (SEAR), and co-solvent flushing ranged from 64% to 81%. If modeling cases are included, the range of percent DNAPL mass removal increases for each technology, but the median value decreases. This is likely due to the fact that treatment duration during the modeling was varied to evaluate sensitivity of remedial performance, rather than treatment being terminated as a result of achieving desired performance levels as is more typical for field applications.
- **Matrix Diffusion:** Modeling results demonstrated that in fractured rock environments with an older DNAPL release, matrix diffusion (diffusion of DNAPL into lower permeability media) has a substantial influence on the distribution of DNAPL mass. If degradation of DNAPL within the lower permeability matrix is limited, back-diffusion of contaminant mass out of the matrix will sustain groundwater concentrations for long periods of time.
- **DNAPL Properties:** The solubility of the DNAPL was observed to influence the resulting net benefit of implementing more aggressive DNAPL treatment technologies over other approaches that rely primarily on dissolution of the DNAPL as the DNAPL mass reduction mechanism (e.g., pump and treat [P&T]). For more soluble DNAPLs such as trichloroethene (TCE), dissolution of the DNAPL is a significant component of the DNAPL mass removal, and incorporating other degradation or mass removal mechanisms (e.g., oxidation, biodegradation, enhanced dissolution) may only result in relatively small incremental increases in DNAPL mass removal.
- **Precipitate Formation:** Through the modeling sensitivity analysis, it was observed that the formation of a manganese dioxide rind (resulting in encapsulation of DNAPL pools and flow bypassing around DNAPL areas) significantly increased the time required to remove TCE DNAPL in ISCO applications using permanganate as the oxidant. This evaluation is specific to permanganate treatment and the corresponding manganese dioxide rind formation; however, it is anticipated that similar results may be observed with other technologies that result in the formation of a precipitate or result in permeability reductions. The influence of the precipitate formation on DNAPL

treatment is anticipated to be particularly pronounced where the precipitate forms within close proximity of the DNAPL phase, as occurs when permanganate reacts with the DNAPL.

1.4 IMPLEMENTATION ISSUES

DNAPL TEST has been designed to be updated in the future to reflect new data. As new field, laboratory, or modeling case studies become available, they can be added to the database. When sufficient new case studies have been added, the statistical analysis can be conducted again to refine statistical relationships. The costs to operate DNAPL TEST are very low. The tool is available for free download at <http://projects.geosyntec.com/DNAPL/dnapltest.aspx> and from the Naval Facilities Engineering Command – Engineering Service Center (NAVFAC ESC) website at <https://portal.navy.mil/go/erb>. The tool will also be available from the ESTCP website in the near future. The time required to run an analysis on the tool is approximately 10-20 minutes.

Given the limitations of the information incorporated into DNAPL TEST, this tool is most effectively used as a preliminary screening for technology selection or as a screening for possible performance limitations for a remedy in place. It cannot replace appropriate site-specific evaluations based on engineering judgment.

DNAPL TEST cannot “predict” technology performance for a particular site but will provide the user with an anticipated range of performance and the ability to compare performance observed for multiple technologies. This information can be used as the basis for developing realistic remedial end goals, as well as developing a short list of potential technologies for a site.

For users interested in obtaining potential technology performance information for a specific site, a Site Specific Analysis will better focus the screening evaluation to include sites that are anticipated to have similar performance. Multiple Site Specific Analyses may be completed for the same site to focus on different areas with different site characteristics. It should be noted that the Site Specific Analysis does require a minimum level of knowledge of conditions at the user’s site, which may limit its usefulness for some sites. Guidance for estimating of these parameters is provided within the tool.

For more general analyses of overall performance trends between parameters and for sites at which key site parameters are unquantified, the General Analysis will be a better option. Modifications to search parameters can easily be changed at any time during the screening process, allowing users to refine their analyses to better meet their needs. Specific examples illustrating a General and a Site Specific Analysis are provided in the User’s Manual, accessible at <http://projects.geosyntec.com/DNAPL/>, to better illustrate how the tool can be effectively used to meet the user’s goals.

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2.0 INTRODUCTION

Multiple technologies have been developed and applied over the past few decades for remediation of chlorinated solvents in the subsurface. The remediation of solvents in the form of DNAPLs is particularly challenging. Factors such as geology, geochemistry, hydrogeology, the composition and distribution of the DNAPL, as well as the presence and absence of other contaminants, play a role in technology selection and performance. To date, despite a multitude of reviews on several individual technologies, no comprehensive studies have been completed that illustrate which technologies generally work best under specific site conditions and desired remedial outcomes or goals.

The main goal of ESTCP project ER-200424 was to address this data gap and assist environmental remediation practitioners in evaluating and selecting appropriate remedial technologies (given particular site conditions and performance goals). More importantly, given that DoD is moving rapidly towards achieving RC at 95% of IRP sites by 2021, the information and screening tool developed as part of this project can be utilized to evaluate existing remedial systems. For those sites where remedies are not meeting established RAOs, the screening tool can assist in determining whether there is a realistic expectation of meeting the RAOs for a given site and technology. The screening tool also can provide an assessment of alternative technologies to consider that may offer a higher likelihood of success.

The primary objective of the project was to develop a user-friendly screening tool that can be utilized by decision makers (i.e., site owners, DoD remedial program managers [RPMs], regulators, and site consultants) during the remedial technology selection or evaluation process to:

- Evaluate potential technology performance at a particular site
- Evaluate potential technology performance in different geological strata at a complex site
- Aid in the selection of feasible technologies for a particular site based on desired performance metrics
- Reduce the uncertainty of estimating and predicting remedial outcomes and implementation costs at DNAPL source zone sites.

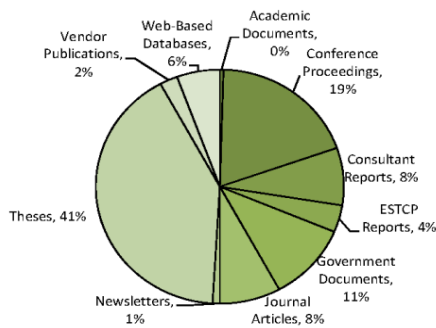
The DNAPL TEST was developed using data from published literature cases and modeling simulations that were used to supplement existing data. Hence, the basis of the screening tool is a database of information derived from case studies of field implementation of various remedial technologies, supported by numerical modeling of targeted technologies to address data gaps, and laboratory studies to provide information on fundamental processes impacting technology performance.

