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(ER-200833)



Improved Field Evaluation of NAPL Dissolution and Source Longevity

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ACRONYMS AND ABBREVIATIONS

AFCEE	U.S. Air Force Center for Engineering and the Environment
bgs	below ground surface
BTEX	benzene, toluene, ethylbenzene, and xylenes
COC	chemical of concern
DNAPL	dense non-aqueous phase liquid
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
GC	gas chromatograph
GMS	Groundwater Modeling System
IPT	integral pumping test
K^{NAPL}	NAPL mass transfer coefficient
LNAPL	light non-aqueous phase liquid
LPZ	Low Permeability Zone
LSZ	Lower Saturated Zone
MCL	maximum contaminant level
MNA	monitored natural attenuation
MTT	mass transfer test
NAPL	non-aqueous phase liquid
PFM	Passive Flux Meter TM
QA/QC	quality assurance/quality control
RAO	remedial action objective
SEAM3D	Sequential Electron Acceptor Model, 3D transport model
SZD	source zone depletion
TEE	thermally enhanced extraction
TOR	time of remediation
USEPA	U.S. Environmental Protection Agency
UST	underground storage tank
UWBZ	Upper Water Bearing Zone
WAFB	Williams Air Force Base

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1.0 EXECUTIVE SUMMARY

The Department of Defense (DoD) needs improved methods for estimating the mass of non-aqueous phase liquids (NAPLs) in subsurface environments contaminated from past releases. In addition, it is still a significant challenge to predict the time needed to achieve specified remedial action objectives (RAOs), with or without NAPL depletion. Credible data are required to support management decisions regarding when and to what intensity active remediation efforts should be pursued at these sites. The primary objective of this project was to evaluate a methodology to improve evaluations of the extent of source remediation required at both light non-aqueous phase liquids (LNAPL) and dense non-aqueous phase liquids (DNAPL) impacted sites.

Current techniques to estimate the persistence of NAPL sources are very uncertain without better specification of the mass of NAPL, the constituents of the NAPL, the NAPL “architecture” (i.e., the geometry of the NAPL distribution in the subsurface), and the dissolution rate of NAPL components in groundwater (referred to collectively in this report as the source zone depletion [SZD] function). The traditional approach to characterizing the SZD function involves estimating NAPL dissolution rates from concentration measurements in discrete locations in the downgradient plume multiplied by an estimated groundwater velocity. However, this approach yields only a snapshot estimate and is subject to large errors in estimating the groundwater velocity due to large spatial variation in aquifer properties. In addition, current interpretations of standard field data typically employ numerical models relying solely on a single estimate of the mass discharge rate from the source, without an estimate of the total source mass and with mass transfer rates estimated from empirical correlation functions.

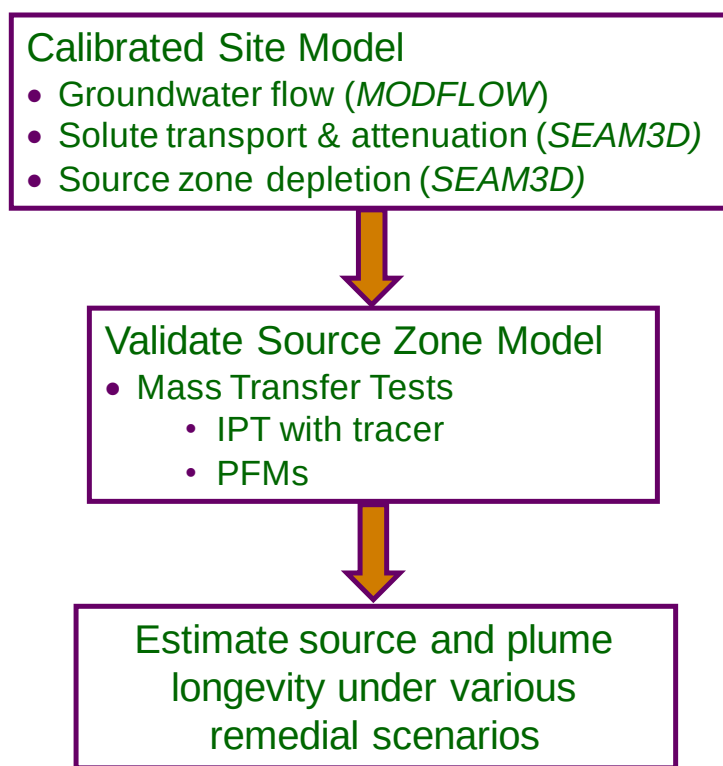
To address deficiencies in field measurements for assessing SZD functions, new approaches were field-tested at Site ST012 on the former Williams Air Force Base (WAFB, now known as Williams Gateway Airport), AZ. In 2001, the Air Force initiated a study to evaluate remedial strategies for NAPL contamination at Site ST012, including field tests and modeling. From 2008 through 2010, the Air Force conducted and evaluated a pilot test of thermally enhanced extraction (TEE) as a suitable technology for reducing the mass and longevity of a multicomponent fuel source (jet fuel) residing in the saturated zone. A rising water table (approximately 4 ft per year) over the last two decades created a submerged smear zone of fuel NAPL spanning a depth of about 75 ft and resulting in a long-term source to groundwater of a number of chemicals of concern (COCs), including benzene and naphthalene.

During the TEE pilot test, a suite of innovative diagnostic techniques were used to evaluate the benefits of partial NAPL source reduction. These techniques included:

- Passive Flux Meters™ (PFMs), which allow simultaneous measurements of groundwater flow velocity and contaminant mass trapped on sorptive resin during the time that the PFM is left in a monitoring well
- Integral pumping tests (IPTs), which measure the contaminant mass in groundwater extracted over time, often with varying extraction rates
- Modeling using the solute transport code Sequential Electron Acceptor Model, 3D transport model (SEAM3D) with an enhanced input SZD function.

Additionally, tracer tests were performed during the IPTs to characterize preferential and asymmetric groundwater flow paths.

The field measurements (IPT and PFMs) were performed both before and after the TEE pilot test within a portion of the NAPL source zone at ST012. The testing provided data related to NAPL architecture and rates of mass transfer from the NAPL to the aqueous phase. The tests measured mass transfer characteristics on length scales varying from a few feet (PFM data) to the 70 ft distance between injection and extraction wells (IPT data) within the TEE cell. Groundwater samples from multiple extraction and monitoring wells provided data on intermediate length scales. To our knowledge, the IPT and PFMs have not been combined previously to provide data for a mass transfer analysis with an appropriate model, with the intent of leveraging the advantage of each technique.



The field data are intended to provide input to a calibrated transport model. SEAM3D is an advective-dispersive numerical solute transport model that simulates the full range of natural attenuation processes in groundwater systems. SEAM3D also explicitly simulates the dissolution of a NAPL source zone based on fundamental mass transfer analyses and a calibrated SZD function for purposes of scaling the results from the TEE test scale to the entire NAPL zone at the site.

The data collected on the various scales before and after the TEE pilot test were synthesized into a working quantitative model of the NAPL architecture and mass dissolution rate for the SEAM3D enhanced SZD function. This approach seeks to circumvent the reliance (or at least reduce the emphasis) on long-term source depletion data to calibrate the SZD function associated with a site solute transport model. The aim is to reduce the uncertainty associated with estimates

of source and plume longevity through the direct measurement of a bulk mass transfer coefficient, which is then used to produce more accurate modeling results of the estimated time of remediation (TOR) for the site. Because of the unique smear zone at Site ST012, the results are applicable to a broader class of sites than just those impacted with LNAPL, including those contaminated with DNAPLs.

Specific quantitative performance objectives for the methodology evaluated during this project focused on three topics:

1. Accurate simulation of the groundwater flow field through a heterogeneous source zone
2. Accurate predictions of the NAPL architecture and contaminant mass discharge in the source zone
3. Accurate simulation of the measured reductions in contaminant mass discharge, which can result from either a reduction in the total NAPL mass or a change in the NAPL composition.

These quantitative objectives were assessed primarily by comparing the SEAM3D numerical model results to the observed field data. In addition, two qualitative performance objectives were evaluated—(1) the ease of implementing the field test procedures and (2) the cost to perform the test.

The success criteria for both the quantitative and qualitative performance objectives were achieved, except at three monitoring locations for the third quantitative performance objective. This variance was the result of uneven thermal treatment across the cell, which was not captured by the modeling assumption of uniform NAPL composition across the cell. Although the solute transport model (SEAM3D) can account for variability in NAPL residual saturation in space, this level of sophistication was not specified in the Demonstration Plan for this project.

The mass transfer tests (MTTs) and associated modeling were able to measure the bulk mass transfer coefficient directly and to relate the absolute source mass to the mass discharge. The methodology resulted in a more accurate SZD function, allowing a more credible prediction of the source longevity and the impacts of partial source reduction. The benefits of using such a methodology include reduced uncertainty, as well as a credible basis for establishing remedial objectives and defining the metrics for source treatment.

The costs of the methodology depend on the existing infrastructure. The costs represent a small increment of the remediation costs if a pump-and-treat system is active at a facility and monitoring wells exist within the source area, or if the installation of such a system is anticipated as part of the site remediation. However, it may represent considerable additional cost at sites where the needed infrastructure for the field testing must be installed. This methodology can be applied at sites with LNAPL or DNAPL and can significantly improve the quality of management decisions.

