ESTCP
Cost and Performance Report

(ER-201032)

Determining Source Attenuation History to Support Closure by Natural Attenuation

November 2013

This document has been cleared for public release; Distribution Statement A

ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT

Project: ER-201032

TABLE OF CONTENTS

Page

TABLE OF CONTENTS (continued)

LIST OF FIGURES

LIST OF TABLES

Page

ACRONYMS AND ABBREVIATIONS

1-D	one dimensional
AFCEC	U.S. Air Force Civil Engineer Center
COC	contaminant of concern
CPT	cone penetrometer testing
CVOC	Chlorinated Volatile Organic Compounds
DCA	Dichloroethane
DCE	Dichloroethene
DHC	*Dehalococcoides*
DNAPL	dense non-aqueous phase liquid
DoD	U.S.Department of Defense
EC	electrical conductivity
ECD	electron capture detector
ESTCP	Environmental Security Technology Certification Program
ft bgs	feet below ground surface
GAC	granular activated carbon
GC	gas chromatography
GSI	GSI Environmental, Inc.
HPT	Hydraulic Profiling Tool
I_k	index of hydraulic conductivity
LIF	laser-induced fluorescence
MAROS	Monitoring and Remediation Optimization Systems
MIP	membrane interface probe
MNA	monitored natural attenuation
MTBE	Methyl tert-butyl ether
NAS	Naval Air Station
NAVFAC	Naval Facilities Engineering Command
O&M	operation and maintenance
OU	operable unit
PID	photoionization detector
PCE	tetrachloroethene
qPCR	quantitative polymerase chain reaction

ACRONYMS AND ABBREVIATIONS (continued)

RACER	remedial action cost engineering and requirements
RI/FS	remedial investigation/feasibility study
RMS	relative mean square
RPD	relative percent difference
RSD	relative standard deviation
SERDP	Strategic Environmental Research and Development Program
TCA	trichloroethane
TCE	trichloroethene
UG	University of Guelph
USEPA	U.S. Environmental Protection Agency
USGS	U.S. Geological Survey
VC	vinyl chloride
VCR	vinyl chloride reductase
VOC	volatile organic compounds
Waterloo APS®	Waterloo Advanced Profiling System

ACKNOWLEDGEMENTS

This demonstration project was funded by the Environmental Security Technology Certification Program (ESTCP), with the main goal of demonstrating the utility of source history modeling of contaminant distributions in lower permeability zones as a line of evidence to support monitored natural attenuation (MNA). Investigators for this project included Dr. Charles Newell (Principal Investigator, GSI Environmental, Inc. [GSI]), Dr. David Adamson (GSI), Dr. Beth Parker (University of Guelph [UG]), and Steven Chapman, M.Sc. (UG). Field work was completed by Mr. Chapman, Adam Gilmore (UG), Dr. Adamson, Nicholas Mahler (GSI), and Poonam Kulkarni (GSI). Several personnel at Stone Environmental, Inc., including Seth Pitkin and Mike Rossi, were instrumental in helping design and implement the field programs. We gratefully acknowledge Michael Singletary, Tim Curtin, and Bill Respet (Naval Facilities Engineering Command [NAVFAC]) for help in identifying and coordinating the work at Naval Air Station (NAS) Jacksonville. Laboratory extractions and analyses of soil samples for volatile organic compounds (VOC) were conducted by Maria Gorecka (UG). The modeling tool that was generated as part of this project was developed by Shala Farhat and Phil DeBlanc (GSI). Additional technical support was provided by Dr. Thomas Sale (Colorado State University) and Doug Mackay (University of California, Davis).

This page left blank intentionally.

EXECUTIVE SUMMARY

This project tested an innovative approach for reconstructing the "source history" at a site (i.e., the concentration trends over time) by using high-resolution soil coring within low permeability (low-k) zones. Essentially, soil cores in these zones serve a similar role as tree rings, in that the cores store information about historic environmental conditions. For contaminants that have migrated into low-k zones via diffusion and slow advection, the concentration versus depth profile can be used to determine if attenuation of the contaminant source in the overlying transmissive zones has occurred. The results can provide an important line of evidence for evaluating the viability of monitored natural attenuation (MNA) at a site.

The project developed a simple transport-based spreadsheet tool—***the Source History Tool***—to generate source history estimates from high-resolution soil core data. The basis for the modeling approach for this project was the one-dimensional (1-D) diffusion equation using Fick's second law. This law defines the diffusion of a chemical in solution in response to a concentration gradient. The analytical solution allows for the concentration at any depth to be determined based on the concentration at the interface. Results were compared to prior source history reconstructions based on detailed numerical modeling.

The Source History Tool calculates the concentrations at the high-k/low-k interface over time that would best represent the vertical concentration profile measured in the sol cores. It develops this pattern by systematically adjusting the interface concentration at various time intervals until a representative "best" fit is obtained. To validate the tool, data were collected from two different source areas located at the Naval Air Station (NAS) Jacksonville, and soil core data from other sites were used to supplement the evaluation. An evaluation of project results yielded the following key conclusions:

1. **The tool proved easy to use, and successfully modeled data from all source areas tested.** A total of 17 source histories were generated during this project (for different compounds and sites), and all of these proved similar to existing estimates and/or site information. As described below, the tool was successful at both of the source areas at NAS Jacksonville. Results showed that using the Source History Tool can provide valuable information for developing and/or refining the conceptual site model by enhancing our understanding of the likely "style" of source history at a site.
2. **Source history was successfully reconstructed at a site with a constant source area concentration over time.** A constant source was predicted for chlorinated ethenes at the first source area (Building 106). This prediction was consistent with the measured soil concentration profiles, where the maximum concentrations were measured at the interface, and the concentrations decreased with distance into the low-k clay. The release date predicted for the near source location, as well as the subsequent arrival dates at downgradient locations, were consistent with site characteristics. In addition, the results confirmed existing evidence of attenuation along the plume flowpath.
3. **The model was also used successfully at a source area with a declining concentration.** Decreasing chlorinated ethene concentrations at the high-k/low-k interface were predicted at the Building 780 source area, and this prediction was consistent with the soil coring data showing peak concentrations occurring several feet

into the low-k clay. This result provided strong evidence for source decay over time. With the exception of 1,2-dichloroethane (DCA), data from co-located cores showed no evidence for decay of chlorinated solvent sources at this site. Again, the release and arrival dates that were predicted by the model were consistent with the available site information.

4. **Understanding the potential impact of degradation is an important component of the source history approach.** The Toolkit incorporates degradation within the low-k zone by including a constituent half-life as an input parameter. While the default assumption is that degradation is minimal in low-k zones, a focused sampling and analysis program was performed to assess biodegradation in the low-k zones at the Building 106 source area. This assessment included use of molecular biological tools, compound-specific isotope analysis, geochemical analyses, and measurements of the relative distribution of parent compounds versus degradation byproducts. The assessment supported the assumption that, at this site, the majority of degradation was occurring in the high-k zone and not the low-k zone.

5. **Several characterization tools proved useful for screening locations for soil coring.** The tools tested during this project included membrane interface probes (MIP), the Waterloo$^{APS\ TM}$, and the Geoprobe Hydraulic Profiling Tool (HPT). These methods are well-suited for determining relative permeability distributions and locating interfaces between low-k and high-k zones.

6. **The uncertainty analysis included in the Toolkit can provide valuable information.** The analysis is not only helpful for understanding the relative sensitivity of various input parameters, but it also can be used to simulate alternative scenarios. For the sites investigated during this project, the results were most sensitive to porosity and tortuosity. The constituent half-life has little impact until values fall below ~10 years.

7. **Proper sample handing, preparation, and analysis methods are critical.** A thorough evaluation confirmed that the protocol used in this project, including methanol preservation in the field, generates high-quality data and should be adopted to the extent possible.