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3.0 DNAPL TEST DEVELOPMENT

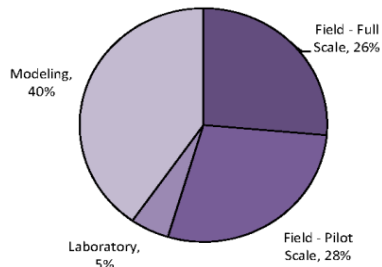
Data on site characteristics and remedial performance were collected for a range of sites and remedial technologies, and compiled into a database as part of the effort. The majority of field and laboratory case studies in the database were collected from a review of publicly available literature, which included both peer-reviewed and grey literature, online databases, guidance documents, consultant reports, and Environmental Protection Agency Superfund Innovative Technology Evaluation (EPA SITE) reports. Figure 1 provides the breakdown of case studies contained within the DNAPL TEST by case study type, reference source, and DNAPL remediation technology.

Breakdown of Case Studies by Information Source



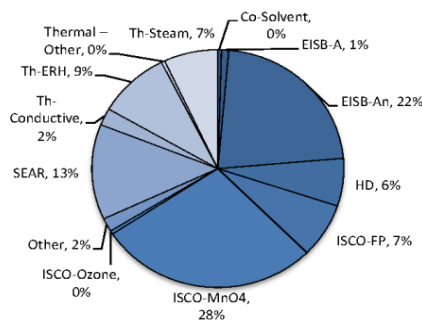
Information Source	Case Studies	Percent
Academic Documents	1	0%
Conference Proceedings	41	19%
Consultant Reports	17	8%
ESTCP Reports	8	4%
Government Documents	23	11%
Journal Articles	17	8%
Newsletters	2	1%
Theses	88	41%
Vendor Publications	5	2%
Web-Based Databases	12	6%

Breakdown of Case Studies by Study Type



Type of Study	Case Studies	Percent
Field - Full Scale	57	26%
Field - Pilot Scale	61	28%
Laboratory	11	5%
Modeling	87	40%

Breakdown of Case Studies by Technology



Technology	Case Studies	Percent
Co-Solvent	1	0%
EISB-A	2	1%
EISB-An	48	22%
HD	14	6%
ISCO-FP	16	7%
ISCO-MnO4	61	28%
ISCO-Ozone	1	0%
Other	4	2%
SEAR	28	13%
Th-Conductive	5	2%
Th-ERH	20	9%
Thermal - Other	1	0%
Th-Steam	15	7%

Figure 1. Breakdown of the case studies included in DNAPL TEST by reference source, case study type, and technology.

3.1 COLLECTION OF FIELD AND LABORATORY CASE STUDIES

The DNAPL TEST screening tool software interfaces with a database that contains raw data from 216 DNAPL remediation case studies. Case studies entered into the database include 129 field and laboratory studies, as well as 87 modeling studies. In order for any case study to be entered into the database, it must have met the following five criteria:

- Information on at least one performance metric (e.g., mass removal, concentration reduction, cost, treatment duration) was available.
- Chlorinated solvent DNAPL was present within the treatment zone.
- The DNAPL remedial technology used was specified in the document.
- The components of the DNAPL were specified (e.g., tetrachloroethene [PCE], TCE, 1,1,1-trichloroethane [1,1,1-TCA]).
- Site characterization data (e.g., hydraulic conductivity, geology/lithology, concentration data) was available.

Once studies were determined to meet the requirements for inclusion in DNAPL TEST, they were entered into the database using a set of database interface forms following a defined protocol (i.e., a set procedure to extract and analyze data from case studies), to ensure consistency between entries.

3.2 DEVELOPMENT OF MODELING CASE STUDIES

To supplement the field case study dataset, numerical modeling simulations were conducted on template sites having frequently encountered site characteristics. Modeling of remediation technologies was completed to provide additional information with regard to long-term performance and other metrics that are difficult to quantify in a field setting (e.g., DNAPL mass destruction, post-treatment groundwater concentration reductions). Five remedial technologies were simulated in both unconsolidated and consolidated media, including anaerobic EISB, ISCO using permanganate, hydraulic displacement (HD) (otherwise known as waterflooding, unconsolidated media only), SEAR, and P&T (unconsolidated media only). As discussed below, the modeling process included sensitivity studies to evaluate the influence of key processes and site parameters on the performance of each remedial technology. P&T was primarily simulated to provide a baseline comparison for the in situ remediation technologies, and these simulations were therefore not included in the screening tool. Modeling was performed using the numerical code DNAPL 3-D-porous media (RX), and the process included sensitivity studies to evaluate the influence of site parameters (e.g., DNAPL type and release volume, fracture aperture, matrix porosity, fraction of organic carbon, fracture spacing, bedrock type, bulk density, matrix tortuosity, hydraulic conductivity, and heterogeneity) on the performance of each remedial technology.

Table 1 provides a summary of the specific processes included in modeling of each technology in each type of porous media.

Table 1. Physical processes incorporated into numerical modeling for each remedial technology.

	P&T	ISCO	EISB	HD	SEAR
Processes Common to Both Unconsolidated and Consolidated Media Simulations	<ul style="list-style-type: none"> • Not applicable (P&T not simulated for consolidated media) 	<ul style="list-style-type: none"> • Physical attenuation mechanisms as with P&T • Reaction of permanganate with both organic carbon in the soil/rock and contaminant • Species-specific diffusion rates 	<ul style="list-style-type: none"> • Physical attenuation mechanisms as with P&T • Biodegradation of TCE and PCE to ethene 	<ul style="list-style-type: none"> • Not applicable (HD not simulated for consolidated media) 	<ul style="list-style-type: none"> • Physical attenuation mechanisms as with P&T • Formation of surfactant micelles • Enhanced dissolution of the DNAPL where micelle concentrations exceed critical levels
Processes Simulated in Unconsolidated Media Runs Only	<ul style="list-style-type: none"> • Physical attenuation mechanisms including DNAPL dissolution, sorption, diffusion, dispersion, dilution, etc. 	<ul style="list-style-type: none"> • Manganese dioxide precipitate formation, resulting pore clogging and reductions in permeability 	<ul style="list-style-type: none"> • Biomass growth and decay • Pore clogging due to biomass growth and related reduction in permeability • Competition for hydrogen with non-dechlorinating biomass 	<ul style="list-style-type: none"> • Physical attenuation mechanisms as with pump and treat • DNAPL redistribution and recovery due to induced hydraulic gradients 	<ul style="list-style-type: none"> • Not applicable (SEAR simulated using similar processes for both media types)

3.3 DEVELOPMENT OF THE DNAPL TEST SCREENING TOOL

A software interface was constructed to allow for a user-friendly means of evaluating the case study information on a site-by-site basis. Recognizing that each site is unique and that performance goals and regulatory constraints will vary from site to site, DNAPL TEST enables the user to select and constrain their analysis to focus on those performance goals, remedial technologies, and site characteristics of interest.