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2.0 INTRODUCTION

2.1 BACKGROUND

DoD needs improved methods for estimating the mass of NAPLs in subsurface environments contaminated from past releases of these compounds. In addition, predicting their persistence into the future and the impact of NAPL source reduction on the time to achieve RAOs at compliance locations remains a significant challenge at these sites. Data are required to support scientifically defensible decisions regarding when and to what intensity active remediation efforts should be pursued at NAPL-contaminated sites before transition to passive remedies such as natural attenuation. The primary objective of this project was to evaluate a methodology to improve decision making on the extent of source remediation required to meet RAOs at both LNAPL and DNAPL impacted sites.

Current techniques to estimate the persistence of NAPL sources are very uncertain without better specification of the mass of NAPL, the constituents of the NAPL, the NAPL “architecture” (i.e., the geometry of the NAPL distribution in the subsurface), and the dissolution rate of NAPL components in groundwater (referred to collectively in this report as the SZD function). The traditional approach to characterizing the SZD function involves estimation of NAPL dissolution rates from concentration measurements in discrete locations in the downgradient plume multiplied by an estimated groundwater velocity calculated from site-specific data.

However, this approach yields only a snapshot estimate and is subject to large errors in estimating the groundwater velocity due to large spatial variation in aquifer properties. In addition, the measurements of downgradient groundwater concentrations and velocities are generally insufficient to differentiate source mass discharge from changes due to biological or chemical degradation occurring in the plume downgradient from the source zone. Further, current interpretations of standard field data typically employ numerical models with the simple input of a contaminant mass discharge rate from the NAPL source zone without an estimate of the total source mass and with mass transfer rates estimated from empirical correlation functions.

To address deficiencies in field measurements for assessing SZD functions, new approaches were field-tested at Site ST012 on the former WAFB. In 2001, the Air Force initiated a study to evaluate remedial strategies for NAPL contamination at Site ST012, including field tests and modeling. From 2008 through 2010, the Air Force conducted and evaluated a pilot test of TEE as a suitable technology for reducing the mass and longevity of a multi-component fuel source (jet fuel) residing in the saturated zone. A rising water table (approximately 4 ft per year) over the last two decades created a submerged smear zone of fuel NAPL (chemicals present in the NAPL include benzene, toluene, ethylbenzene, and xylenes [BTEX] and naphthalene), spanning a depth of about 75 ft and resulting in a long-term source to groundwater of a number of COCs, including benzene, naphthalene, and other constituents of fuel NAPL.

The Air Force independently pursued an innovative combination of newly developed diagnostic techniques to conduct an evaluation of the benefits of partial NAPL source reduction. These included PFMs, IPTs, and modeling using the solute transport code SEAM3D with an enhanced input SZD function. SEAM3D is an advective-dispersive numerical solute transport model that simulates the full range of natural attenuation processes (biodegradation, sorption, dilution and

dispersion, volatilization, and diminishing source mass discharge) in groundwater systems. SEAM3D also explicitly simulates the dissolution of a NAPL source zone based on fundamental mass transfer analyses and a calibrated SZD function for purposes of scaling the results from the TEE test scale to the entire NAPL zone at the site. Additionally, tracer tests were performed during the IPTs to characterize preferential and asymmetric groundwater flow paths.

The field measurements (IPT and PFMs) were performed both before and after the TEE pilot test within a portion of the NAPL source zone at ST012. The testing provided data related to NAPL architecture and rates of mass transfer from the NAPL to the aqueous phase. The tests measured mass transfer characteristics on length scales varying from a few ft (PFM data) to the 70-ft distance between injection and extraction wells (IPT data) within the TEE cell. Groundwater samples from multiple extraction and monitoring wells provided data on intermediate length scales. The data collected on the various scales before and after the TEE pilot test were synthesized into a working quantitative model of the NAPL architecture and mass dissolution rate for the SEAM3D enhanced SZD function.

Multi-scale field measurements during the IPT are collectively referred to as the “MTT.” The IPT was performed by injecting clean water in the center of the test cell and extracting groundwater from six extraction wells located on a circular periphery, although other injection-extraction configurations were possible (e.g., a single dipole with intermediate monitoring wells). The concentration of a dissolved compound increased as the water traveled through the NAPL-bearing soils to the extraction wells, controlled by the component’s equilibrium solubility in water and the local mass transfer. The combined mass removal rate at the extraction wells defined a bulk mass transfer coefficient for the soil volume flushed with clean water.

Groundwater flow was assessed by injecting a bromide tracer pulse in the center well and by observing breakthrough curves at each of the monitoring wells. Tracer arrival times in monitoring wells corresponded to flow velocities at specific depths and, when compared to the known mean groundwater velocity, provided indications of preferential and asymmetric flow. PFMs were deployed in the monitoring wells to further assess the rates of mass transfer. The PFMs provided data on the vertical distribution of contaminant and groundwater fluxes within the monitoring wells. Flux is defined as the mass of groundwater or contaminant passing through a given cross-sectional area per unit time. The mass discharge (in units of mass per time) can be calculated from flux measurements by integration of the mass flux values over the cross-sectional area of interest. Data collected during the pre- and post-TEE MTTs were interpreted using SEAM3D.

The flow chart shown in Figure 1 outlines the general procedure for the methodology in which results of an MTT are integrated into a numerical modeling framework to calculate the TOR under various remedial scenarios. This approach seeks to circumvent the reliance (or at least reduce emphasis) on long-term source depletion data to calibrate the SZD function associated with a site solute transport model. The aim is to reduce the uncertainty associated with estimates of source and plume longevity through the direct measurement of a bulk mass transfer coefficient, which is then used to produce more accurate modeling results of the TOR.

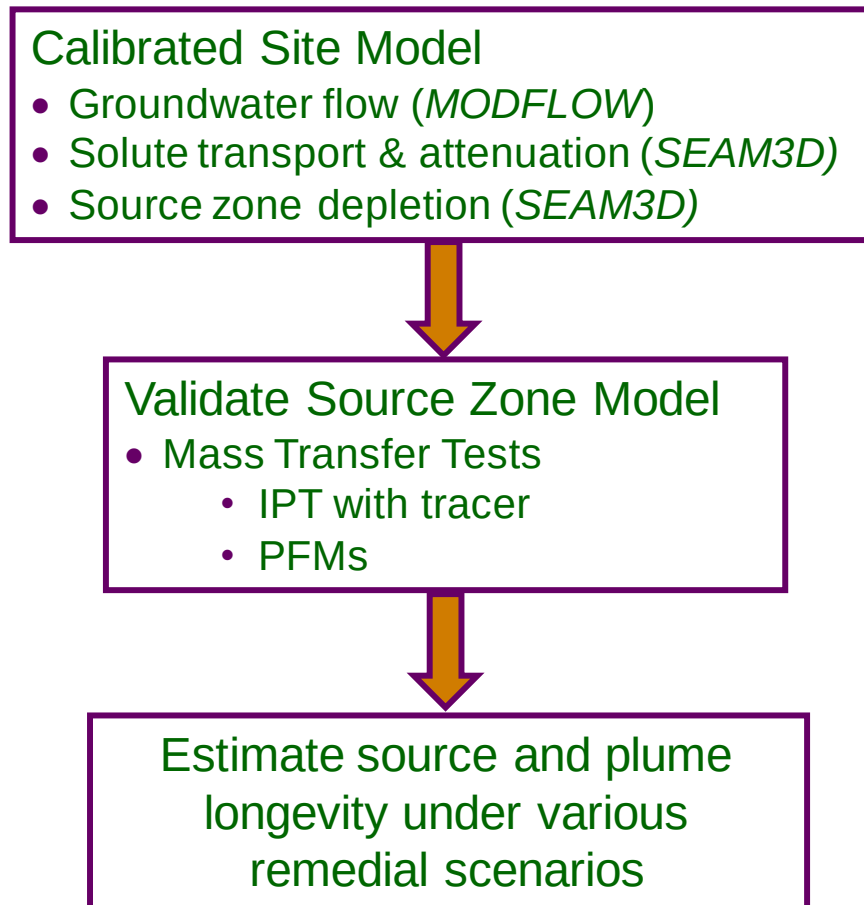


Figure 1. Flow chart outlining the methodology of combining mass transfer testing and source zone remediation with the SEAM3D site model to reduce uncertainty associated with the SZD function and its use in long-term simulations to estimate TOR.

To our knowledge, the IPT and PFMs have not been combined previously to provide data for a mass transfer analysis with an appropriate model, with the intent of leveraging the advantage of each technique. Because of the unique smear zone at Site ST012, the results are applicable to a broader class of sites than just those impacted with LNAPL, including those contaminated with DNAPLs.

2.2 OBJECTIVES OF DEMONSTRATION

The Air Force intended to generate data that could be used for decision making based on improved characterization of the NAPL contamination at ST012 through the analysis of the pre- and post-TEE MTTs. The MTTs and TEE pilot test were performed by the Air Force's contractor, BEM Systems, Inc. The primary ESTCP activities were in support of the post-TEE MTT and development and evaluation of the proposed methodology for application to other NAPL impacted sites.

The performance objectives are described in Section 5.0. All performance objectives were met during the demonstration with the exception of one objective at some monitoring locations. The explanation for this variance is presented in Section 7.3.

2.3 REGULATORY DRIVERS

Aqueous solubilities of common NAPL constituents found at DoD facilities often greatly exceed drinking water standards, including federal maximum contaminant levels (MCLs). Mass dissolution of fuel components from NAPL can result in concentrations at locations near the source zone persistently above the MCLs for hundreds of years if left untreated.