8. **The costs for high-resolution soil coring may be justified if it allows use of MNA.** For a site where source history method was applied at a scale similar to that used for this project, the stand-alone costs were approximately $161K, or $1150 per vertical foot (cored), with $35.8K of this cost due to project-specific reporting. For a full-scale application of this approach where it leads to selection of MNA, the estimated life cycle cost is 23% less than enhanced in situ bioremediation (which may not be effective in low-k zones), and 75% less than pump-and-treat.

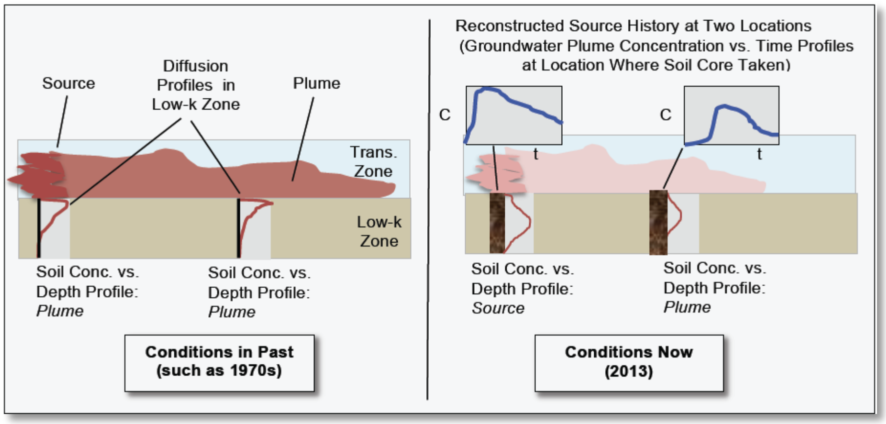


Figure ES.1. Example of how source reconstruction using soil core data works. High-resolution analysis of soil cores collected in 2013 show the style of the source history of the groundwater point at the location the core was collected.

This page left blank intentionally.

1.0 INTRODUCTION

1.1 BACKGROUND

One of the key constraints on our ability to select remedies for closing sites contaminated by chlorinated solvents is that there is typically only a short time interval where monitoring data are available to assess trends. This problem is exacerbated in situations where source material is expected to be present because of uncertainty about plume stability versus source stability. In particular, this hinders an evaluation of monitored natural attenuation (MNA) as a remedy, despite the fact that recent historical surveys of MNA have determined that it was a feasible remedy in over 75% of the sites where it was included in the evaluation, either alone or in conjunction with an active treatment technology (McGuire et al., 2004; Newell, 2006). Often concentration trends are difficult to discern, even with the use of advanced statistical tools such as U.S. Air Force Civil Engineer Center's (AFCEC) Monitoring and Remediation Optimization Systems (MAROS) tool, such that insufficient evidence is available to demonstrate that natural attenuation is viable. This can delay the decision-making process until more data can be collected and evaluated, and any supplemental data is gathered to support a "lines of evidence" approach that is not necessarily definitive or reflective of long-term trends.

Furthermore, regulators frequently adhere to a conceptual model of an unchanging, non-attenuating source zone, and insist on source remediation projects to replace or augment natural attenuation. As a result, site managers often are faced with implementing a costly technology and demonstrate performance in terms of mass removal efficiency, even though estimates of the mass present or remaining in a source zone are typically difficult to make and are subject to significant uncertainty given the limitations in monitoring data and investigation resolution, especially as subsurface releases age over time.

To aid in the selection of MNA as a long-term remedy, we propose a new approach that allows for a reconstruction of *long-term source histories* that extend back to the beginning of the original source release. Methods developed by Parker et al. (2004, Chapman and Parker 2005, 2008)—specifically the collection of closely spaced soil concentration measurements at discrete depths in low permeability zones within and downgradient of source zones to provide insight into historic concentration trends at interfaces with the low permeability zones—provide a focused way to reconstruct long-term source histories that extend back to the beginning of the original source release.

1.2 OBJECTIVES OF THE DEMONSTRATION

The overall objective of this ESTCP project is to reduce the uncertainty associated with assessing long-term concentration trends for use in remedy selection at sites with chlorinated solvent contamination in soil and groundwater. This is based on the hypothesis that diffusion of contaminant mass into and out of low permeability geologic strata within a source zone provides a method of reconstructing the source history by obtaining detailed soil concentration profiles within these less transmissive layers, along with measurement of relevant transport parameters controlling the advective – diffusive development of the profile. Specific objectives include:

1. Determine if existing models can be updated to determine source histories.

2. Conduct a field demonstration to collect data for model validation and protocols for sampling and analysis.
3. Develop a simple, user-friendly modeling tool (and associated guidance) for site managers to apply this methodology and to aid in interpretation of results.

These objectives were examined at several sites by completing high resolution soil and groundwater sampling within high and low permeability zone interfaces in source zone(s) and also the downgradient plume(s). The sampling program was aimed at defining the mass distribution in low permeability zones. These high-resolution characterization data can then be used as input data for the diffusion model. The result is a historical reconstruction of the source concentration history at the interface over time. In cases where the characteristic back diffusion profile from locations within the source and in the downgradient plume are encountered in the low permeability zones, they can be used to demonstrate a declining concentration trend resulting from source depletion that has occurred in the time elapsed following initial contaminant releases. This is done by back-calculating possible scenarios for the source loading (i.e., concentration history at the low permeability interface) that would have resulted in the measured soil concentration profile in the low permeability layers as the result of diffusion-dominated transport in these layers.

1.3 REGULATORY DRIVERS

A key outcome of this project is developing a methodology that can be used to help break the logjam of sites where natural attenuation has been proposed but not accepted by regulators due to concerns that the source is not being treated fast enough, or where routing monitoring data do not show definitive trends. A long-term source history from the beginning of releases at a site to present time would help confirm a site conceptual model that shows attenuation is a significant process for both the source and the plume, and it generates data that are well-suited for use in predicting future concentration and attenuation trends. This approach has the potential to eliminate source removal as a necessary step at some sites prior to adopting natural attenuation as a long-term remedy, which reduces the complexity of remedy selection and accelerates implementation. The key requirement is the presence of low permeability strata within or downgradient of the source zone. Given the increased understanding of the role of small-scale permeability contrasts in enhancing transport, as well as the potential long-term storage of mass within fine-grained intervals, the potential exists for low permeability zones to serve as a contributor to source and plume behavior at even moderately heterogeneous sites. Consequently, the methods proposed in this project have wide applicability to many Department of Defense (DoD) sites.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

The lack of long-term temporal information about contaminant concentrations in source zones makes it more difficult for site managers to make a data-driven argument for MNA as a suitable long-term remedy, especially given that conventional conceptual models often neglect or dismiss source attenuation that can occur over the decades that have generally elapsed at most sites since initial dense non-aqueous phase liquid (DNAPL) releases occurred. This line-of-thinking does not take into account increasing evidence that source strength *does* decrease over time as natural processes deplete mass from the source zone. Recent research has shown that many sources—and perhaps most—do show significant attenuation over the relatively long time periods since releases occurred, i.e., 20 to 50 years, the age of many of the sources the DoD now has to manage (Newell et al., 2006).

We propose a new approach that allows for a reconstruction of *long-term source histories* that extend back to the beginning of the original source release. Methods developed by Parker et al. (2004, Chapman and Parker 2005, 2008)—specifically the collection of closely spaced soil concentration measurements at discrete depths in low permeability zones within and downgradient of source zones to determine source loadings—provide a focused way to reconstruct long-term source histories that extend back to the beginning of the original source release. Evaluation of such datasets from this technology using modeling tools developed as part of this demonstration places us in a far better position to make informed and cost-effective decisions about managing and closing these sites.