The remedial technologies evaluated in DNAPL TEST include ISCO, thermal technologies (including thermal conductive heating [TCH], steam flooding, electrical resistive heating [ERH] and microwave heating), surfactant flushing (SEAR) and co-solvent flushing, HD, EISB, and chemical reduction with zero-valent iron (ZVI). For these technologies, DNAPL TEST provides a summary of observed remedial performance for a number of performance metrics, including decrease in the DNAPL mass in the subsurface, decrease in volatile organic compound (VOC) concentrations in soil and groundwater, achievement of maximum contaminant levels (MCLs) in groundwater, rebound in groundwater concentrations after termination of treatment, duration of treatment, achievement of remedial goals (including achieving desired reductions in DNAPL mass, groundwater and soil concentrations, and contaminant mass discharge and/or flux, as well as achievement of site closure or reduction of groundwater concentrations to below MCLs), and unit treatment cost.

3.4 DEVELOPMENT OF DATA QUALITY RANKINGS

Data Quality Rankings (DQRs) were designed to provide DNAPL TEST users an assessment of the relative quality of the data upon which their analyses are based. They are not to be interpreted as a judgment on the quality of the modeling, field, or laboratory work described in each case study, as this would require a detailed evaluation of the technical aspects of each case study and more detailed information than typically available. Rather, the DQRs have been developed to use certain key indicators to provide an assessment of the quality of each case study, based on readily available information.

There are some limitations to this approach. For example, some well-implemented case studies may have been assigned lower DQRs in DNAPL TEST if detailed reports could not be obtained by the project team and insufficient information was available to develop a full assessment of the DQR. The converse situation may also occur, with a poorly implemented program being assigned a higher DQR if more information was available describing the implementation or if the remediation program was implemented more recently.

While such ratings cannot be developed with complete objectivity, efforts were made to minimize subjectivity by automating the DQR calculation. The DQR calculation reflects the following five criteria:

- A – Quality of the information source
- B – Age of the study
- C – Type and density of DNAPL assessment methods and locations
- D – The methodology used and amount of information available for pretreatment performance monitoring
- E – The methodology used and amount of information available for post-treatment performance monitoring.

Case studies receive an integer ranking between 1 and 3 (3 being highest) for each of these criteria (criteria ranking assignment described below), and the DQR is their weighted average calculated as follows:

$$\text{DQR} = 0.1A + 0.2B + 0.2C + 0.25D + 0.25E$$

The average was weighted according to the following rationale:

- A: Information sources vary in reputability (e.g., a peer-reviewed journal article versus a technology vendor's project description). However, this criterion does not weigh as highly as other criteria that reflect the completeness of the data record.
- B: Older studies were ranked lower than more recent studies to account for improved technology application resulting from lessons learned from previous technology applications and ongoing technology developments.

- C: The density of sampling and methods used to characterize the DNAPL are an important subset of site characterization activities.
- D and E: The completeness of site characterization and monitoring (e.g., hydrogeological parameters, area or volume treated, and assessment of performance metrics, particularly DNAPL mass removal), both before and after treatment, are the most important indicators of data quality.

For use in DNAPL TEST, DQRs were considered low if the value was ≤ 1.8 out of 3.0, medium if the DQR ranged from >1.8 to <2.4 , and high if the value was ≥ 2.4 .

The average DQR as well as the number of studies included in the analysis is shown on the bottom left corner of General Analysis input screens. This information is automatically updated as the user changes selection criteria.

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4.0 DNAPL TEST SCREENING TOOL STRUCTURE

DNAPL TEST allows users to customize their analysis to meet their own objective by providing two options: a General Analysis or a Site Specific Analysis.

- ***The General Analysis Option***, in which the user can query the database of case studies for general performance information. In this option, the user can refine the search to include specific technologies, case study type, data quality rankings, and site characteristics, and the tool will generate reports of average and select individual performance data from case studies matching the search criteria. With the General Analysis, the user can query the database of case studies for general performance information by refining their search to include specific technologies, case study type, data quality rankings, and site characteristics. The tool will generate reports of average and select individual performance data from case studies matching the search criteria.
- ***The Site Specific Analysis Option***, in which the user is given the opportunity to tailor the analysis to provide performance information from case studies with specific characteristics. Using this alternative, the user is asked to input characteristics of the site of interest and specify other search criteria (e.g., specify data quality rankings and case study types to be included, geologies, DNAPL types). DNAPL TEST then searches for case studies with statistically similar site characteristics (i.e., case studies with site characteristics that are anticipated to have similar technology performance) for performance metrics where correlations between technology performance and site characteristics were observed (see Section 3.4 for more details). For performance metrics where correlations were not observed, case studies that meet the user-specified search criteria are included in the analysis. The Site Specific Analysis output reports provide more details of case-study-specific performance as well as average and min/max performance trends. Output reports are also provided on an individual performance metric basis as well as technology-specific basis. With the Site Specific Analysis, the user can input characteristics of the site of interest and specify other search criteria (e.g., specify data quality rankings and case study types to be included, geologies, DNAPL types). DNAPL TEST then searches for case studies with statistically similar site characteristics for performance metrics where correlations between technology performance and site characteristics were observed. The Site Specific Analysis output reports provide more details of case-study-specific performance as well as average and min/max performance trends. Output reports also are provided on an individual performance metric basis as well as technology-specific basis.

The basis of the Site Specific Analysis is a statistical evaluation that identified and quantified correlations between site parameters and performance metrics. This evaluation was completed in a two-step process. In the first step, a series of correlation tests were conducted to identify linear associations between a given site parameter and a given technology performance metric. A 5% level of significance was used as the criteria for statistically significant linear correlations. In the second step, site parameter, performance metric pairs that showed a statistically significant correlation were analyzed using simple linear regression methods. Regression quantified the sensitivity of the technology performance to each site parameter and also was used to calculate a

range of site parameters values given a particular technology performance value via a 95% confidence interval.

A total of nine pairs for all technologies was found to have statistically significant correlations.

- For EISB, reduction in DNAPL mass correlated to hydraulic conductivity.
- For SEAR, reduction in DNAPL mass was correlated to the areal extent of the DNAPL zone, pre-remediation DNAPL mass, and the volume of the DNAPL zone.
- For thermal (steam), treatment duration was correlated to the volume of the DNAPL zone, and for thermal (resistive), reduction in DNAPL mass was correlated to the area and volume of the DNAPL zone, and treatment duration was correlated to the pre-remediation DNAPL mass and electrode spacing.

5.0 PERFORMANCE ASSESSMENT

5.1 VERIFICATION OF DNAPL TEST SOFTWARE CODE

Verification of the DNAPL TEST software code was conducted through completion of a site-specific technology performance analysis for two well-characterized sites at which remediation has been completed. The characteristics of the case studies identified for the screening tool analysis were compared to the filtering criteria and confirmed to be appropriate for inclusion in the analysis. Validation of the General Analysis search function was also verified with site characteristics compared to filter criteria. Finally, cross-checking of output statistics to actual case study data confirmed that the statistics were being calculated correctly.