3.0 SITE DESCRIPTION

3.1 SITE LOCATION

Throughout its history, pilot training was the primary mission of WAFB. A wide variety and large number of aircraft were based at WAFB, including prop-driven and jet aircraft. Within WAFB, Site ST012 is the location of the former liquid fuels storage area, which encompasses approximately 13 acres within WAFB (Figure 2). Fueling operations were conducted at the base from 1941 until 1991.



Figure 2. Location of the former Williams AFB and Site ST012.

A substantial portion of the remaining cleanup at WAFB addresses fuel releases at ST012. Soil and groundwater at ST012 have been affected by releases of JP-4 and avgas. These releases are attributable to multiple documented fuel releases between 1977 and 1989 and other undocumented releases during base operations over a 50-year period. All underground storage tanks (USTs) and the associated fuel distribution lines were removed from ST012 in early 1991.

3.2 SITE GEOLOGY/HYDROGEOLOGY

The site vertical profile (0 – 245 ft below ground surface [bgs]) is a heterogeneous mix of alternating fine-grained and coarse-grained units. Coarse-grained units range in thickness from less than 1 ft to more than 20 ft, and a few of the larger units appear to be continuous across the site. The geologic materials in the saturated zone have been subdivided into four main hydrostratigraphic units:

- The Upper Water Bearing Zone (UWBZ), extending vertically from the water table (currently at approximately 160 ft bgs) to 195 ft bgs
- The Low Permeability Zone (LPZ), extending from approximately 195 ft to 210 ft bgs
- The Lower Saturated Zone (LSZ), extending from approximately 210 ft to 240 ft bgs
- The Aquitard, occurring at approximately 240 ft bgs.

The LPZ effectively separates the deeper LSZ from the shallower UWBZ with respect to remediation. Pumping tests have shown the two zones act independently on the timescale of remediation. As a result of this independence, the MTT described previously was applied in each zone.

The water table beneath ST012 has been rising at an average rate of about 3.4 ft per year for the last two decades and is expected to continue to do so for some period of time, with the potential for further degradation of groundwater from fuel constituents currently in the vadose zone. In the 1960s and early 1970s, regional groundwater levels declined due to extensive withdrawal and to diversion or retention of major sources of groundwater recharge for flood control (BEM Systems, 2010). During the fuel releases at Site ST012, the estimated low level for the water table was 232 ft bgs. Water level data for wells located on and near the former WAFB show groundwater levels have been rising steadily since about 1978. Groundwater within the LSZ, once apparently unconfined, now appears to be under semi-confined conditions.

3.3 CONTAMINANT DISTRIBUTION

Select results of previous site investigations are presented in Appendix C to the Final Report for this ESTCP demonstration (ESTCP, Improved Field Evaluation of NAPL Dissolution and Source Longevity, Final Report).

Fuel contamination, including mobile and immobile NAPL present in the saturated zone, serves as a continuing source for dissolved-phase groundwater contamination. The total mass and distribution of NAPL in the saturated zone is not known; however, field evidence suggests NAPL is smeared across all but the lower 10 to 15 ft of the LSZ (as a result of initial fuel infiltration and the subsequent rising water table from an estimated low of 232 ft bgs). NAPL may be preferentially present trapped in the upper portions of coarse-grained layers underlying fine-grained layers or within fine-grained layers, particularly near interfaces with coarse-grained layers.

The TEE pilot test was designed to address groundwater impacted by smeared fuel contamination in the saturated zone, consisting of the UWBZ, LPZ, and LSZ. The TEE test cell was located within the lateral footprint known to be contaminated with smeared NAPL.

The UWBZ was spanned by a single screen in each of the monitoring wells from about 170 to 195 ft bgs. These wells are referred to as the “A-horizon” wells. The LSZ was divided into two subunits with separate monitoring well screens for each. The fine-grained soils are found in the upper two-thirds of the LSZ (referred to as the “B-horizon”) and were monitored with screens that extended from about 205 to 220 ft bgs. The dominant coarse interval found at bottom of the LSZ was referred to as the “C-horizon.” C-horizon screens were located from about 230 ft to 245 ft bgs, extending into the underlying Aquitard. The C-horizon was found to contain very little residual NAPL as compared to the A- and B-horizons; however, this interval is the most transmissive. Figures in Appendix C to the Final Report illustrate the placement of the TEE test cell within the historic boundaries of detected NAPL and the interpreted plume of dissolved benzene in the C-, B-, and A-horizons.

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4.0 TECHNOLOGY

As described in Section 1.0, the Air Force has independently pursued development of an MTT to provide parameters that define the SZD function quantitatively at Site ST012 in sufficient detail to reduce the uncertainty in site-specific estimates of the TOR and subsequent remedial decisions on the extent of NAPL source depletion required to meet a TOR goal. The measurements were performed both before and after a pilot test of TEE within a portion of the source area at ST012, providing a measured mass removed and the resulting change in the mass discharge rate. Typically, IPTs and PFMs are applied downgradient from a NAPL zone, but this novel application within the source zone was intended to define the SZD term in greater detail.

4.1 TECHNOLOGY DESCRIPTION

The MTT within the source zone sought to generate data suitable for estimating NAPL mass and describing the source zone function for alternative NAPL architectures (e.g., ganglia versus pooled distribution of NAPL) in the source zone. For such estimates, mass transfer coefficients specific to the NAPL architecture must be determined. The Final Report describes the individual elements of the MTT, the unique characterization of NAPL obtained from the approach, and the calibration of the SZD function using the model SEAM3D. The MTT is briefly summarized in this section.

The MTT: Integral Pumping Test with PFMs Deployed in the Source Zone

At Site ST012, IPTs were implemented in the portion of the source zone where the TEE pilot test was performed and included tracer testing and PFM deployment. The IPT was performed by injecting clean water in the center of the test cell and extracting on the periphery through six extraction wells. A pulse of bromide tracer was introduced to assess the flow velocities. PFMs were installed in 12 monitoring wells within the test cell after the flows and concentrations had stabilized in response to the steady central water injection. The MTTs were performed both before and after the TEE pilot test, although conditions were not identical between the two MTTs.

The conceptual cross-section of the MTT illustrated in Figure 3 shows clean water traveling through soil containing residual NAPL with extraction at the periphery of the NAPL contamination. As the water travels through the NAPL zone, contaminants are dissolved into the flowing water according to groundwater flow paths, the architecture of the residual NAPL, and the rate of mass transfer. Measurements of the groundwater flow rate and concentrations at extraction after a complete pore volume sweep yield a pseudo-steady state mass dissolution rate for this imposed flow condition. If the imposed flow rate is low, the water may become saturated with dissolved contaminant yielding no information on the rates of mass transfer beyond such saturation. This condition is labeled “Low Flow” in Figure 3. A higher flow that does not become saturated is also illustrated in Figure 3 and labeled “Desired Flow.” Concentrations measured in intermediate monitoring well screens provide mass dissolution rates for horizontal subsets of the soil volume. Arrays of PFMs deployed in the monitoring wells can further segregate and refine the concentration and flow data vertically. An advantage of the PFMs for this application over other vertically discrete sampling devices is the additional capability to

measure groundwater fluxes allowing contaminant mass fluxes, not just concentrations, to be measured as a function of depth.