The behavior of source material following release is strongly influenced by heterogeneities in subsurface environments, which contribute to the complexity of site characterization and remediation strategies. In particular, abrupt contacts between highly transmissive and less transmissive zones are common in most geologic settings. The presence of these layers of differing permeability in a source zone and in the downgradient plume zone also means that a portion of the contaminant mass is subject to diffusion into and storage within the low-k zones. This occurs as high concentrations of aqueous-phase contaminants in high-k zones come into contact with lower permeability zones. Over time, contaminants migrate into the lower permeability zones (e.g., silts, clays, fractured bedrock) via vertical advection and slow diffusion.

In particular, the diffusion process is predictable and controlled by concentrations at the interface as well as characteristics of the lower permeability zone, which can be measured on core samples or estimated with good certainty. This "source loading" process can result in the long-term storage of substantial contaminant mass as dissolved and sorbed phase within the low permeability zones. The contaminant storage capacity in these lower permeability zones is generally greatly enhanced by sorption; given these zones typically contain higher organic carbon content. At a later time, even if no DNAPL remains, plumes can be sustained by the slow release ("back diffusion") of mass from the low permeability zones into the higher permeability zones (Liu and Ball, 1998a, 1998b, 2002; Parker et al., 2004; Chapman and Parker, 2005; Seyedabbassi et al., 2012).

The nature of the current contaminant profiles in the low permeability zone can be used to infer the concentration history at the interface. For example, a soil profile with decreasing concentrations from the interface to deeper portions of the low-k zone is consistent with a constant source (i.e., continued loading via diffusion). Alternatively, a soil profile where the peak concentration is located some distance into the low-k zone (and not at the interface) is consistent with a decreasing source (i.e., back diffusion). This shows how the present-day profiles can be used to provide insight into the “style” of the past concentration history at the interface.

The technical approach focuses on the collection of high-resolution depth-discrete data from low permeability zones and then using a diffusion-based transport model to “reconstruct” the historical source loading. A schematic of the technology and its benefits are shown in Figure 1 and Figure 2. The specific sampling methodology used during this project will involve the collection of depth-discrete soil samples near geologic interfaces and into the low permeability zone for subsequent laboratory extraction and analysis to generate a detailed contaminant profile with depth. Supporting measurements of parameters such as porosity and organic carbon content are also made on samples to be used in assessment and modeling. In cases where the characteristic back diffusion profile from locations within the source and in the downgradient plume are encountered, they can be used to demonstrate a decreasing concentration trend resulting from source decay and/or active remedial measures that has occurred in the time elapsed following release (assuming a reasonable estimation of the time of release can be made) (Figure 1). This is done by back-calculating the source loading (i.e., concentration history at the low permeability interface) that would have resulted in the measured soil concentrations in the low-permeability layers as the result of diffusion-dominated transport in these layers.

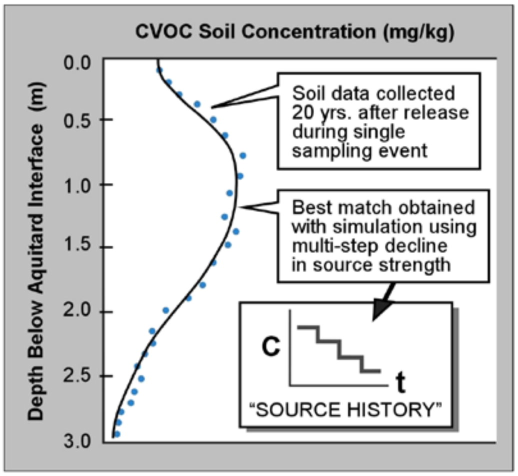


Figure 1. Conceptual model of the source history approach.

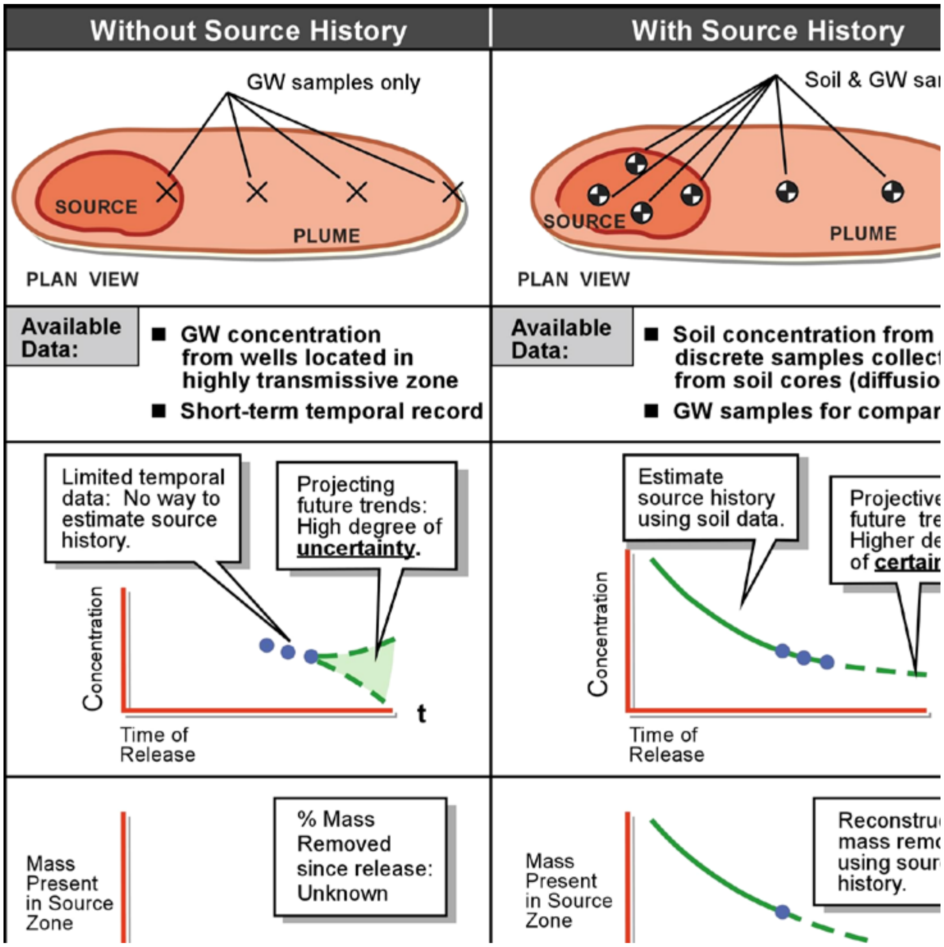


Figure 2. Example of benefits of reconstructing source history for MNA decision-making.

The utility of this method is outlined in the right-hand panels in Figure 2. The concentration "signature" within the low permeability zones can be used to estimate the source strength behavior over time, with the potential to quantitatively establish that significant attenuation has occurred since the time of initial DNAPL releases. Compare this to the typical case where only a limited temporal record is available from monitoring of groundwater concentrations in wells generally positioned in the higher permeability zones (left-hand panels of Figure 2), such that the true extent of source attenuation cannot be adequately appreciated because the majority of source decay occurred prior to the collection of the groundwater monitoring data. This hampers an evaluation of the attenuation potential at a site, both in terms of what has already occurred and what can be expected to occur in the future.

A key objective of this project is to help break the logjam of sites where natural attenuation has been proposed, but not accepted by the regulators due to concerns that the source is not being treated fast enough. Consequently, the methods proposed in this project have wide applicability to most or all DoD sites. A long-term source history from the time when contaminant releases first occurred at a site to present time would help confirm the site conceptual model that shows attenuation is a significant process for both the source and the plume at the majority of sites, and it generates data that are well-suited for use in predicting future attenuation trends. At some sites, this approach has the potential to reduce the need for further source treatment because it would show that significant mass has already been removed from the source zone over time via natural processes and that the source strength and input to the plume is also declining over time. This can serve to accelerate the selection and implementation of less costly approaches like MNA at many sites, allowing more focused application of scarce funds to sites where more active remedial measures can have more impact on reducing risk. The key requirement is the presence of low permeability strata within or downgradient of the source zone in which contaminant transport is largely diffusion-controlled.