5.2 DNAPL TECHNOLOGY PERFORMANCE EVALUATION

General observations on trends in technology performance are discussed in further detail below. This information was developed from an analysis of general trends seen from the field case studies and supplemented with additional information gleaned from the results of the numerical modeling simulations.

5.2.1 Reductions in Groundwater Concentrations

The influence of various site characteristics and technology implementation parameters on achievable reductions in groundwater concentrations for each DNAPL remediation technology was evaluated as part of the numerical modeling studies and the statistical correlation evaluations. Of the site characteristic and technology implementation parameters that were evaluated statistically, none were found to statistically correlate to reductions in groundwater concentrations. Similar observations were seen from the numerical modeling exercise, with the exception of the duration of treatment (i.e., longer treatment durations generally resulted in greater reductions in groundwater concentrations). Longer treatment durations in the modeling also generally resulted in greater removal of DNAPL mass.

The graph below (Figure 2) illustrates the correlation between the reduction of DNAPL mass and groundwater concentration reductions that occurred throughout the active treatment phase. The data included in this plot includes results observed both in field case studies (open symbols) as well as in the numerical modeling studies (closed symbols). Groundwater concentrations correspond to concentrations observed at the termination of treatment and do not reflect rebound post-treatment (if any). Overall, there appears to be an approximate 1:1 correlation between the amount of DNAPL mass that is removed from the subsurface and the corresponding reductions in groundwater concentrations that result (with some deviations as discussed below). This overall relationship between DNAPL mass and groundwater concentration reductions is generally independent of remedial approach, which suggests that the greatest influence on remedial performance from a groundwater concentration reduction perspective is the degree of DNAPL mass removal. Therefore, as a rule of thumb, if 50% groundwater concentration reductions are the remedial goal, it is likely that removal of approximately 50% of the DNAPL mass will be required. Similarly, if achievement of MCLs is desired (typically representing >99% reduction in groundwater concentrations), then >99% removal of the DNAPL mass will likely be required.

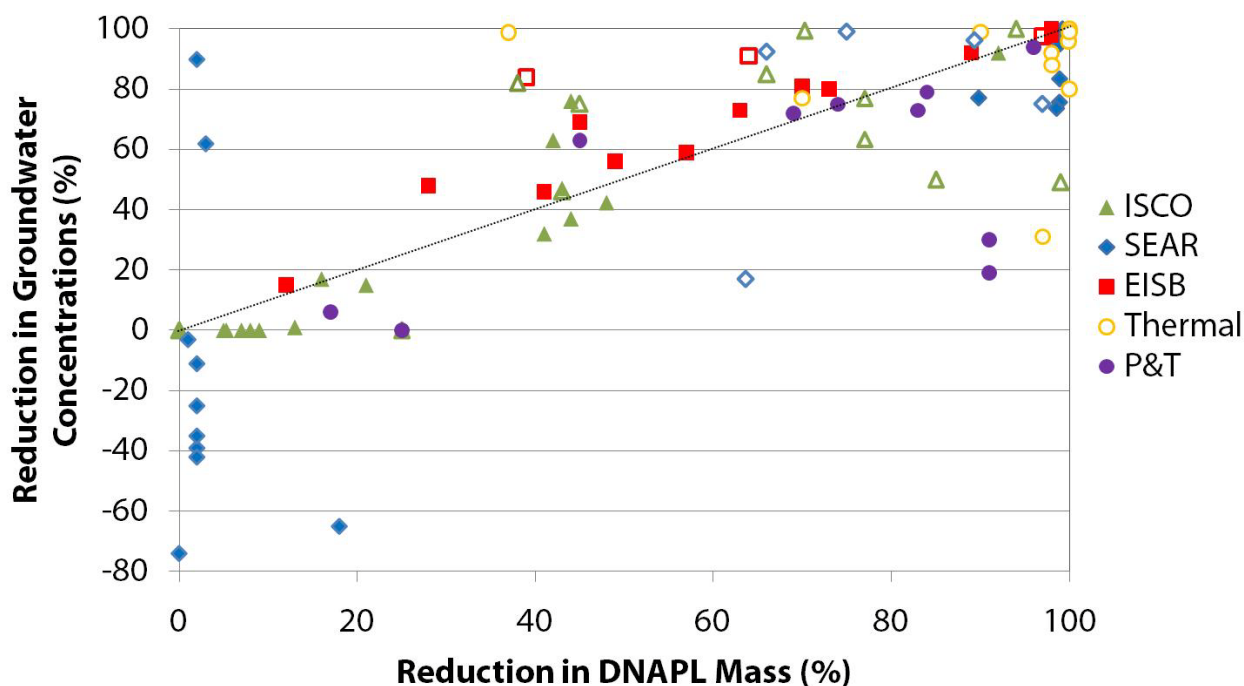


Figure 2. Relationship between reduction of mass in the system at the start of remediation and groundwater concentration reductions by remedial technology.

Open symbols represent field case studies; closed symbols represent modeling case studies.

Slight deviations from the above behavior are evident for a couple of technologies. For example, for EISB, the resulting DNAPL removal—groundwater concentration reduction pairs consistently plot above the 1:1 line—indicate that the groundwater concentration reduction achieved with EISB is consistently greater than the corresponding reduction in DNAPL mass removal, even after treatment is terminated. As a result, slightly less DNAPL mass removal is required for EISB to achieve concentration reductions similar to ISCO, for example. This greater reduction in groundwater concentrations during EISB may reflect the fact that the more permeable regions are treated preferentially, and EISB also exhibits a “sustained treatment” effect that keeps concentrations reduced after treatment for several years (Adamson et al., 2011), as discussed in Section 5.2.7 on post-treatment rebound.

Another example of slight deviation from this behavior is the consistent plotting of groundwater concentration reduction—DNAPL removal pairs for P&T below the 1:1 line. This behavior suggests that greater reductions in DNAPL removal are required for P&T to achieve similar reductions in groundwater concentrations. Thermal case studies tend to cluster at the upper range of the reduction in DNAPL mass and groundwater concentrations (i.e., typically >90-99% mass removal and corresponding reductions in groundwater concentrations are achieved) because thermal technologies are very effective at achieving near complete mass removal when designed appropriately and the treatment zone encompasses the entire DNAPL zone.

At sites where ISCO has been applied, the groundwater concentration reduction—DNAPL mass removal pairs plot consistently on both sides of the 1:1 line—indicate that a reasonable predictor for groundwater concentration reductions would be the reduction in DNAPL mass for ISCO technologies. Conversely, the variability in the position of groundwater concentration reduction—DNAPL mass removal pairs for sites where SEAR has been applied—varies widely on both sides of the 1:1 line. It should be noted that the variability at the low end of the DNAPL removal range occurs in the modeling studies and may be an artifact of the modeling assumptions.