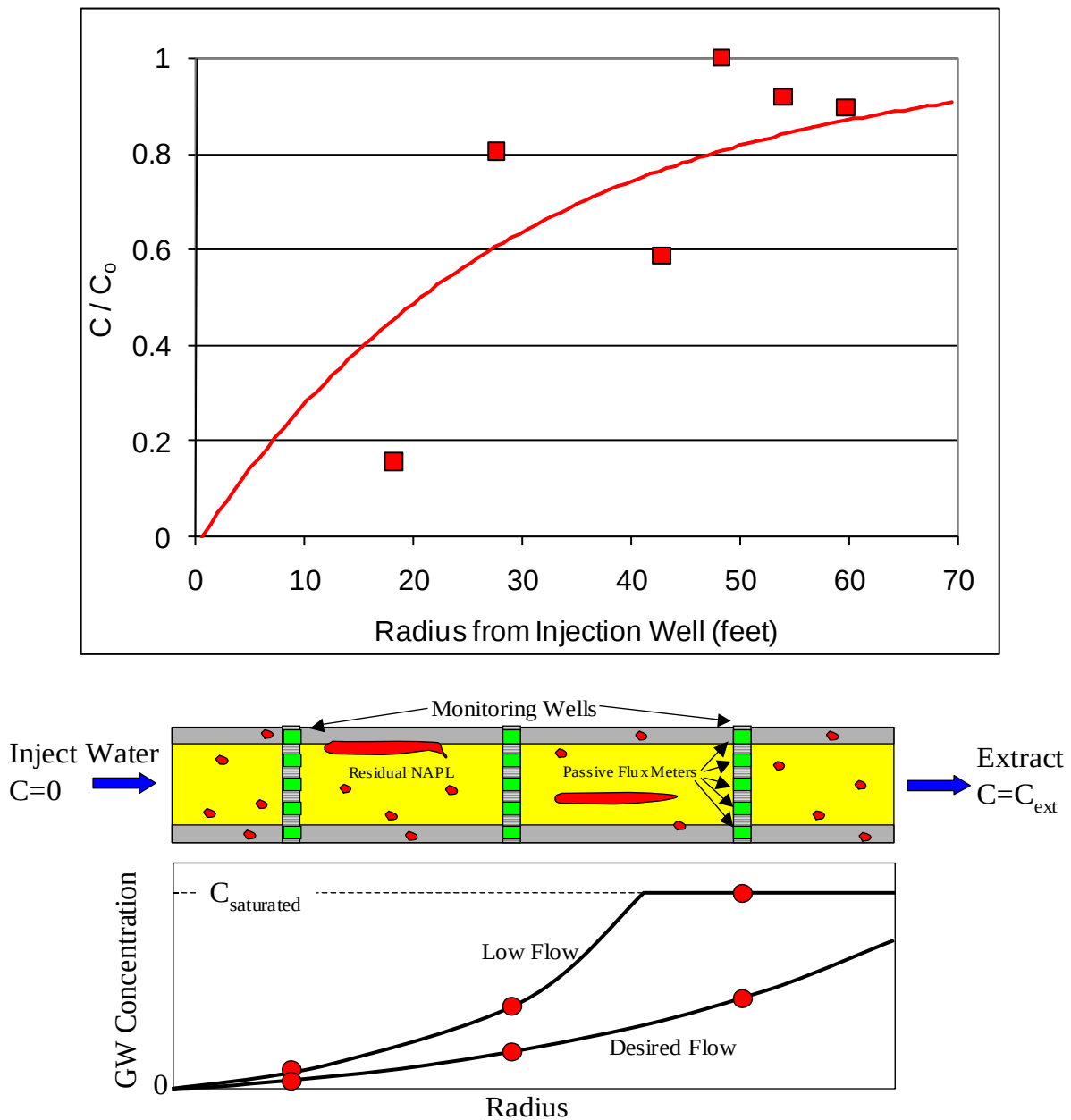


Figure 3. Conceptual application of IPT and PFMs.

Circles represent concentration measurements in groundwater samples from monitoring wells along the groundwater flow path.

The MTT provides dynamic data more suitable to transient SZD function evaluation than the traditional approach of monitoring relatively static groundwater concentrations downgradient of a source coupled with water level-derived estimates of groundwater velocity. The combined application of the IPT and PFMs in the source zone during the MTT has significant potential to improve the accuracy of estimates of vertical and horizontal NAPL distribution and mass discharge from a defined source zone.

4.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

Detailed listings of the advantages and limitations of IPTs, PFMs, and SEAM3D are provided in the Final Report.

The overall methodology developed herein is an innovative combination of field measurements on various scale lengths including PFMs and IPTs with a bromide tracer (the MTT), and modeling using SEAM3D with an enhanced input SZD function. Primary advantages of the overall methodology are:

- It provides a robust and defensible testing and model for evaluating multiple scenarios of various magnitudes of source zone reduction (i.e., partial source depletion) and the impact on plume longevity in support of decision making with respect to meeting site-specific RAOs.
- This methodology represents a novel approach for estimating and constraining model input parameters that result in more accurate predictions of source depletion and plume longevity. Typically, the source term for site models is calibrated to historical data sets without any direct measurement of source parameters (e.g., field-scale mass transfer coefficient). Through application of the source zone model to data generated through the MTTs, uncertainty in estimating the TOR (i.e., time to reach compliance) can be significantly reduced.

Another advantage of the overall technology is cost savings through leveraging site assets and completed modeling studies. Specifically, existing site infrastructure (pumping/injection and monitoring wells) may be adapted and utilized for MTTs. Well-documented site models for groundwater flow and solute transport may serve as a starting point for implementing SEAM3D and updating the site model for estimates of the TOR for a range of points of compliance.

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5.0 PERFORMANCE OBJECTIVES

Specific quantitative performance objectives for the methodology evaluated during this project were related to three topics:

- Groundwater flow field through a heterogeneous source zone.
- NAPL architecture and contaminant mass discharge in the source zone.
- Reduction in contaminant mass discharge resulting from a reduction in NAPL mass or a change in NAPL composition.

These quantitative objectives were assessed primarily by comparing the SEAM3D numerical model results to the observed field data. Two qualitative performance objectives were evaluated: the ease of implementing the field test procedures and the cost to perform the test.

The performance objectives, their data requirements and success criteria, and the overall evaluation of the results are summarized in Table 1 and discussed in greater detail in Section 7.0.

Table 1. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Estimate of source zone hydrogeologic parameters	<u>Pre- and post-TEE data:</u> Monitoring well data in the TEE cell: ▪ Bromide tracer histories ▪ PFM alcohol depletion results ▪ Water levels Injection rate of water and extraction rate of groundwater in the TEE cell	Average PFM velocity within a factor of two of average velocity based on injection rate Arrival times of tracer peaks at monitoring wells within a factor of two of estimates based on PFM velocity measurements	The success criteria were achieved for both tracer and PFM data at all monitored locations. With increasing distance from the injection well, the match with tracer data eroded as a result of bromide sensor limitations, the influence of unsteady pumping from perimeter extraction wells, and, possibly, heterogeneity not captured in the geologic model.
Estimate of source zone contaminant parameters	<u>Pre- and post-TEE data:</u> MTT data in the TEE cell: ▪ Hydrocarbon concentrations at monitoring wells ▪ PFM mass flux results Dissolved phase concentration data from monitoring wells in the TEE cell and near source	Pre-TEE test: Range of results for NAPL mass within range of pre-TEE estimates derived from independent measures Post-TEE test: Mean error between observed equilibrium source zone concentrations and simulated concentrations using SEAM3D within one order of magnitude	The pre-TEE criterion was successfully achieved. The model also accurately captured transient and steady-state concentration responses of both BTEX following injection of clean water during the pre-TEE MTT. The post-TEE success criterion was met, even with variable treatment and variable NAPL composition across the test cell.

Table 1. Performance objectives. (continued)

Performance Objective	Data Requirements	Success Criteria	Results
Estimate of reduction in contaminant mass discharge as a result of partial source reduction	<u>Pre- and post-TEE data:</u> MTT data in the TEE cell: ▪ Hydrocarbon concentrations at extraction and monitoring wells ▪ PFM mass flux and water velocity results ▪ Injection and extraction rates in the TEE cell ▪ Mass of contaminants extracted <u>TEE Pilot Test Data:</u> ▪ Mass of contaminants extracted during pilot test	Correlation of change in mass discharge rate between pre- and post-TEE MTTs to the measured mass removed Mean error between observed equilibrium source zone mass discharge at extraction wells and that simulated with SEAM3D within one order of magnitude	The post-TEE modeling of benzene concentrations and mass discharges matched nearly exactly the observed mass removed from the test cell during the TEE pilot test. The mean error between the observed equilibrium source zone mass discharge and that simulated with SEAM3D was well within one order of magnitude in the two wells closest to the injection well. The objective was achieved in the deep interval of other wells, but the error exceeded one order of magnitude in the shallow screens of the three monitoring wells closest to extraction wells. The exceedances resulted from variable thermal treatment across the cell, which was not captured by the modeling assumption of uniform NAPL composition across the cell.
Qualitative Performance Objectives			
Ease of simultaneous implementation of an IPT and PFMs	<u>Pre- and post-TEE data:</u> Monitoring well data in the TEE cell: ▪ Bromide tracer histories ▪ Hydrocarbon concentrations in monitoring wells Injection rate of water and extraction rate of groundwater in the TEE cell.	Ease in determination of the optimal timing and duration of PFM deployment within the IPT	This performance objective was successfully met as PFMs were not deployed until equilibrium concentrations were observed in the TEE cell. Possible skewing of PFM results by NAPL floating in the wells was mitigated by well purging and a PFM “swipe” test.
Incremental costs of IPT and PFM deployment	Operational cost data	Segregation of PFM and IPT incremental costs above those of ongoing operations	PFM and IPT costs were readily segregated from other costs with an existing pump-and-treat system in place. Costs to install a temporary pump-and-treat system are contingent on site-specific conditions such as depth to water, contaminant, concentrations, discharge requirements, and required pumping rates.

The success criteria for both the quantitative and qualitative performance objectives were achieved, except at three monitoring locations for the third performance objective. This variance was the result of uneven thermal treatment across the cell, which was not captured by the modeling assumption of uniform NAPL composition across the cell. Although the SEAM3D can account for variability in NAPL residual saturation in space, this level of sophistication was not specified in the Demonstration Plan for this project.

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6.0 TEST DESIGN

At ST012, the innovative MTT and data analyses described in Section 4.0 were applied before and after the application of the TEE technology in the pilot test cell. In addition, as described in this section, the MTT was performed in two intervals of the saturated zone, UWBZ and the LSZ, within the test cell.

The primary purpose of the pre-TEE MTT in the saturated zone was to determine the rate of dissolution (i.e., mass loading) of hydrocarbon constituents from residual NAPL to water flowing through the pilot test area under known conditions. These measurements were interpreted to assess the individual NAPL constituent mass loading to groundwater under natural flow conditions and used as input for solute transport modeling. The MTT was repeated after the TEE pilot test to provide data for the fate and transport modeling to calculate the reduced mass loading of COCs to groundwater in the source area of ST012 after a measured mass of contaminants was extracted (i.e., partial source reduction). These data, along with other TEE pilot test performance data, allowed forecasts of the mass loading of COCs to groundwater in the source area of ST012 resulting from various scenarios of TEE implementation.