This demonstration project specifically addresses sites where chlorinated solvents have impacted soil and groundwater, but it also has potential applicability at other DoD sites where other contaminants of concern (COC) are present, such as fuels, methyl tert-butyl ether (MTBE), perchlorate, and explosives.

With respect to cost benefits, the proposed approach provides valuable information to base decisions on whether or not to implement or continue an active source treatment or control remedy versus natural attenuation. These decisions necessarily rely on a quantitative assessment of contaminant mass both in terms of the percentage of mass remaining, the contaminant loading to the downgradient plume, and the rate of attenuation that has occurred since the time of release and expected future rates of attenuation. As a consequence, these data allow stakeholders to better evaluate whether remediation goals will be achieved within a reasonable time frame without the implementation of aggressive source treatment technologies. For those sites where source treatment is eliminated, the potential cost savings is significant.

2.2 TECHNOLOGY DEVELOPMENT

The source history reconstruction approach that has been used as part of this project is an extension of a methodology that has been previously applied by members of the project team (Parker and Cherry, 1995; Parker et al., 2004, 2008; Chapman et al., 2005) (Table 1). Previous work related to estimating source loading over time was also presented in a series of papers by Liu and Ball (1998a, 19998b, 1999, 2002) that summarized field and modeling work at Dover Air Force Base.

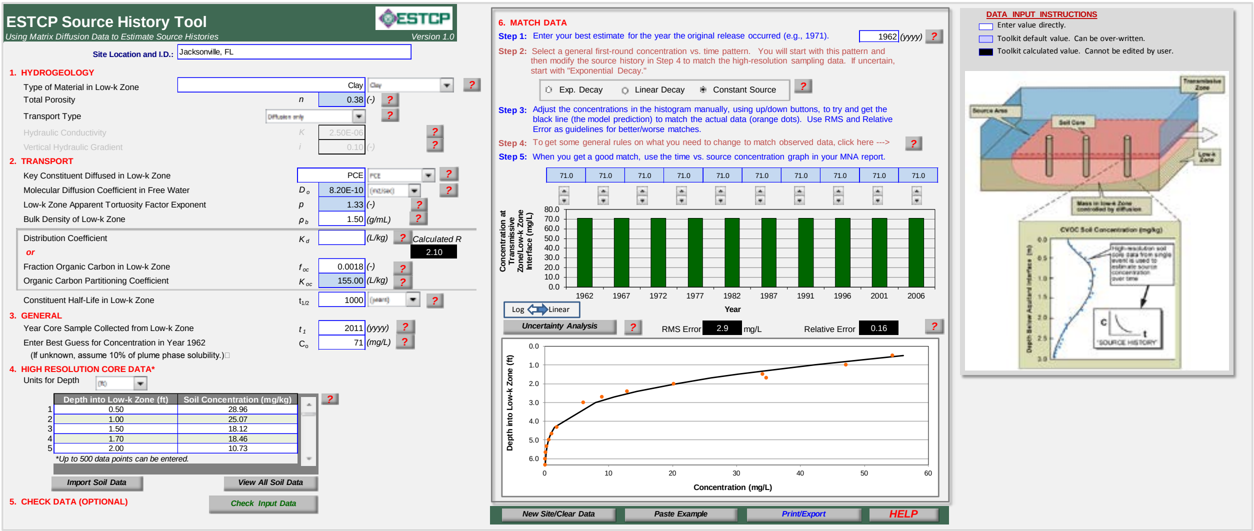
Table 1. Chronological summary of the development of the technology.

Time Period	Description of Technology Development
1980s	• Experimental results demonstrate influence of diffusion within heterogeneous media (particularly fractured media) on DNAPL fate and transport (e.g., Sudicky et al., 1985; Sudicky, 1986; Schwille, 1988) • Initial implementation of field methods for drive-point based depth-discrete subsurface characterization (e.g., cone penetrometer testing [CPT], GeoProbe, HydroPunch)
1990s	• Increased recognition that diffusion of DNAPL into fractured porous media and other low permeability matrices can influence contaminant transport long after initial release (e.g., Parker et al., 1994, 1996, 1997; Liu and Ball, 1998a, 1998b, 1999) • Further development and commercialization of field methods that are aimed at high-resolution subsurface characterization of chlorinated solvents (e.g., Waterloo Profiler, membrane interface probe [MIP], laser-induced fluorescence [LIF])
2000-present	• Further improvement and industry acceptance of field characterization methods that are suitable for investigating low permeability media (e.g., U.S. Environmental Protection Agency [USEPA] Triad Approach) • Detailed source characterization at several sites coupled with analytical and numerical modeling efforts to estimate source loading and back diffusion effects (Parker et al., 2004, 2008; Chapman et al., 2005; Mackay et al., 2000; Liu and Ball, 2002) • Release of several technical guidance documents that highlight influence of matrix storage and release on contaminant transport and remediation (AFCEC, 2007; Sale et al., 2008) • Development of the Matrix Diffusion Toolkit (ESTCP ER-201126; currently under review by the ESTCP program office)

Note that the reconstructed "source histories" were not always the focus of the characterization activities described above but established the potential efficacy of this approach at other sites. Similar, the modeling completed during the studies described above largely relied on numerical groundwater flow and solute transport models (e.g., HydroGeoSphere) that, while commercially-available and very powerful, require considerable expertise to learn and apply at a specific site. The current ESTCP demonstration project is intended to build on the potential that was established by these earlier studies. This is accomplished by systematically characterizing contaminant profiles at several sites and using this data to develop and calibrate a readily-accessible tool for evaluating the profiles and aiding stakeholders in decision making.

The basis for the modeling approach used during this project is the one-dimensional (1-D) diffusion equation (e.g., Freeze and Cherry, 1979) using Fick's second law. This law defines the diffusion of a chemical in solution in response to a concentration gradient. The analytical solution allows for the concentration at any depth to be determined based on the concentration at the interface: The goal of the approach being tested as part of this project is to use the vertical concentration profile within the low permeability zone to establish the interface concentration versus time pattern that would best represent this profile. This is done by systematically adjusting the interface concentration at various time intervals until a representative "best" fit is obtained.

The tool generated by this project is a simple spreadsheet-based model that follows this approach and provides a source history estimate that best represents the soil concentration profile (see Figure 3). It also includes a vertical advection term and a first-order decay term to understand the potential impacts of these processes on contaminant fate and transport in addition to diffusion and sorption processes. A comprehensive User's Manual was completed as part of this project and is included as an Appendix to the Final Report.



ESTCP Source History Tool
Using Matrix Diffusion Data to Estimate Source Histories
Version 1.0

Site Location and I.D.: Jacksonville, FL

1. HYDROGEOLOGY
Type of Material in Low-k Zone: Clay
Total Porosity n: 0.38 (-)
Transport Type: Diffusion only
Hydraulic Conductivity K: 2.50E-06
Vertical Hydraulic Gradient i: 0.10 (-)

2. TRANSPORT
Key Constituent Diffused in Low-k Zone: PCE
Molecular Diffusion Coefficient in Free Water D_o: 8.20E-10 (m2/sec)
Low-k Zone Apparent Tortuosity Factor Exponent p: 1.33 (-)
Bulk Density of Low-k Zone ρ_b: 1.50 (g/mL)
Distribution Coefficient K_d: (L/kg)
or
Fraction Organic Carbon in Low-k Zone f_{oc}: 0.0018 (-)
Organic Carbon Partitioning Coefficient K_{oc}: 155.00 (L/kg)
Calculated R: 2.10
Constituent Half-Life in Low-k Zone $t_{1/2}$: 1000 (years)

3. GENERAL
Year Core Sample Collected from Low-k Zone t_1: 2011 (yyyy)
Enter Best Guess for Concentration in Year 1962 C_o: 71 (mg/L)
(If unknown, assume 10% of plume phase solubility.)