5.2.2 DNAPL Mass Removal

Table 2 provides a summary of DNAPL mass removal achieved for the various technologies for field case studies only and for both field and modeling studies for technologies where modeling was completed (shown in parentheses). As seen in Table 2, near complete removal of the DNAPL mass has been achieved by the majority of the technologies, the one exception being hydraulic displacement, which relies on mobilization of the DNAPL phase as the primary DNAPL removal mechanism. Capillary forces acting upon the DNAPL phase effectively trap smaller blobs and ganglia of residual DNAPL, and enhancement of pressure gradients to levels high enough to mobilize residual DNAPL is unlikely to be achievable. Therefore, hydraulic displacement can only achieve partial removal of the DNAPL but may be (1) a cost-effective means of stabilizing a source zone (i.e., eliminating the potential for future pool mobilization to deeper depths), (2) a cost-effective means of removing large quantities of DNAPL mass in a short period of time, and (3) a pretreatment step as it results in an increase in the DNAPL surface area-to-volume ratio, which is beneficial for mass-transfer driven remedial technologies.

Table 2. Summary of DNAPL mass removal achieved with the various technologies for field case studies only and where modeling studies are also included
(shown in parentheses).

Technology	No. of Studies	Median % DNAPL Mass Removal	Range in % DNAPL Mass Removal
Aerobic EISB	1	39%	--
Anaerobic EISB	3 (15)	64% (63%)	48% to 97% (12% to 98%)
Hydraulic Displacement	0 (13)	(31%)	(9% to 45%)
ISCO – Fenton’s Reagent	4	68%	38% to 99%
ISCO – Permanganate	5 (19)	77% (44%)	70% to 99% (1% to 100%)
SEAR	2 (27)	81% (72%)	66% to 98% (0% to 99%)
Co-solvent Flushing	1	64%	--
Thermal – TCH	2	NA	NA
Thermal – ERH	15	94%	37% to 98%
Thermal – Steam	9	96%	79% to 100%

As seen by the median percentage DNAPL mass removal in Table 2, thermal technologies typically achieve high levels of DNAPL mass removal (94% to 96%). Median removals for the remaining technologies including anaerobic EISB, ISCO, SEAR, and co-solvent flushing ranged from 64% to 81% for the field case studies. When modeling case studies are included, the ranges are larger and the medians tend to be lower; however, this is more likely because treatment duration during the modeling was varied to evaluate sensitivity of remedial

performance, rather than treatment being terminated as a result of achieving desired performance levels, as is more typical for field applications.

5.2.3 Influence of Matrix Diffusion

The potential influence of matrix diffusion into lower permeability media and the resulting influence of back-diffusion on remedial performance were investigated as part of the sensitivity study for the numerical modeling. The numerical modeling included simulations of ISCO (permanganate) treatment of TCE and PCE diffused into fractured clay, and EISB, ISCO, and SEAR treatment of TCE diffused into fractured rock matrices of various porosities (i.e., ranges typical for shale, granite, and sandstone) and fraction organic carbon content (which governs the level of influence that sorption/desorption mechanisms dictate contaminant behavior within the matrix).

Through incorporating various fate and transport processes into the numerical model (e.g., sorption/desorption of TCE onto organic matter within the matrix, degradation of amendments both within the fractures and matrix, constituent-specific forward- and back-diffusion into and out of the matrix), the following was demonstrated:

- The significance of matrix diffusion in a particular fractured rock environment will have a substantial influence on the distribution of DNAPL and VOC mass at the start of remediation, particularly if the DNAPL release is not recent. Fractured rock types that exhibit higher matrix porosity, higher fracture density, lower mean fracture apertures (contributing to lower groundwater velocities) or higher matrix fraction organic carbon (e.g., sandstone and shale) may exhibit a much higher fraction of VOC mass present in the matrix. Large amounts of sorbed and aqueous VOCs in the matrix may correspond to a decrease in DNAPL mass present, particularly if the DNAPL release is not recent. In many simulations in this work, more than 97% of the DNAPL released was present as sorbed VOC mass in the matrix at the end of the site aging stage. In contrast, where factors contribute to a significant amount of DNAPL remaining in the fractures (DNAPL release is recent, matrix diffusion is low, DNAPL type has low solubility, etc), then groundwater flow rates through the source zone may be low, impacting delivery of amendment. The impact of any treatment must be considered in the context of the distribution of DNAPL and VOC mass prior to treatment application.
- For sites where degradation/transformation of the contaminant phase within the lower permeability matrix is limited, back-diffusion of contaminant mass from the matrix will sustain groundwater concentrations for long periods of time. This can occur, for example, due to pore size restrictions on the ability of microorganisms to penetrate the matrix, or natural organic matter in the matrix consuming permanganate during forward diffusion, or amendments with high reactivity that react and degrade faster than they can diffuse very far into the matrix. As a result, treatment primarily occurs within the fracture network and the rate of reduction of contaminant mass contained within the matrix is limited to the rate it can back-diffuse out of the matrix, which is very slow. Moreover, it can be difficult and costly to continue to deliver amendments in the advection-dominated fractures for a long enough period (i.e., years) to effectively address contaminant mass via back diffusion. Due to the majority of the contaminant

mass being unavailable in such cases, in situ treatment is unlikely to have a substantial net benefit in terms of reducing treatment durations over containment approaches like pump and treat. Reduction in overall treatment costs over pump and treat may be achieved if an approach with lower operation and maintenance (O&M) costs is used (e.g., EISB). This scenario (i.e., insubstantial matrix treatment) can occur at sites (1) with a very tight matrix (e.g., granite); (2) with high VOC mass loading in the matrix but limited ability for diffused amendment to be effective in the matrix (SEAR, possibly EISB); (3) dominated by large horizontal apertures (such that mean residence time for amendment in the source zone is low); (4) with treatment approaches that depend on advective flushing of the contaminant mass for ex situ treatment (e.g., P&T); or (5) that require the use of amendments that do not persist for very long in the subsurface (e.g., oxidants).

- Where degradation/transformation can occur within the lower permeability matrix, and thus treatment effectiveness is less influenced by back-diffusion to the fractures, in situ treatment times are likely to be shorter than flushing technologies such as P&T, and post-treatment rebound of groundwater concentrations will be less likely to occur. This scenario (i.e., substantial matrix treatment) is expected to occur for sites where significant VOC mass is stored in the matrix (e.g., sandstone) and the amendment can penetrate and react effectively in the matrix (e.g., ISCO in a low- fraction of organic carbon [f_{oc}] matrix, possibly EISB). Note that this latter example assumes that significant rates of biodegradation can be attained and sustained within the matrix; there is little data currently available to quantify such rates.
- Where significant amounts of DNAPL have accumulated and remain in fractures, then treatment approaches that depend on advective flushing may provide significant benefit in DNAPL mass reduction. This scenario may apply for sites that have a tight matrix (e.g., granite) and for technologies that directly target DNAPL (e.g., SEAR).
- Where DNAPL has accumulated in dead-end fractures, DNAPL removal may again be limited for technologies such as SEAR that rely on delivery of the amendment directly to the non-aqueous phase liquid (NAPL) phase.