With the data from these applications of the MTT at ST012, the procedure was evaluated for application to other NAPL sites. This section provides the details of the field measurements and data analyses. Details on the TEE pilot test and the design and construction of the TEE treatment system can be found in the TEE Pilot Test Work Plan (BEM Systems, 2007).

The layouts of injection wells, extraction wells, and monitoring wells used in the MTTs and the TEE pilot test at ST012 in the LSZ and UWBZ are depicted in Figure 4 and Figure 5, respectively. The test cell was located within a portion of ST012 where substantial accumulation of NAPLs was known to exist. This location provided a suitable setting for evaluation of the effectiveness of TEE to treat source areas, and the configuration of wells afforded the opportunity to test the technology for assessing the NAPL architecture and mass transfer characteristics. TEE was expected to have varying degrees of effectiveness in removing individual components of the NAPL as a result of their varying chemical properties. BTEX compounds were expected to be highly amenable to treatment via TEE because of their relatively high vapor pressures and high aqueous solubility. Naphthalene is less volatile and was expected to undergo a lesser degree of removal from the NAPL in response to TEE. However, naphthalene has a very high aqueous solubility compared to other semivolatile fuel components, and its solubility increases markedly with temperature. Also, during the TEE pilot test, more soil treatment and higher temperatures occurred near the steam injection wells, and less treatment and lower temperatures were observed with increasing distance from the central steam injection wells (LSZ-07 and UWBZ-07 in Figure 4 and Figure 5, respectively).

The testing was conducted within a single treatment cell having a diameter of about 140 ft and across the two vertical zones represented by the LSZ and UWBZ. Each zone contained a central injection well surrounded by six perimeter extraction wells screened across the full depth of the zone in the treatment cell. The test cell also contained six monitoring well nests (three screens) within the cell interior.

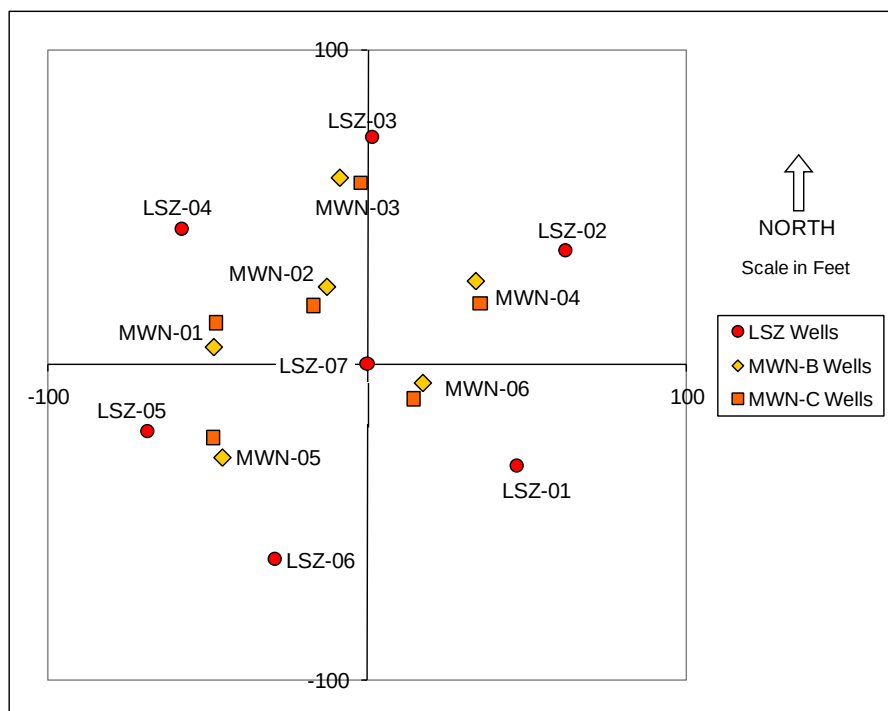


Figure 4. Layout of central injection (LSZ-07), peripheral extraction (LSZ wells), and monitoring wells (MWN wells) in the LSZ.

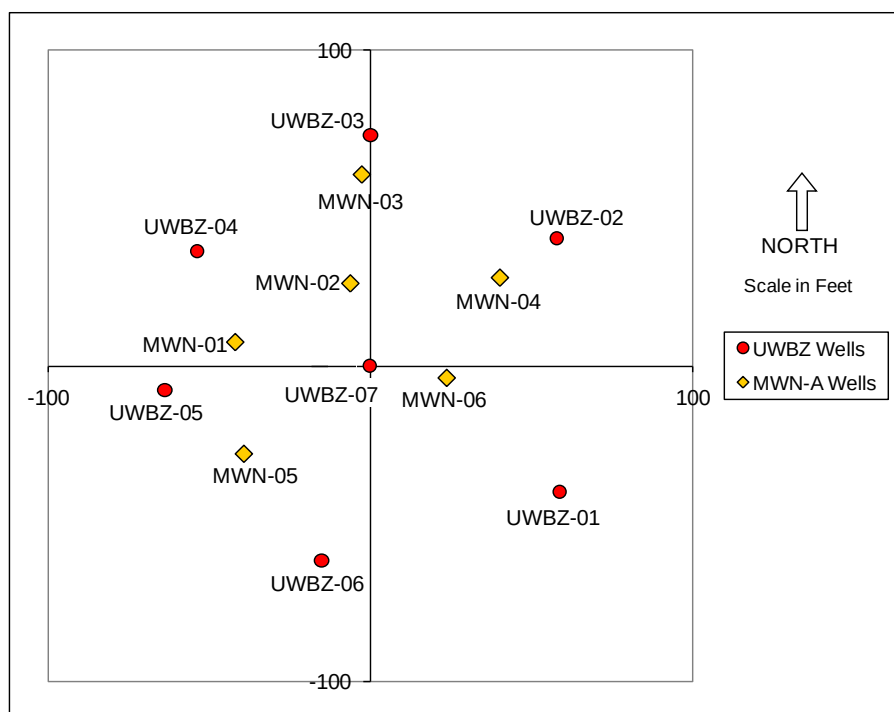


Figure 5. Layout of central injection (UWBZ-07), peripheral extraction (UWBZ wells), and monitoring wells (MWN wells) in the UWBZ.

The interior monitoring wells provided groundwater and vapor samples for assessing the performance of the pilot test, tracer and contaminant concentration data for the IPT, and locations for deployment of the PFMs. The monitoring wells in the LSZ included six screens in the C-horizon and six screens in the B-horizon, as shown in Figure 4. The UWBZ had six monitoring wells with single screens spanning the full depth of the A-horizon (i.e., UWBZ) as indicated on Figure 5. The approximate vertical interval for the testing spanned about 80 ft. For this depth interval, the target volume for the test cell was about 46,000 cubic yards.

The testing within each zone (LSZ and UWBZ) occurred in the following sequence both before and after the TEE pilot test:

1. Establish steady groundwater extraction in the six perimeter wells.
2. Establish steady central water injection.
3. Measure groundwater concentrations in monitoring wells and extraction wells throughout the MTT.
4. Introduce bromide tracer pulse in the water injection.
5. Measure bromide breakthrough curves at select monitoring well screens.
6. Deploy PFMs at select depths and in select monitoring well screens.
7. Retrieve PFMs.
8. Terminate MTT and proceed with other Air Force tasks.

A timeline summarizing the field activities in each zone is provided in Figure 6.

	2008					2009												2010	
Task	A	S	O	N	D	J	F	M	A	M	J	J	A	S	O	N	D	J	F
Baseline Sampling - Soil Sampling (2004) - Groundwater Sampling (2006)																			
LSZ Pre-TEE MTT - Tracer Test - PFM Deployment (B-horizon)																			
UWBZ Pre-TEE MTT - Tracer Test - PFM Deployment (A-horizon)																			
TEE Pilot Test																			
Post-TEE Cooling & Monitoring																			
LSZ Post-TEE MTT - Tracer Test - PFM Deployment (B-horizon)																			
UWBZ Post-TEE MTT - PFM Deployment (A-horizon)																			
Soil and Groundwater Sampling																			

Figure 6. Field testing time line.

Refer to Section 5.0 of the Final Report for a full description of baseline characterization activities, treatability study results, field testing, sampling methods, and sampling results.

7.0 PERFORMANCE ASSESSMENT

The methodology of the MTT was evaluated before and after the TEE pilot test at WAFB according to five quantitative and qualitative criteria. Table 1 presents a summary of each objective, data requirements, success criteria, and evaluation of success for each objective, and this section provides details supporting this summary. Though data were collected in both the UWBZ and LSZ during the MTTs, the quantitative performance objectives were evaluated using data only from the LSZ due to the intensity of the modeling efforts.

A numerical groundwater flow and solute transport model (see Appendix F to the Final Report) and an analytical model were used for assessing the quantitative performance objectives, beginning with estimates of source zone hydrogeologic and contaminant NAPL dissolution parameters. Although the complexity of ST012 required a comprehensive numerical model, at sites that are relatively homogeneous, an analytical model may be sufficient.

The success criteria for both the quantitative and qualitative performance objectives were achieved, except at three monitoring locations for the third performance objective. This variance was the result of uneven thermal treatment across the cell, which was not captured by the modeling assumption of uniform NAPL composition across the cell. Although the SEAM3D can account for variability in NAPL residual saturation in space, this level of sophistication was not specified in the Demonstration Plan for this project.