4. HIGH RESOLUTION CORE DATA*
Units for Depth: (ft)

	Depth into Low-k Zone (ft)	Soil Concentration (mg/kg)
1	0.50	28.96
2	1.00	25.07
3	1.50	18.12
4	1.70	18.46
5	2.00	10.73

Up to 500 data points can be entered.

5. CHECK DATA (OPTIONAL)

6. MATCH DATA
Step 1: Enter your best estimate for the year the original release occurred (e.g., 1971). 1962 (yyyy)
Step 2: Select a general first-round concentration vs. time pattern. You will start with this pattern and then modify the source history in Step 4 to match the high-resolution sampling data. If uncertain, start with "Exponential Decay."
○ Exp. Decay ○ Linear Decay ● Constant Source
Step 3: Adjust the concentrations in the histogram manually, using up/down buttons, to try and get the black line (the model prediction) to match the actual data (orange dots). Use RMS and Relative Error as guidelines for better/worse matches.
Step 4: To get some general rules on what you need to change to match observed data, click here --->
Step 5: When you get a good match, use the time vs. source concentration graph in your MNA report.

1962	1967	1972	1977	1982	1987	1991	1996	2001	2006
71.0	71.0	71.0	71.0	71.0	71.0	71.0	71.0	71.0	71.0

RMS Error: 2.9 mg/L
Relative Error: 0.16

DATA INPUT INSTRUCTIONS
☐ Enter value directly.
▨ Toolkit default value. Can be over-written.
■ Toolkit calculated value. Cannot be edited by user.

Figure 3. The Source History Tool.
The software tool is an Excel spreadsheet model that allows the user to input site-specific (or default) information obtained from soil cores (left hand side of screen) to estimate the source history associated with these data (right-hand side of screen).

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The technology couples a detailed site characterization approach in lower permeability zones with transport modeling to reconstruct the source history at a site. Technology performance is a function of site properties. Subsurface contaminant distribution and geology, including specific depths where high and low permeability zones are encountered, must be known or established as part of the characterization efforts. Geologic complexity can affect the outcome as well, for example sites with relatively simple geology and abrupt contacts between high and low k zones provide greater potential for meaningful insight on source attenuation history versus sites with greater geology complexity such as transitional changes between high and low k zones.

Table 2. Advantages and potential limitations of the technology.

Advantages	Limitations
May reduce need to implement costly source treatment technology	Requires presence and delineation of interface between two geologic strata with contrasting permeabilities
Increases acceptability of MNA as a remedy	Presence of multiple sources and/or commingled plumes can complicate analysis
Investigation is minimal in footprint and requires no permanent installations	Collection of high-resolution data can be costly at sites with complex geology or deep contamination
Improved understanding of contaminant fate and transport at a site and potential for back diffusion, even if characteristic diffusion profile in low k layer is not obtained	Modeling may generate multiple "source histories" solutions, such that some user knowledge is required to narrow down solutions to most appropriate
Applicable to multiple contaminant types	Occurrence of reactions (abiotic or biotic), non-linear sorption, etc. within the low k zones can complicate analysis

3.0 PERFORMANCE OBJECTIVES

The technical performance objectives for the project are listed in Table 3, with a full description provided in Section 6.0.

Table 3. Performance objectives for the field demonstration.

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
1. **Reconstruct source history – accuracy**	Data from depth-discrete and matrix-specific field samples (soil extracts, groundwater), source history estimate (modeling results)	Source history captures the style of measured field data: relative percent difference (RPD) ≤ ±30% for majority of paired depth-discrete data (e.g., measured soil concentration versus modeled soil concentration at same depths	***NO*** - Only 7 of 17 source histories met criterion - Criterion overly restrictive and not very representative - Passes "eyeball test" for style
		Source history captures the style of measured field data: Ratio of relative mean square (RMS) error to maximum measured concentration for 75% source history estimates ≤ 0.3 (30%)	***YES*** - 17 of 17 source histories met criterion - More representative metric
2. **Reconstruct source history – precision**	Data from depth-discrete and matrix-specific field samples (soil extracts, groundwater), source history estimate (modeling results)	Similar source history generated from duplicate datasets from same location at same site: i) RPD ≤ 30% at majority of time points; or ii) same temporal concentration trend using non-parametric statistical test	***YES*** - Same source history trend (constant) observed using data from duplicates – confirmed using Mann-Kendall - RPD < 30% for 10 of 10 datapoints
3. **Reconstruct source history – sensitivity**	Data from depth-discrete and matrix-specific field samples (soil extracts, groundwater), source history estimate (modeling results); Monte Carlo sensitivity analysis	Quantify sensitivity of source history to individual input parameters: i) same temporal concentration change trend following ±10% change in each input parameter; ii) same style in soil volatile organic compound (VOC) versus depth profile following ±50% change in each input parameter	***YES*** - No changes to temporal concentration trends No changes to style of soil VOC versus depth profiles
4. **Comparison of modified data collection method with standard data collection methods**	Matrix-specific field samples (soil extracts, groundwater)	Identify consistent trends between field extracts analyzed using University of Guelph (UG) methods versus Encore samplers analyzed at commercial lab: $R^2 \geq 0.9$ using regression analysis for paired data	***NO*** - $R^2 = 0.83$ Significant low bias in unpreserved Encores contributed excessive variability

Table 3. Performance objectives for the field demonstration (continued).

Performance Objective	Data Requirements	Success Criteria	Success Criteria Achieved?
Quantitative Performance Objectives			
4. **Comparison of modified data collection method with standard data collection methods (continued)**	Matrix-specific field samples (soil extracts, groundwater)	Identify consistent trends between soil extracts analyzed at UG versus soil extracts analyzed at commercial lab: RPD ≤ ±30% for majority of paired data	***YES*** • RPD < 30% for 37 of 39 analytes • Pattern relatively consistent for all analytes
		Median relative standard deviation (RSD) of duplicates analyzed at UG < ±10% (i.e., similar to acceptable RSD for duplicates analyzed at commercial lab)	***YES*** • Median RSD = 7%
Qualitative Performance Objectives			
Ease of use	Feedback from field personnel regarding time required for data collection and ease of implementing methods	Single mobilization required per site to collect adequate level of data	***PARTIAL*** • Second mobilization required to accommodate expanded scope of work • Methods were easy to implement
Selection of appropriate locations	Historical site data used to select locations for detailed data collection	Assess what previous historical data was used to select locations and how this improved the results.	***YES*** • Existing data were sufficient to select test areas • Multiple coring locations per site proved valuable

4.0 SITE DESCRIPTION

4.1 SITE LOCATION

The sites selected for the demonstration were two separate source areas (Building 106 and Building 780 at operable unit [OU]3) at Naval Air Station (NAS) Jacksonville. NAS Jacksonville is a large site located within the city limits of Jacksonville, Florida, with at least eight OUs that are part of extensive investigation and cleanup efforts under Superfund. OU3 is a 134-acre area located in the eastern part of the facility near the eastern boundary (St. Johns River) and south of the flightline (Figure 4).

Building 106 Source Area: This building was the former dry cleaner for the air station and is located in the north/northwest portion of OU3. It was operated as a dry cleaner beginning in 1962 and was believed to have used approximately 150 gallons of tetrachloroethene (PCE) per month until 1990 or so when dry cleaning operations were discontinued and the building was demolished shortly thereafter. This area was identified as a potential source of contamination in 1993. Currently, the immediate area remains free of structures and is paved. It is surrounded by surface parking and there are several large buildings and access roads on all four sides. Interim remedial measures, including air sparging and soil vapor extraction, were implemented at the site in 1998 as part of the Record of Decision for OU3, but were discontinued following an optimization review completed in 2004-2005 (as part of the Five-Year Review). As of early 2013, the need for additional remedies was currently being evaluated as part of an addendum to the original remedial investigation/feasibility study (RI/FS) (from 2000). Based on communication with site personnel, it is understood that a large-scale pilot test of electrokinetic methods for enhancing biostimulation was scheduled to be implemented in a portion of the source area sometime in 2013.