The maximum rebound of concentrations in the fracture can occur years after termination of treatment, which has implications with respect to designing and interpreting the results of performance monitoring programs. The limitations of diffusion also imply that complete mass removal is not going to be achievable in a reasonable time frame in fractured clay or rock environments, and that partial mass removal to target reductions in groundwater concentrations and mass flux may be a more appropriate remedial goal.

5.2.4 DNAPL Properties

The solubility of the DNAPL was observed to influence the resulting net benefit of implementing more aggressive DNAPL treatment technologies over other approaches such as monitored natural attenuation (MNA) or P&T that rely primarily on dissolution of the DNAPL as the DNAPL mass reduction mechanism. For more soluble DNAPLs such as TCE, dissolution of the DNAPL is a significant component of the DNAPL mass removal, and incorporating other

degradation or mass removal mechanisms (e.g., oxidation, biodegradation, enhanced dissolution) may only result in relatively small incremental increases in DNAPL mass removal. However, introducing other mass removal mechanisms can potentially result in more significant enhancements over dissolution alone for lower solubility DNAPLs such as PCE.

5.2.5 Impact of Precipitate Formation on Technology Performance

The impact of precipitate formation on treatment performance for ISCO applications using permanganate as the oxidant was investigated as part of the numerical modeling sensitivity study. The formation of manganese dioxide rind specific to permanganate injections can result in encapsulation of the DNAPL (particularly pools) and flow bypassing around DNAPL areas (Conrad et al., 2002). Once the rind forms around the DNAPL, the rate at which permanganate can contact the DNAPL becomes diffusion limited, and the rate of DNAPL mass removal slows significantly as a result. Ongoing diffusion of dissolved contaminant phase through the rind occurs as well, and rebound of concentrations post-treatment is common as a result.

Table 3 illustrates the results of the numerical modeling sensitivity study (West et al., 2008) where 3 kilograms of TCE DNAPL were assumed to be evenly distributed throughout a 1 cubic meter (m³) volume of homogeneous sand. The simulation continued until all TCE mass was removed from the domain for several scenarios, including:

- Dissolution of the DNAPL only
- Dissolution of the DNAPL for 10 years, then either (1) 1 year permanganate amendment followed by dissolution only; (2) 2 years permanganate amendment followed by dissolution only; and (3) continuous treatment with permanganate until all of the TCE mass had been degraded. To illustrate the impact of rind formation on treatment performance, two sets of runs were completed, one with rind formation and the second without rind formation.

As seen in Table 3, the formation of the rind significantly increased the time required to remove the TCE DNAPL (14 years) when compared to the scenario with no rind being formed (8 years). Where only partial treatment with permanganate was completed, the encapsulation of the remaining DNAPL phase resulted in a longer persistence of TCE (25 years) than if no treatment had been completed (20 years).

Table 3. Results of the sensitivity study completed to investigate the potential influence of manganese dioxide rind formation during permanganate treatment.

(West et al., 2008)

Scenario	DNAPL Lifespan
Dissolution only	20 yrs
1 yr treatment with permanganate with rind, followed by dissolution	25 yrs
2 yr treatment with permanganate with rind, followed by dissolution	25 yrs
Continuous treatment with permanganate without rind formation	7 yrs
Continuous treatment with permanganate with rind formation	14 yrs

The influence of the manganese dioxide rind formation in consolidated media environments will vary, depending on where the rind forms. Rind formation and the associated permeability reductions in fractures is anticipated to have a much larger influence on technology performance than formation of the manganese dioxide rind in the matrix, where contact with the contaminant is already diffusion-limited. Similar behavior as seen in the numerical modeling sensitivity study has been observed at the field scale, a prime example being the Watervliet Arsenal site (Goldstein et al., 2004).

The above examples are specific to permanganate treatment and the corresponding manganese dioxide rind formation; however, it is anticipated that similar results may be observed with other technologies that result in the formation of a precipitate or result in permeability reductions. The influence of the precipitate formation on DNAPL treatment is anticipated to be particularly pronounced where the precipitate forms within close proximity of the DNAPL phase, as occurs when permanganate reacts with the DNAPL.

5.2.6 Benefits of Partial DNAPL Mass Removal

Figure 3 illustrates near- and long-term groundwater concentration reductions, DNAPL mass removal, and reduction in contaminant mass flux from the source area for four different partial DNAPL treatment scenarios based on the base case modeling scenario (i.e., TCE DNAPL source, moderate heterogeneity and permeability, etc.), including:

- Treatment with ISCO (permanganate) or EISB for approximately 2 years only
- Treatment with ISCO or EISB for approximately 2 years followed by MNA, assuming physical attenuation mechanisms only (e.g., DNAPL dissolution, dispersion, sorption, etc., no biological attenuation)
- Continuous treatment with ISCO or EISB for 10 years
- Continuous treatment with ISCO or EISB for 30 and 20 years, respectively.

As seen in Figure 3, ongoing treatment results in increasing groundwater concentration reductions, removal of DNAPL mass, and reduction in mass flux from the downgradient source zone boundary for both ISCO and EISB. Interestingly, the results achieved with 2.3 years of ISCO implementation followed by 7.7 of MNA were not much less than those achieved with 10 years of active treatment. The benefit achieved with ongoing treatment appears to be less for ISCO than for EISB; in particular the further removal of DNAPL mass. This trend reflects the impact that the formation of the manganese dioxide rind has on the DNAPL removal efficiency when using permanganate, as discussed above. Similarly, continuing ISCO treatment beyond 10 years to 30 years has little to no net benefit in reducing groundwater concentrations at the downgradient source boundary or the site conditions evaluated.