7.1 PERFORMANCE OBJECTIVE: ESTIMATE OF SOURCE ZONE HYDROGEOLOGIC PARAMETERS

This quantitative performance objective was to validate a method of measuring groundwater velocities through the source zone and interpreting these data to produce hydraulic conductivity estimates. Specifically, the PFM data included measurements of groundwater flux, which were to be used to generate vertical profiles of velocity variation. Assuming a uniform applied head, the velocity profiles were to be used to calculate soil hydraulic conductivity profiles. Analysis of the pre- and post-TEE MTTs, including tracer test results, was accomplished using local models implemented in the Groundwater Modeling System (GMS) platform using MODFLOW. Starting with a calibrated site model for ambient groundwater flow at ST012, the approach involved refining the existing model to simulate flow and transport only within the TEE cell and simulating the groundwater pumping and water injection during the MTTs, both pre-TEE and post-TEE.

Data requirements for this objective included stratigraphic data within the TEE cell such as boring logs of soil type, water levels in monitoring and extraction wells, transient concentration response of tracer at monitoring wells within the TEE cell, PFM results, and pre-TEE and post-TEE monitoring well data collected at source zone monitoring wells and wells located downgradient and adjacent to the TEE cell. Additional hydrogeologic input parameters were derived from readily available site reports and data collected in association with the TEE pilot test. MTT data included pumping and injection rates, water level data, injection tracer concentrations, and monitoring well tracer data. Results from the PFMs were to provide a secondary means of model calibration of NAPL parameters (NAPL mass, composition and mass transfer coefficient) and a more detailed delineation of vertical hydraulic conductivity variations.

A primary determinant of success for this objective was that the range of vertically discrete water velocities from PFM data was consistent with measured injection and extraction rates. Specifically, the average of the PFM groundwater velocity measurements should have been within a factor of two (i.e., +100% / -50%) of the average velocity based on a mass balance of the measured injection rate. A second independent measure was provided by the slug injection of a tracer mixed into the injected water. The arrival times of tracer peaks at monitoring wells should have been within a factor of two of time estimates based on PFM velocity measurements.

The success criterion was achieved at all monitored locations. For both the pre- and post-TEE tracer tests, the local SEAM3D model of the TEE cell captured breakthrough characteristics related to travel time and the rise to peak concentrations at monitoring wells closest to the injection well (wells 18 and 28 ft away). At both wells, the model matched the time of travel with a differential between the observed and simulated breakthrough time varying by no more than a factor of two. Differences in the time of travel may be a result of temporal variability in the withdrawal rates at the peripheral pumping wells in the TEE cell. At more distal monitoring wells, the tracer concentration decayed to levels close to the detection limit of the bromide sensor. As such, modeling results achieved a better match with the observed data at wells closer to the injection well relative to the more distant monitoring wells.

Vertical distributions of Darcy velocity derived from the PFMs in individual monitoring wells and simulated flow rates with depth calculated with the groundwater flow model compared favorably for all monitored wells. An excellent match was achieved in the wells closest to the injection well (18 and 28 ft from the injection well). However, the vertical location of the PFMs in some wells may have missed a thin layer of high permeability sand. Overall, the results provide a good match, particularly in the fine sand layers, and met the success criterion.

7.2 PERFORMANCE OBJECTIVE: ESTIMATE OF SOURCE ZONE CONTAMINANT PARAMETERS

This quantitative performance objective was to validate a method to determine source zone parameters applicable to prediction of NAPL mass discharge and source longevity under different remedial strategies related to the extent of source removal required. Starting with a calibrated local model of the TEE cell from the first objective, source zone parameters (i.e., input to the SEAM3D NAPL Package) were determined through calibration to the hydrocarbon concentrations at monitoring wells within the TEE cell and mass flux measurements based on PFM results. After simulating the pre-TEE MTT results, the process was repeated for the post-TEE test to evaluate mass removal, compositional changes, and post-remediation mass transfer rates following completion of the TEE pilot test.

Data requirements for this objective included hydrostratigraphic and compound-specific data within the TEE cell such as boring logs of soil type, transient responses of hydrocarbon concentrations at monitoring wells within the TEE cell, PFM results, and pre-TEE and post-TEE monitoring well data collected at source zone monitoring wells and wells located downgradient and adjacent to the TEE cell. Additional hydrogeologic input parameters were derived from readily available site reports and data collected in association with the TEE pilot test. MTT data included pumping and injection rates, water level data, injection concentrations, and monitoring well data (hydrocarbon concentrations). Results from the PFMs were to provide a secondary

means of model calibration. Historical pre-TEE monitoring well data collected at source zone monitoring wells and wells located downgradient and adjacent to the TEE cell (i.e., within the hydrocarbon plume) were also used. Post-TEE data were collected after concentrations stabilized and the site cooled to near ambient temperatures.

Previous estimates of the NAPL mass in the TEE cell were based on groundwater and soil hydrocarbon concentration data and NAPL thicknesses measured in wells. These values were updated during the TEE pilot test based on literature values and the observed mass removed during the TEE pilot test, and the initial mass estimate used in the SEAM3D modeling was based on these updated values. The pre-TEE model simulations were expected to accurately match the breakthrough and short-term equilibrium concentrations of benzene data at TEE cell monitoring wells.

The objective associated with the post-TEE test was considered successful if the equilibrium source zone concentrations and simulated concentrations using SEAM3D were within one order of magnitude. Similar to the pre-TEE success criteria, the analysis was deemed successful if the SEAM3D simulations matched the post-TEE benzene concentrations measured at TEE cell monitoring wells.

During the pre-TEE MTT, the local SEAM3D transport model accurately captured transient concentration responses of both benzene and TEX following injection of clean water and also the equilibrium concentrations during extended flushing. The model input variables that most directly controlled the equilibrium concentrations were the NAPL mass transfer coefficient (K^{NAPL}), NAPL saturation (i.e., NAPL mass) and the NAPL composition, specifically the benzene mass fraction. Estimates of typical residual NAPL saturations for specific soil types (Charbeneau and Adamski, 2010) were employed in the model initial condition, and K^{NAPL} were varied to match the concentration data measured in the monitoring wells. The success criterion for the pre-TEE MTT was met since simulated benzene concentrations nearly exactly matched the observed concentrations.

For the post-TEE test, the observed concentrations in the TEE cell showed much greater variability among the monitoring wells compared to the pre-TEE case. This variability was primarily the result of variable treatment within the cell that likely yielded a non-uniform NAPL composition in the cell. The soils around the monitoring wells closest to injection received much more thermal treatment than those near the periphery. Despite the variable treatment, the success criterion to match the post-TEE concentrations with modeling within an order-of-magnitude was met.

To support the numerical modeling results, in particular the assumed mass transfer coefficients, a more simplistic analytical model was derived for determining bulk K^{NAPL} from the pseudo steady-state concentration data, and these values were compared to values calculated from correlations in the literature based on flow through a uniformly distributed NAPL. This large difference was expected as the heterogeneities in a real subsurface tend to discourage contact between flowing water and residual NAPL, whereas the flow is forced through the residual NAPL in laboratory column studies. These data suggest that literature correlations based on a

uniformly distributed NAPL in a homogeneous soil would overpredict the rate of mass transfer in heterogeneous field settings by two to three orders of magnitude.

The average bulk mass transfer coefficients estimated from the analytical model range from 0.0076 to 0.104 d⁻¹. The values employed in the numerical modeling ranged from 0.05 to 0.5 d⁻¹, and therefore may have modestly overpredicted the mass dissolution rate in the source zone, but they were of the same order of magnitude. Overall, the MTTs and associated modeling were successfully able to directly measure a bulk mass transfer coefficient and relate the source mass to the mass discharge, which resulted in a more accurate SZD function for estimating source persistence and the benefits of partial source reduction for reduction of the TOR.

7.3 PERFORMANCE OBJECTIVE: ESTIMATE OF REDUCTION IN CONTAMINANT MASS DISCHARGE AS A RESULT OF PARTIAL SOURCE REDUCTION

This quantitative performance objective was to validate a method for estimating the reduction of mass discharge resulting from partial removal of NAPL mass from a source area. The goal was to evaluate the potential benefit of a remediation approach for partial mass removal required to meet a specified cleanup metric. This important performance objective was to be met by synthesizing the field measurements of groundwater velocity and mass transfer described in the previous two Performance Objectives.

Data requirements for this objective included hydrostratigraphic data within the TEE cell, transient concentration responses of hydrocarbon concentrations at monitoring wells within the TEE cell, PFM results, and pre-TEE and post-TEE monitoring well data collected at source zone monitoring wells and wells located downgradient and adjacent to the TEE cell. In addition, the total mass of contaminant removed from the test cell during the TEE pilot test was used. Other data required for the objective were described in the prior two objectives.

A primary criterion of success for this objective was correlating the change in mass flux between pre- and post-TEE MTTs to the mass removed from the test cell during the TEE pilot test. This criterion is complex and was determined from multiple applications of SEAM3D to match mass transfer data as described in Objective 4.2. The model was first calibrated to the pre-TEE mass transfer data and then to the post-TEE mass transfer data. Within a reasonable number of iterations, the mass subtracted from the pre-TEE model of the test cell to achieve a calibration to the post-TEE data was to have been within $\pm 50\%$ of the observed mass removed from the test cell during the TEE pilot test. In addition, the mean error between the observed equilibrium source zone mass discharge and that simulated with SEAM3D was not expected to exceed one order of magnitude.