Building 780 Source Area: This building housed a paint stripping and solvent recycling operation and currently is used as a general (non-hazardous) recycling facility. The building occupies a relatively small footprint (approximately 1000 m^2 including outbuildings) and is located in the northern portion of OU3 (approximately 200 meters NE of Building 106). Currently, the area surrounding Building 780 includes several other permanent structures of various sizes, and all spaces where no buildings are present are paved. The exact start date for solvent use is unknown but it reportedly occurred throughout the 1970s and 1980s to strip paints from aircraft and parts (as well as disposal of spent jet fuels). It was identified as a potential source of contamination in 1990 when high concentrations of VOCs were encountered in exposed subgrade soils during major construction activities at the site. Subsequent investigation activities identified elevated concentrations of multiple types of VOCs (primarily chlorinated ethenes and chlorinated ethanes) as well as numerous inorganics in the soil and groundwater. In 1998, a soil-vapor extraction system and a groundwater pump-and-treat system were implemented at Building 780 to address contamination associated with this source as part of the Record of Decision. These systems were shut down temporarily following the 2004-2005 optimization review. Similar to the situation at Building 106, further remedial activities are being evaluated as additional data are collected at the site in support of an addendum to the 2000 RI/FS.

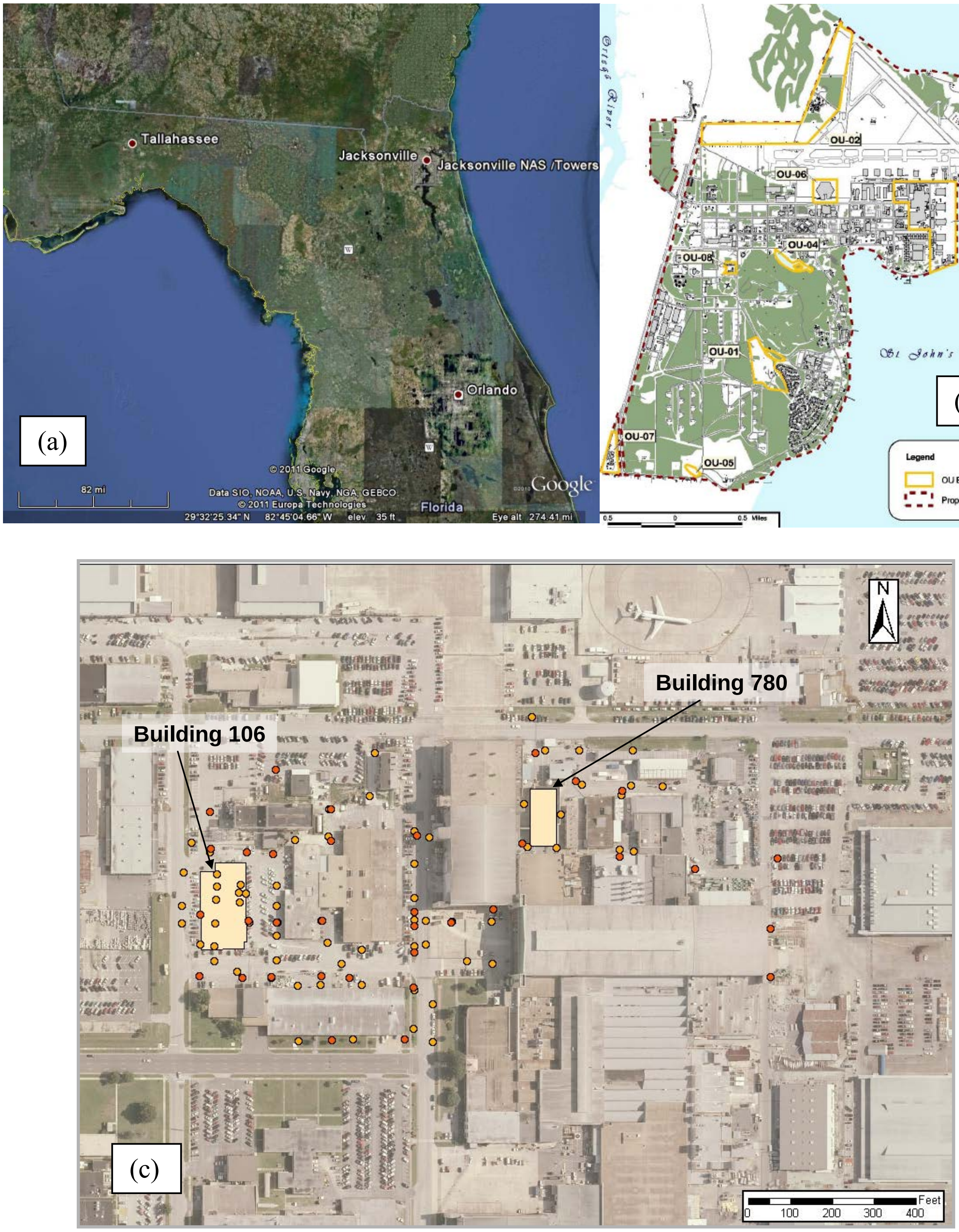


Figure 4. (a) Location of NAS Jacksonville; (b) various operating units at the site; (c) site map of OU3 at NAS Jacksonville.

Figure 4c shows only a portion of OU3, specifically the focus areas for the current project, including Building 106 and Building 780. Colored dots represent investigation points (primarily MIP and/or CPT) that were part of previous site characterization activities.
(Modified from figure supplied by site manager)

4.2 SITE GEOLOGY AND HYDROGEOLOGY

The site geology and hydrogeology at OU3 have been extensively characterized as part of previous investigations at the site (U.S. Geological Survey [USGS], 1998; 2000). Below the surface fill, interbedded layers of sand, clayey sand, sandy clay, and clay are encountered to depths of approximately 150 feet below ground surface (ft bgs). Each of these layers are somewhat discontinuous and not encountered at all locations, but the upper soil intervals are generally dominated by sands. Laterally extensive clays have been encountered in the northern portion of the site in particular. These investigations established that the clays were generally first encountered at depths of 10 to 20 ft bgs and ranged in thickness between 2 and 10 ft. In this portion of the site, the clay is often present as two smaller lenses, separated by thin sublayers of sandier soils. In general, similar stratigraphy was encountered at the two source areas that are part of this project (Building 106 and Building 780). More complex layering (i.e., thinner and more discontinuous clay layers) has generally been observed near Building 780.

The deposits at OU3 form a surficial aquifer unit that consists of two different layers within the northern portion of the site: 1) unconfined upper sand layer that extends from the surface to the depth of the clay (approximately 10 to 20 ft bgs); and 2) an intermediate sand layer that is confined by the clay (Table 4). Because releases of hazardous materials occurred with the upper layer and came into contact with the low permeability clay, the upper layer of this surficial aquifer is the focus of the current investigation. Groundwater in the surficial aquifer generally flows in an easterly direction away from the Building 106 source area and northeasterly from the Building 780 source area. Groundwater is first encountered at depths between about 4 to 7 ft bgs, and water levels reportedly vary little throughout the year. Hydraulic gradients in the surficial aquifer are relatively small, in the range of about 0.001 to 0.005.

A summary of hydrogeologic information is provided in Table 4. Based on the length of the plumes associated with the Building 106 and Building 780 source areas (a minimum of several hundred feet) and the assumed release timeframe (30 – 50 years ago), the 70 ft/yr groundwater velocity is likely a more representative value for further modeling efforts.

Table 4. Summary of NAS Jacksonville OU3 stratigraphy.