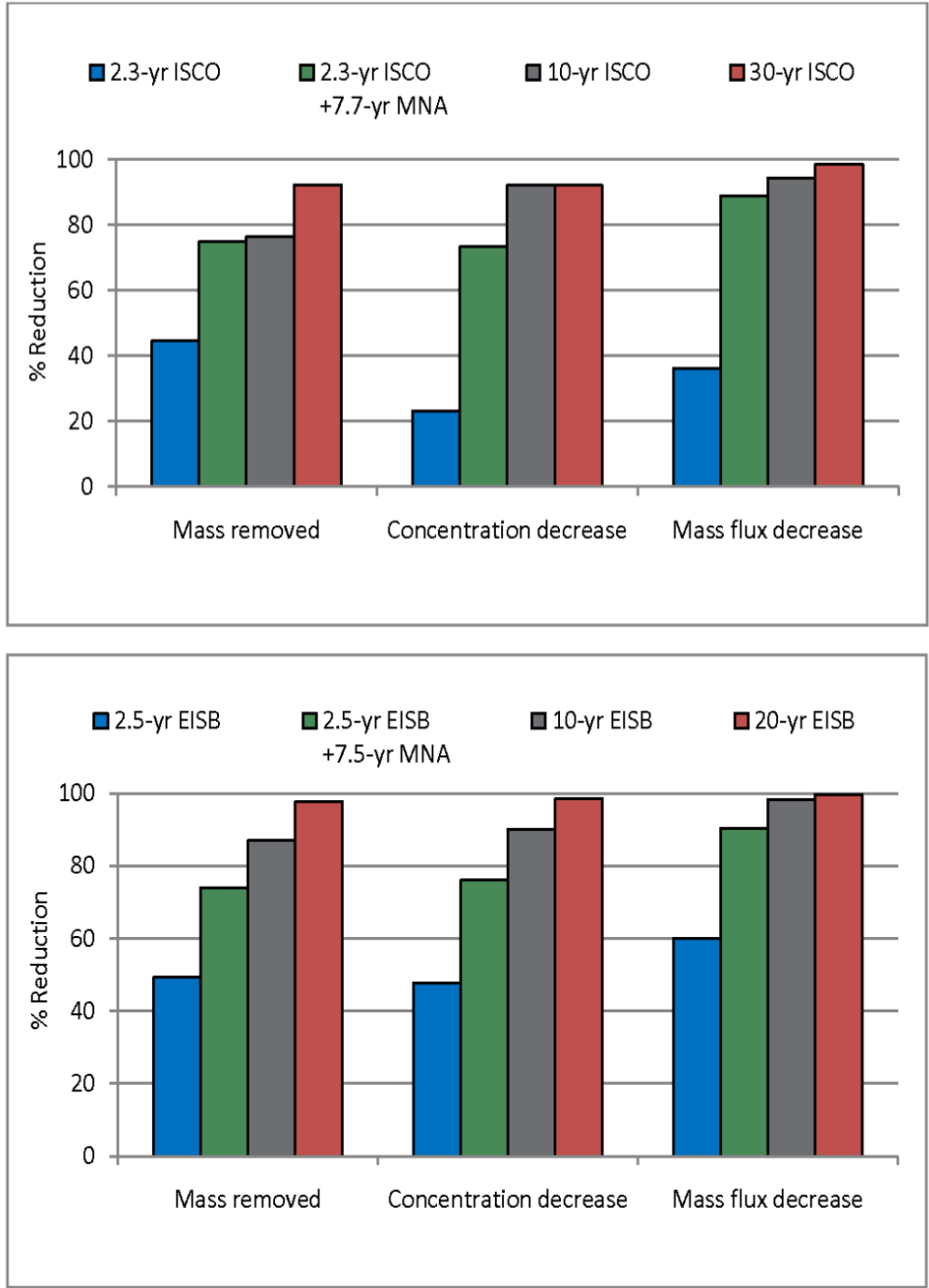


Figure 3. Comparison of technology performance in terms of mass removal, concentration reduction, and mass flux reduction after either 2.5 or 10 years of active treatment using either ISCO or EISB.

5.2.7 Post-Treatment Rebound of Groundwater Concentrations

Table 4 summarizes post-treatment rebound of groundwater concentrations observed at field sites included in the screening tool database. Rebound was defined as a significant (i.e., >20%) increase in groundwater concentrations after treatment was terminated, in comparison to concentrations observed at the end of active treatment. Technologies not included in Table 4 did not have any case studies reporting rebound behavior in the screening tool database.

Table 4. Summary of post-treatment groundwater concentration rebound behavior observed at field sites.

Technology	Site Observing Rebound Post-Treatment	Percentage of Sites with Rebound
Anaerobic EISB	3 of 13 sites	23%
ISCO – Fenton’s Reagent	5 of 7 sites	71%
ISCO – Permanganate	8 of 11 sites	73%
ISCO – Ozone	1 of 1 sites	100%
SEAR	2 of 3 sites	67%
Thermal – ERH	0 of 9 sites	0%
Thermal – TCH	0 of 3 sites	0%

As seen in Table 4, rebound was not observed at any of the thermal sites and was observed at only a small proportion (23%) of the anaerobic EISB sites. The lack of rebound at thermal sites is due to the high proportion of DNAPL mass removed, while at EISB sites, rebound is suppressed due to ongoing bioactivity for a period of time upon termination of active treatment due to the biomass using decaying biomass as a nutrient source (Adamson and Newell, 2009). Rebound may also be suppressed at EISB sites potentially due to other processes including back diffusion of electron donor that migrated into lower-permeability regions and possibly enhanced abiotic degradation under reducing conditions (Adamson et al., 2011).

In comparison, rebound was observed at the majority of ISCO and SEAR sites (>67%), where partial DNAPL mass removal is typically achieved and treatment effectively terminates once amendment injection is terminated. Fractured rock sites saw concentration rebound due to back diffusion of contaminants stored in the matrix after the fractures have been flushed and cleaned. The back-diffusion, and thus the concentration rebound, is more significant for scenarios with a higher proportion of the VOC mass stored in the matrix (e.g., longer time since DNAPL release, higher solubility DNAPL, higher matrix porosity, higher fracture density, lower mean apertures, higher matrix f_{oc}). This rebound behavior is consistent with observations reported in an independent study completed by McGuire et al. (2006).

5.2.8 Treatment Costs

Limited cost data was available for the case studies collected in DNAPL TEST, as case-study-specific costs are rarely discussed in publicly available literature sources. Table 5 presents a summary of the costs available, presented as costs per unit volume of the treatment zone. Costs are normalized by treatment volume in an effort to provide comparable values between both large and small remedial implementations. It should be recognized that, although unit costs

reduce some of the variability in costs related to treatment scale, they can still be skewed in cases where the treatment volume size is small. For example, the ISCO permanganate application that had a unit cost of \$60,000 per m³ in Table 5 below was a 1 m³, highly instrumented research demonstration that is not representative of larger scale costs.

Table 5. Breakdown of unit costs by treatment technology.

Technology	No. of Case Studies Reporting Costs	Median Unit Cost (\$/m³)	Range in Unit Costs (\$/m³)
Aerobic EISB	1	\$100	--
Anaerobic EISB	4	\$270	\$9 - \$630
ISCO – Fenton’s Reagent	4	\$260	\$51 - \$770
ISCO – Permanganate	5	\$240	\$35 - \$60,000
SEAR	3	\$8,200	\$5,500 - \$41,000
Co-solvent Flushing	1	\$23,000	--
Thermal – TCH	2	\$270	\$150 - \$380
Thermal – ERH	11	\$170	\$42 - \$720
Thermal – Steam	4	\$170	\$18 - \$390

As seen in Table 5, median unit costs for EISB, ISCO, and thermal technologies are of similar order of magnitude (\$100 to \$270/m³) with similar ranges in unit costs as well (\$9 to \$770/m³). Costs for co-solvent flushing and SEAR for the case studies included in the screening tool database are an order of magnitude higher, although a limited number of case studies for these technologies was available with cost data, and the range in costs may not therefore be representative of costs for all sites.