The local solute transport model described for the first two objectives was used to calculate the mass flux of benzene at monitoring wells. In the field, this was directly determined using PFMs installed in the B interval monitoring wells during the latter phase of both the pre- and post-TEE MTTs. For the pre-TEE MTT, a reasonable match between the observed and calculated benzene mass flux in each model layer was obtained, meeting this performance objective. Results for the post-TEE MTT were favorable at the monitoring wells nearest to the injection well. At the more distant wells, the observed benzene mass flux from the PFMs was over an order of magnitude

greater than the model-simulated results. As described previously, the benzene concentrations in the TEE cell showed much greater variability among the monitoring wells after treatment as compared to the pre-TEE values. This variability was likely the result of variable treatment within the cell that yielded a non-uniform NAPL composition in the cell. The mean error between the observed equilibrium source zone mass discharge and that simulated with SEAM3D for the post-TEE MTT was well within one order of magnitude in the two wells closest to the injection well but exceeded one order of magnitude in the three monitoring wells closest to the extraction wells.

Estimates of initial NAPL mass for both the pre- and post-TEE model simulations were based on field measurements and analyses associated with the TEE pilot test, including the observed mass removed from the cell during the TEE pilot test. The reasonable match between observed and simulated benzene mass flux at most monitoring locations during the MTTs validates these estimates.

7.4 PERFORMANCE OBJECTIVE: EASE OF SIMULTANEOUS IMPLEMENTATION OF AN IPT AND PFMS

This qualitative performance objective was to assess the ease of deploying PFMs during an IPT. A primary concern was the timing and duration of PFM placement. Because of soil heterogeneities, different soil volumes are swept for different duration times by the injected water. Hence, equilibrium between aquifer material with flowing water, lesser permeable soils, and contaminated soil volumes was difficult to assess. Optimally, PFMs would not be deployed until nearing this equilibrium to avoid sample collection over a period of changing NAPL constituent concentrations. This objective evaluates the method of determining the timing and duration of PFM deployment. An additional potential complication was that a thin layer of floating NAPL could skew results by contaminating the outside of a PFM during placement.

Data requirements for this objective included hydrostratigraphic data within the TEE cell, injection and extraction rates, and transient concentration responses of tracer at monitoring wells. In addition, each well with PFMs was monitored for the existence of a NAPL layer in the well casing prior to deployment and again before retrieval.

Criteria for success in determining the optimal timing and duration of PFM deployment within the IPT were qualitatively evaluated from the consistency and utility of PFM data. For example, NAPL smearing on a PFM during deployment could yield locally high concentrations of benzene or other petroleum hydrocarbons. If the adsorbent in the PFM was saturated with contaminants, the duration of deployment may have been too long. The length of the deployment period was determined from concentrations measured in the monitoring well and estimates of local groundwater velocity based on head gradients.

This performance objective was successfully met as PFMs were not deployed until equilibrium concentrations were observed in the TEE cell. The Pre-TEE MTT included a tracer test that verified a volume-based calculation for the timing of the PFM deployment. The total pore volume of the target soil volume was calculated and the PFMs were not deployed until this volume of clean water had been injected. The tracer concentration histories identified soil heterogeneities and preferential flowpaths where the injected water flowed. The tracer results

indicated more than two pore volumes of water passed through flowpaths prior to the PFM deployment. The contaminant concentrations in the monitoring wells were measured during the water injection and were observed to stabilize before PFM deployment.

An additional concern was the possibility of a thin layer of floating NAPL skewing results by contaminating the outside of a PFM during placement. All wells were bailed of any visible NAPL and purged of three well volumes just prior to the deployment of the PFMs. In addition, a “swipe” test was performed whereby a dummy PFM was installed and immediately withdrawn and sampled for any NAPL contact. A small fraction of the PFM results were slightly adjusted based on the results of the swipe test.

7.5 PERFORMANCE OBJECTIVE: INCREMENTAL COSTS OF IPT AND PFM DEPLOYMENT

This performance objective was to estimate the incremental costs of performing an integral pumping test in a source zone and the deployment of PFMs for vertical delineation of flow and contaminants. Data requirements included operational costs of an existing pump and treat system or the costs for a temporary extraction and treatment system, costs for field technicians to implement the IPT, and costs for deployment and analysis of PFMs.

Success of this criterion was achieved if PFM and IPT incremental costs could be segregated and compared to baseline operating costs.

PFM and IPT costs were successfully segregated and are presented in Section 8.0.

8.0 COST ASSESSMENT

This section provides information to reasonably estimate costs at other sites for implementing the MTT procedures and interpreting the data. A primary determinant for the total cost to perform the testing is the existence of operating infrastructure to pump and treat relatively large quantities of contaminated groundwater for days or weeks. If pump-and-treat is active at a facility and monitoring wells exist within the source area, or if the installation of such a system is anticipated as part of the site remediation, the cost of performing the mass transfer testing is almost solely for the analytical data. Sites requiring such infrastructure usually involve a NAPL source and involve pump-and-treat as part of more intensive technologies such as electrical resistance heating, steam injection, surfactant floods, recirculating chemical oxidation, etc. The costs for data analyses in the form of modeling to determine the source strength and mass transfer characteristics are less variable than the field implementation; however, the modeling costs do vary with the complexity of the site, the intensity of data collection, and the experience of the modeler.

Costs for implementing the methodology at Site ST012 were analyzed, and a cost model was developed that incorporated the elements needed to implement the methodology at other sites. The cost elements considered in the cost model for implementing the MTT at a site are summarized in Table 2. Surface infrastructure typically involves a permanent or temporary facility for the treatment of contaminated groundwater and permitted discharge into a sanitary sewer. Groundwater pumping tests to characterize aquifer permeability are common; however, durations are typically 72 hours or less. This short duration allows pumped water to be treated off site but is generally too short for the MTT described in this report. The quantities of water pumped in the MTT would typically require a permitted treatment and discharge facility. Costing of such a facility is not unique to the MTT and standard practice can be followed.

The existence or need for the installation of subsurface infrastructure is also non-unique for costing, and standard practice can be employed. However, the location and density of injection, extraction, and monitoring wells for the mass transfer testing may be different from existing infrastructure. Often, extraction and monitoring wells are placed downgradient from sources rather than within the source area. This practice is driven by the expectation that (1) monitoring wells within a NAPL source will yield little data other than measures of equilibrium solubility between the NAPL and groundwater, and (2) extraction wells should be placed downgradient for containment of the dissolved plume. For sites with an appreciable groundwater velocity and an aged NAPL source, monitoring wells within the source area are not likely to be in equilibrium with the NAPL and can provide valuable information on the mass dissolution rate. Similarly, extraction from within the source area can also provide containment as well as mass removal, though the rate of extracted groundwater must be higher and the water generally requires a greater degree of treatment than the downgradient water. Hence, extraction and monitoring wells installed in a NAPL source area to support an MTT would have significant value beyond the testing period.

Table 2. Cost model for the MTT field effort.

Cost Element	Data Tracked During the Demonstration	Costs	
Surface infrastructure	- Operational groundwater treatment and discharge system - No unique requirements	Standard practice	
Subsurface infrastructure	- Extraction/injection well installation - Monitoring well installation - Groundwater extraction pumps - No unique requirements	Standard practice	
Baseline hydrogeologic characterization	- Hydrogeologic assessment of boring logs, pumping tests, etc. - Review of available site investigation data and reports	Standard practice	
Baseline contaminant characterization	- Collect groundwater samples from extraction and monitoring wells before injection and extraction - Analysis of groundwater samples for contaminants of concern - Review of available site investigation data and reports	Standard practice	
MTT plan	- Conceptual design of MTT (e.g., flow rates, duration, sampling frequencies, sampling equipment) - Preparation of a test plan	Project engineer, 40 hr	\$5000
Integral pumping test	- Establish pseudo-steady-state flow field in the source zone and maintain flows for desired period of flushing (minimum one equivalent pore volume within the source zone) - Sample and analyze groundwater from extraction and monitoring wells at frequencies specified in the test plan - Measure water levels across the test area as specified in the test plan	Standard practice—assume 8 sampling/monitoring events during the integral pumping test. For example, during a 4-week test, two samples per week are collected from each sampling location and analyzed for COCs by the appropriate method. The current project utilized a calibrated, on-site gas chromatograph (GC) with off-site quality assurance/quality control (QA/QC).	
Tracer test	- Purchase and meter tracer (e.g., potassium bromide) into injected water - Calibrate, deploy, and monitor submersible bromide sensors in monitoring wells	Field technician, 16 hr Project engineer, 8 hr Unit: \$/lb for tracer Unit: \$/sensor per rental week or purchase	\$1200 \$1000 \$50/lb \$1700 sensor purchase
PFM deployment	PFM deployment, retrieval, and analyses	Vendor: Lump sum	\$50,000
Data analyses	See Table 3		
Waste disposal	Standard disposal, no cost tracking	NA	

Baseline characterizations are assumed to be part of the standard site investigation, and a good conceptual site model is assumed to accompany any remedial effort. Hence, the baseline hydrogeologic and contaminant characterizations are not included in assessing the cost of the MTT and standard practice can be followed. However, the mass transfer testing is intended to add an order-of-magnitude improvement to the characterization of the site and conceptual site model for evaluating cleanup options. Hence, the cost model for this technology demonstration only addresses the incremental costs of performing the field measurements and the additional data analyses including computer modeling.