Unit	Soil Type	Typical Thickness (ft)	Hydraulic Conductivity (ft/day)
			Maximum
Surficial	Sand	10-20	20
	Clay	2-10	0.001

Notes: (1) Units are described starting at the surface and then proceeding to deeper depths (surface fill not included); (2) Hydraulic conductivities represent field-based measurements when available; (3) Model values cited in site investigation reports used for units where field-based measurements were not performed.

4.3 CONTAMINANT DISTRIBUTION

Building 106 Source Area: Constituents of concern include PCE, trichloroethene (TCE), and associated degradation products (including 1,1-dichloroethene [DCE], cis-1,2-DCE, trans-1,2-DCE, and vinyl chloride [VC]). In the one permanently-installed monitoring well in the area (MW-28 located immediately east of the former building), total chlorinated volatile organic coumpound (CVOC) concentrations in 1998 approached 30 mg/L with PCE as the major constituent. Concentrations in this well have fluctuated over time but remain well above regulatory screening limits for several chlorinated ethenes. Similarly high levels were seen in a series of temporary piezometers that were installed in the area and monitored periodically during the period from 2000 to 2004 when the interim remedy was operating. There are several locations where the concentration of metabolites (particularly cis-1,2-DCE) exceed the concentration of parent compounds. The most recent groundwater data from February 2010 suggest that concentrations are significant (total CVOCs approx. 6 mg/L in MW-28) with evidence of extensive biodegradation.

Building 780 Source Area: Constituents of concern at Building 780 include 1,1,1-trichloroethane (TCA), methylene chloride, PCE, TCE, and associated degradation products (including 1,1-dichloroethane [DCA], 1,2-DCA, 1,1-DCE, cis-1,2-DCE, trans-1,2-DCE), as well as several aromatic hydrocarbons (benzene, toluene, xylenes). During early characterization of the site (1990), total CVOC concentrations exceeded 200 mg/L in the one permanently-installed monitoring well in the area (MW-780-1 located immediately west of Building 780). Concentrations decreased markedly in this well by 2000. Concentrations of chlorinated ethenes and ethanes varied widely in the series of temporary piezometers that were installed and monitored during the early 2000s. The most recent groundwater data indicated that total VOC concentrations are < 100 µg/L and the number of constituents detected is much more limited (cis-1,2-DCE, trans-1,2-DCE, TCE, and VC).

Limited soil concentration data have been collected at the two source areas but confirm that significant contaminant mass is associated with the lower permeability soils. As part of a direct-push investigation in 2006, soil samples were collected at various locations near Building 106 and Building 780. Depths of these samples typically coincide with the start of the lower permeability clays identified across OU3. These data demonstrate that near the Building 106 source area, the VOC profile is generally dominated by PCE (maximum concentration of 77 mg/kg), with higher contributions from lesser chlorinated ethenes at downgradient locations. At Building 780, the highest concentrations by far were encountered within the source area at the southeast corner, including 5100 mg/kg of 1,1,1-TCA and >100 mg/kg of PCE, TCE, and toluene. Note that these soil concentrations are much higher than what would be estimated based on groundwater samples in the area (which collect primarily from sandy intervals), reflecting the influence of mass storage within lower permeability zones in the surficial aquifer. Also of note are that 1,1,1-TCA concentration data exhibit significant spatial variability at this site; large drops in the concentration of this constituent are seen over small distances.

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The field program was designed to collect high-resolution depth-discrete data from low permeability zones at multiple sites and then to reconstruct the historical source history at each site using a diffusion-based transport model. The specific sampling methodology used during this project involved the collection of depth-discrete soil samples near geologic interfaces with lower-k zones to generate a detailed contaminant profile with depth within these zones.

A similar protocol was followed at each site (Figure 5). Specifically, multiple locations were characterized at each site to generate several vertical soil profiles to serve as input data for source history modeling. While the focus was on source areas, downgradient locations were also included at each site. At each location, high-resolution soil sub-sampling (Figure 6) was preceded by detailed vertical stratigraphic profiling to provide guidance for selecting sampling depths.

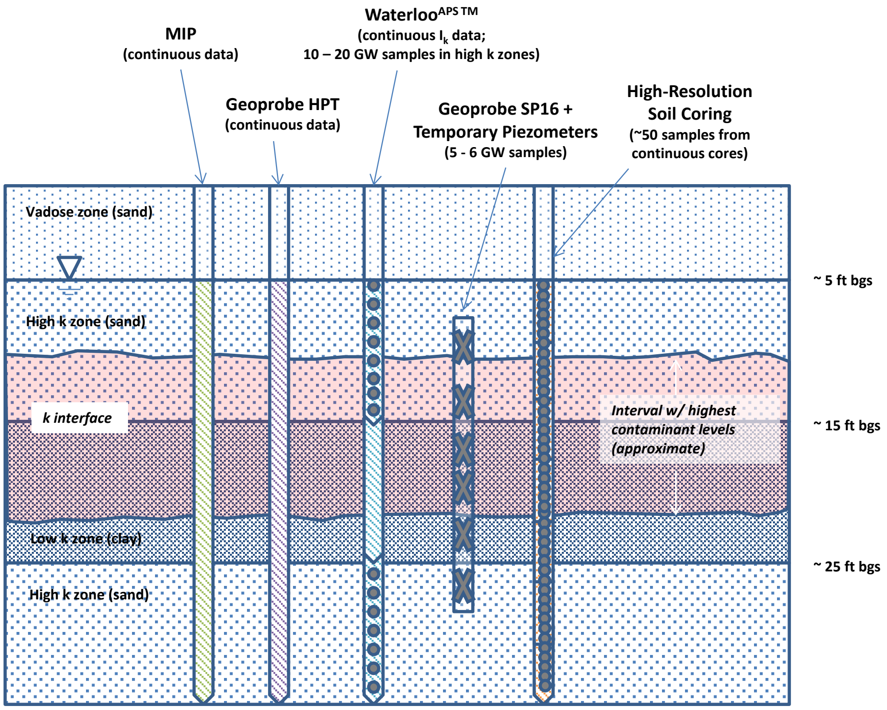


Figure 5. Characterization methods used during field demonstration at NAS Jacksonville.

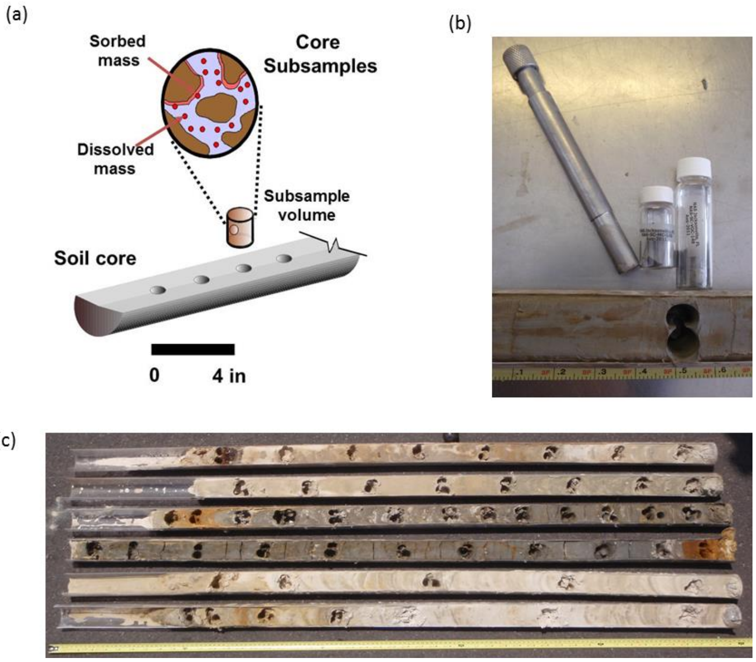


Figure 6. Overiew of high-resolution soil sub-sampling.
(a) schematic, (b) stainless steel subsampler and samples from one depth (one preserved in methanol for VOCs, one for moisture content), and (c) example of subsampled cores from OU3-4 (collected from 5-35 ft bgs).