6.0 CONCLUSIONS

In conclusion, observations on technology performance can be made based on the modeling results and field case study data collection completed to date. Some of these are summarized below:

- **Reductions in Groundwater Concentrations:** None of the site characteristic or technology implementation parameters that were evaluated as part of the statistical analysis were found to have a statistical correlation with reductions in groundwater concentrations; however, there does appear to be a relationship between the amount of DNAPL mass removed from the subsurface during treatment and reduction in groundwater concentration. This relationship appears to be independent of treatment technology.
- **DNAPL Mass Removal:** Near complete mass removal has been achieved with all technologies with the exception of hydraulic displacement. In field studies, the highest DNAPL mass removal was observed in thermal treatment case studies (94% to 96%), and the median mass removed for anaerobic EISB, ISCO, SEAR, and co-solvent flushing ranged from 64% to 81%. If modeling cases are included, for each technology the range of percent DNAPL mass removal increases, but the median value decreases. This is likely due to the fact that treatment duration during the modeling was varied to evaluate sensitivity of remedial performance, rather than treatment being terminated as a result of achieving desired performance levels as is more typical for field applications.
- **Matrix Diffusion:** Modeling results demonstrated that in fractured rock environments, with an older DNAPL release, matrix diffusion (diffusion of DNAPL into lower permeability media) has a substantial influence on the distribution of DNAPL mass. If degradation of DNAPL within the lower permeability matrix is limited, back-diffusion of contaminant mass out of the matrix will sustain groundwater concentrations for long periods of time.
- **DNAPL Properties:** The solubility of the DNAPL was observed to influence the resulting net benefit of implementing more aggressive DNAPL treatment technologies over other approaches, primarily on dissolution of the DNAPL as the DNAPL mass reduction mechanism. For more soluble DNAPLs such as TCE, dissolution of the DNAPL is a significant component of the DNAPL mass removal, and incorporating other degradation or mass removal mechanisms (e.g., oxidation, biodegradation, enhanced dissolution) may only result in relatively small incremental increases in DNAPL mass removal.
- **Precipitate Formation:** Through the modeling sensitivity analysis, it was observed that the formation of a manganese dioxide rind (resulting in encapsulation of DNAPL pools and flow bypassing around DNAPL areas) significantly increased the time required to remove TCE DNAPL in ISCO applications using permanganate as the oxidant. This evaluation is specific to permanganate treatment and the corresponding manganese dioxide rind formation; however, it is anticipated that similar results may be observed with other technologies that result in the formation of a precipitate or result in

permeability reductions. The influence of the precipitate formation on DNAPL treatment is anticipated to be particularly pronounced where the precipitate forms within close proximity of the DNAPL phase, as occurs when permanganate reacts with the DNAPL.

DNAPL TEST has been designed to be updated in the future to reflect new data. As new field, laboratory, or modeling case studies become available, they can be added to the database. When sufficient new case studies have been added, the statistical analysis can be conducted again to refine statistical relationships.

The costs to operate DNAPL Test are very low. The tool is available for free download at <http://projects.geosyntec.com/DNAPL/dnapltest.aspx> and from the NAVFAC ESC website at <https://portal.navy.mil/go/erb>. The tool will also be available from the ESTCP website in the near future. The time required to run an analysis on the tool is approximately 10-20 minutes.

Given the limitations of the information incorporated into DNAPL TEST, this tool is most effectively used as a preliminary screening for technology selection or as a screening for possible performance limitations for a remedy in place. It cannot replace appropriate site-specific evaluations based on engineering judgment.

Specific applications of the screening tool could include the following:

- Assessment of a realistic level of performance for a particular remedial technology given specific site conditions
- Comparison of potential remedial performance between various technologies for specific site conditions
- Comparison of potential remedial performance of a particular technology in different geological strata at a complex site
- Performance of sensitivity analyses on key site parameters to optimize remedial performance.

DNAPL TEST cannot “predict” technology performance for a particular site but will provide the user with an anticipated range of performance and the ability to compare performance observed for multiple technologies. This information can be used as the basis for developing realistic remedial end goals, as well as for developing a short list of potential technologies for a site.

For users interested in obtaining potential technology performance information for a specific site, a Site Specific Analysis will better focus the screening evaluation to include sites anticipated to have similar performance. Multiple Site Specific Analyses may be completed for the same site to focus on different areas with different site characteristics. It should be noted that the Site Specific Analysis does require a minimum level of knowledge of conditions at the user’s site, which may limit its usefulness for some sites. Guidance for estimating these parameters is provided within the tool.

For more general analyses of overall performance trends between parameters and for sites at which key site parameters are unquantified, the General Analysis will be a better option. Modifications to search parameters can easily be changed at any time during the screening process, allowing users to refine their analyses to better meet their needs. Specific examples illustrating a General and a Site Specific Analysis are provided in the User's Manual, which is accessible at <http://projects.geosyntec.com/DNAPL/>, to better illustrate how the tool can be effectively used to meet the user's goals.

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7.0 REFERENCES

- Adamson, D.T., and C.J. Newell. 2009. Support of Source Zone Bioremediation through Endogenous Biomass Decay and Electron Donor Recycling, *Bioremediation Journal*, 13(1): 29-40.
- Adamson, D.T., T.M. McGuire, C.J. Newell, and H. Stroo. 2011. Sustained treatment: Implications for treatment timescales associated with source-depletion technologies, *Remediation Journal*, 20(2): 27-50.
- Conrad, S.H., R.J. Glass, and W.J. Peplinski. 2002. Bench-scale visualization of DNAPL remediation processes in analog heterogeneous aquifers: surfactant floods and in situ oxidation using permanganate, *Journal of Contaminant Hydrology*, 58: 13– 49.
- Goldstein, K.J., A.R. Vitolins, D. Navon, B.L. Parker, S. Chapman, and G.A. Anderson. 2004. Characterization and pilot-scale studies for chemical oxidation remediation of fractured shale. *Remediation*, no. 14: 19-37.
- McGuire, T.M., J.M. McDade, and C.J. Newell. 2006. Performance of DNAPL Source Depletion Technologies at 59 Chlorinated Solvent-Impacted Sites. *Groundwater Monitoring and Remediation*, 26: 73-84.
- West, M.R., G.P. Grant, J.I. Gerhard, and B.H. Kueper. 2008. The influence of precipitate formation on the chemical oxidation of TCE DNAPL with potassium permanganate, *Advances in Water Resources*, 31 (2): 324-338.

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APPENDIX A
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