For this demonstration, MODFLOW and SEAM3D were utilized to complete the numerical modeling. SEAM3D is available at no cost to DoD employees and DoD's on-site contractors. The current cost to purchase SEAM3D via the GMS platform is \$3850 for a single license, which includes MODFLOW. The five primary tasks for data analyses and reporting associated with implementation of a comprehensive numerical model of mass transfer testing are listed in Table 3 along with the estimated labor effort required to complete them. As described previously, the costs for computer modeling depend on the size and complexity of the site. Prior to developing the TEE cell model, data were reviewed, and an assessment of the NAPL source was performed. Development of a modeling plan included a description of the conceptual model, detailed plans for construction of the numerical model, and assembly of input parameters. Implementation of the TEE cell model involved model calibration of groundwater flow in parallel with calibration of the tracer transport model. Following this step, the model was applied to simulate the observed pre-TEE MTT observed data. The procedure for model implementation was repeated for simulating the post-TEE MTT.

Table 3. Cost model for the MTT data analysis.

Cost Element	Data Tracked During the Demonstration	Costs	
Initial model setup	Determine appropriate model domain and develop numerical grid.	Project engineer, 16 hr	\$2000
	Translate boundary conditions: Site model to local model.	Project engineer, 4 hr	\$500
	Combine regional and local boring information to develop three-dimensional depiction of hydrostratigraphy in area of interest and translate to model layering and property assignment.	Project engineer, 56 hr	\$7000
Source zone hydrogeologic parameters	Simulate transient behavior of hydraulic heads under induced gradient conditions and compare to observed system response at monitoring wells—develop acceptable state of calibration with respect to head conditions.	Project engineer, 40 hr	\$5000
	Simulate transport of conservative (nonreactive) tracer compound; evaluate appropriateness of model specifications using tracer breakthroughs at the monitoring well locations as calibration data.	Project engineer, 112 hr	\$14,000
	Compare model-predicted resultant flows (resultant vector through cell) to PFM-derived Darcy velocity results—achieve acceptable match between simulated and observed conditions.	Project engineer, 40 hr	\$5000

Table 3. Cost model for the MTT data analysis. (continued)

Cost Element	Data Tracked During the Demonstration	Costs	
Source zone contaminant parameters	Evaluate appropriate time period over which MTT is to be simulated; determine what simplification steps may be required to provide reasonable simulation times (e.g., steady state vs. transient flow).	Project engineer, 16 hr	\$2000
	Initialize SEAM3D NPL package using observed NAPL composition and residual saturation data; simulate Phase I of MTT at outset of forced gradient conditions (injection/extraction); compare to sampling performed within monitoring well network.	Project engineer, 56 hr	\$7000
	Extend transport simulation through period corresponding to PFM deployment; compare model results (resultant flow versus simulated concentration) to PFM-derived mass flux measurements at monitored locations.	Project engineer, 56 hr	\$7000
Reduction in contaminant mass discharge as a result of partial source reduction	Repeat SEAM3D simulations for post-treatment case; initialize model using observed post-treatment NAPL composition and residual saturation.	Project engineer, 32 hr	\$4000
	Revise mass transfer coefficient (model input), as necessary, within area of influence to minimize error; evaluate sensitivity to input parameters (i.e., NAPL composition, residual saturation).	Project engineer, 56 hr.	\$7000
Reporting	Summarize results.	Project engineer, 56 hr	\$7000
	Finalize report and develop appendices describing modeling steps.	Project engineer, 112 hr	\$14,000

9.0 IMPLEMENTATION ISSUES

9.1 IMPLEMENTATION ISSUES DURING THE PILOT TEST

Implementation issues encountered during field testing are discussed in this section, including those specific to the IPT and PFMs.

The injection of water is relatively simple; however, a forced flow IPT requires an extended period of injection and extraction, along with tracer tests, to demonstrate attainment of a pseudo-steady-state condition for flow and NAPL mass dissolution. Water injection may require a separate injection permit in some areas. At sites without an existing pump-and-treat system, the mass transfer testing described in this report may be cost-prohibitive.

An on-site laboratory is recommended to analyze water samples to reduce costs and to allow near real-time concentration data. Shipping samples off-site with standard turn-around times is generally not practical or cost effective. Certified laboratory data are not required for the IPT, as the data are used for engineering purposes.

The PFMs are supplied, deployed, and interpreted by a single vendor, which could result in a long lead time for deployment (e.g., on the order of months). PFMs are not a direct measurement of flux; professional judgment and interpretation are required to obtain usable results. The vendor analysis of data generated by the PFMs is not transparent; calibration procedures and data were not supplied, nor was the method of translating measured data into flux data.

An additional concern regarding the PFMs was the possibility of a thin layer of floating NAPL skewing results by contaminating the outside of a PFM during placement. In this demonstration, all wells were bailed of any visible NAPL and purged of three well volumes just prior to the deployment of the PFMs. In addition, a “swipe” test was performed whereby a dummy PFM was installed and immediately withdrawn and sampled for any NAPL contact. A small fraction of the PFM results were slightly adjusted based on the results of this swipe test. The accuracy of this correction is somewhat uncertain, however, and care should be taken to avoid using PFMs in wells that contain NAPL.

9.2 IMPLEMENTATION OF THE METHODOLOGY AT OTHER SITES

Remediation time frames for reaching site-specific RAOs at compliance locations are largely dependent on the persistence of a contaminant source zone flux combined with the natural attenuation capacity of the groundwater system (Chapelle et al., 2004). At present, studies demonstrating the use of computational tools to predict TOR have been limited by a lack of well-documented sites where source zone remediation has resulted in a reduction in groundwater contaminant concentrations that satisfy regulatory mandates within a reasonable timeframe. However, numerical and analytical models serve an ever increasing role as a tool for decision makers at sites where source zone remediation combined with monitored natural attenuation (MNA) may be a viable long-term remedial option.

Using the steady-state site solute transport model as a starting point, simulations were conducted to determine which model input parameters associated with the source zone exerted the greatest impact on TOR estimates for Site ST012. Results of the sensitivity analysis are summarized in Figure 7 using sensitivity coefficients for three parameters: (1) NAPL mass, (2) percent benzene in the multicomponent source, and (3) K^{NAPL} . The results show the relative importance of each input parameter in terms of controlling TOR for this specific site model. Results of this analysis for this site show the least sensitivity to K^{NAPL} . However, historically K^{NAPL} has been the most challenging parameter to measure in field settings, and attempts at estimating field-scale K^{NAPL} have relied upon very long-term groundwater monitoring data (e.g., 20 to 40 years of data), which is costly to obtain. The methodology evaluated in this demonstration thus improves the accuracy of the model parameter that has historically been the most difficult and costly to estimate.

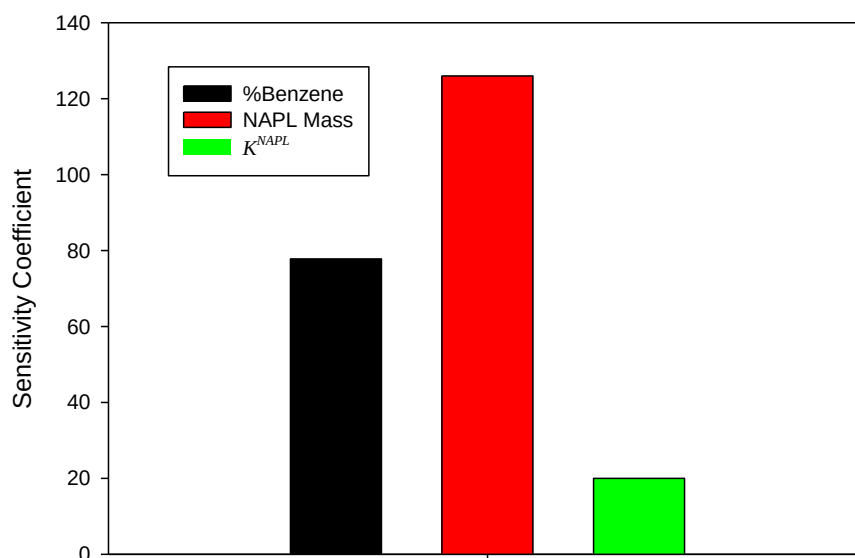


Figure 7. Sensitivity analysis for time to reach 5 µg/L of benzene at a specific point of compliance at Site ST012 based on MNA only and natural source depletion.

The MTTs and associated modeling were successfully able to measure directly a bulk mass transfer coefficient and relate the absolute source mass to the mass discharge, which resulted in a more accurate SZD function for estimating of source persistence and the result of partial source reduction.

If pump-and-treat is active at a facility and monitoring wells exist within the source area, or if the installation of such a system is anticipated as part of the site remediation, the costs of the methodology are almost solely for the analytical data and associated analyses and are a small increment of site operating costs in comparison to the scientifically defensible data collected. This methodology can be applied at sites with LNAPL or DNAPL and can improve the scientific defensibility of decisions regarding when and to what extent active source remediation efforts should be pursued.

10.0 REFERENCES

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- Chapelle, F.H., M.A. Widdowson, J.S. Brauner, E. Mendez, and C.C. Casey. 2004. Methodology for estimating times of remediation associated with monitored natural attenuation, USGS Water Resources Investigation Report 03-4057, 51 pp.
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APPENDIX A

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