5.2 BASELINE CHARACTERIZATION ACTIVITIES

The field component of this project involved a detailed subsurface characterization at multiple locations at several sites. These efforts involved the use of screening-level characterization tools at many locations (e.g., MIP, Waterloo Advanced Profiling System [Waterloo APS®], Geoprobe Hydraulic Profiling Tool [HPT®]—see Section 5.4) followed by high-resolution soil coring (Figure 5). As such, there was no separate baseline characterization component to this project.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

Treatability and lab-based studies were not a component of this project.

5.4 FIELD TESTING

For the two source areas at OU3 at NAS Jacksonville, Figure 7 displays the locations characterized at the former Building 106 source area and the Building 780 source area.

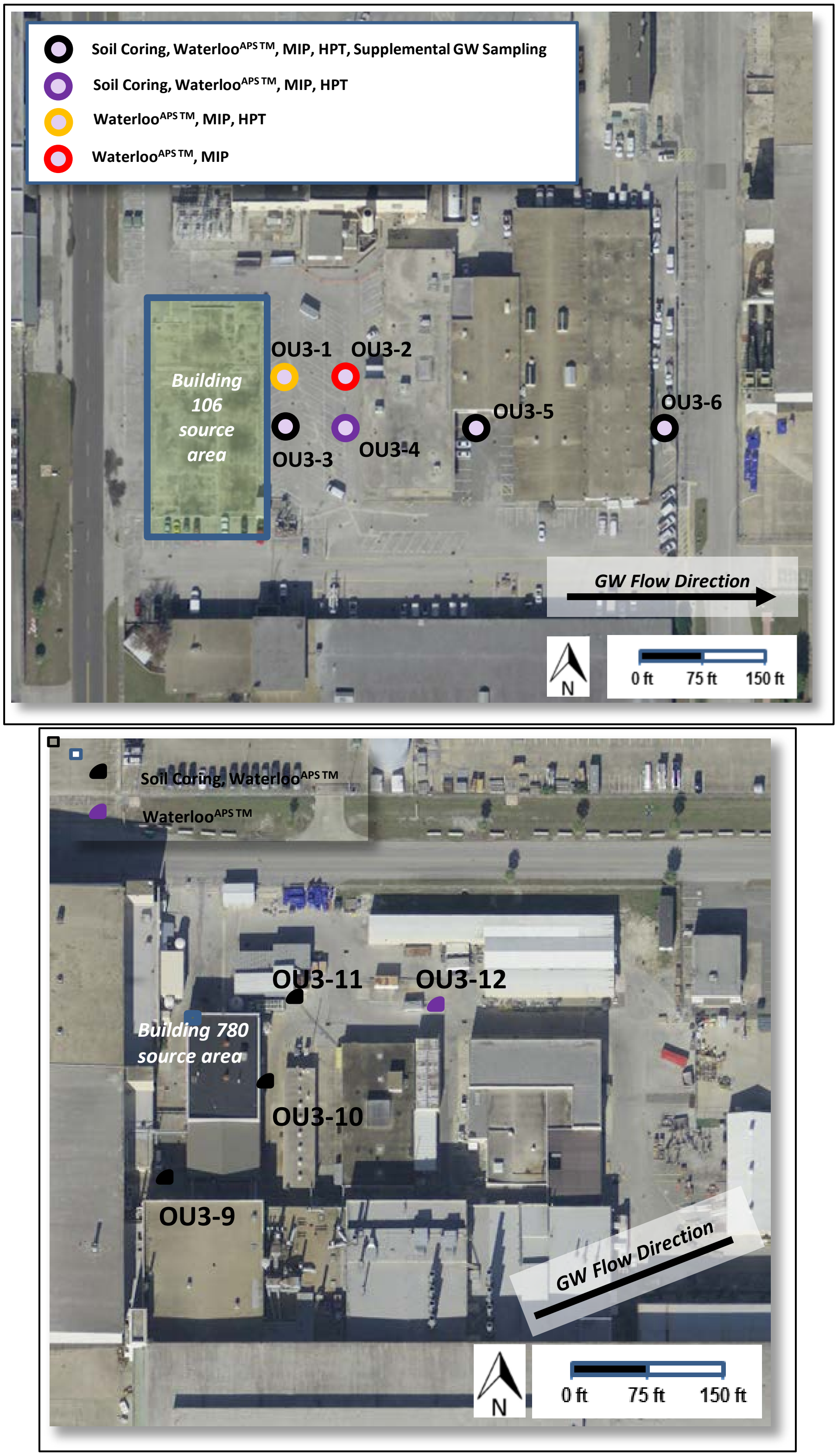


Figure 7. Test locations for field demonstration at OU3.
Former Building 106 Source Area (top panel) and Building 780 (bottom panel) at NAS Jacksonville.

Screening-level characterization was completed at multiple locations with the follow objectives: (1) provide initial information on hydrostratigraphy and contaminant profiles inform conceptual site models; (2) identify promising locations for further soil coring; (3) generate high-resolution profiles for side-by-side comparison of depth-discrete data collected using each method. Three different screening-level characterization tools were used at one or more of the source areas.

- MIP was used to screen potential locations for more detailed investigations and to guide subsequent soil sampling activities. As part of a joint investigation with Strategic Environmental Research and Development Program (SERDP) ER-1740, an objective was to examine an MIP as a tool for low permeability zone investigations and develop a recommended standard operating protocol for these zones (Adamson et al., 2013). MIP does not provide hydraulic conductivity profiling data or actual VOC concentrations in soil or groundwater, limiting its utility for this more quantitative demonstration. As such, MIP was used a supplemental tool for the purposes of this project.
- Waterloo$^{APS\ TM}$ was used to detail vertical characterization and was completed at two of the source areas. This is a subsurface data acquisition system developed by Stone Environmental, Inc. (Montpelier, VT), an adaptation of the original Waterloo Groundwater Profiler Tool (Pitkin et al., 1999) that collects both discrete-depth groundwater samples and an integrated set of companion data in a single, continuous direct push. Specifically, it allows real-time collection of hydrostratigraphic data (i.e., index of hydraulic conductivity or Ik) as the tooling is advanced, allowing identification of optimum sampling locations and k interfaces.
- The Geoprobe HPT tool provides a real-time indication of hydraulic conductivity via logging water injection rates and pressures during advancement of the tool using a direct-push rig. Software tools are available for evaluating the data including use of empirical correlations for direct estimation of hydraulic conductivity. The tool also includes an electrical conductivity (EC) sensor array providing another means of assessing presence of lower k (i.e., silt and clay-rich) zones.

Soil coring was then completed at multiple locations to: (1) generate high-resolution input data for the source history model by determining the soil VOC concentration profile with the low-k zones; (2) quantify specific biomarkers as a line of evidence for biodegradation; and (3) compare various sampling and analysis methods. At each location, cores were obtained using a direct push rig (Geoprobe Model 6620DT) within several feet of the previously-characterized locations. Continuous cores were collected in liners from an interval starting near the surface to a depth several feet through the targeted low-k unit at each location. Soil samples were collected from each core at closely-spaced vertical intervals with a sampling frequency based on data obtain during the Waterloo$^{APS\ TM}$ characterization and visual inspection of cores, as well as experience of the field team for characterizing contamination in low permeability zones. At a minimum, soil samples were collected every 1 foot within the intervals of interest, and higher collection frequencies (i.e., as tight as every 2 to 6 in) were used within intervals with fine-grained material.

Finally, targeted groundwater sampling was completed at select locations to: (1) generate complimentary VOC concentration data for understanding and calibrating soil VOC profiles; and (2) understand geochemical conditions and other potential lines of evidence for biodegradation. This consisted of multi-level groundwater sampling using: Waterloo$^{APS\ TM}$, which was used to collect samples in the zones of higher permeability; and the Geoprobe SP16 sampling system and temporary piezometers in both high and low-k zones.

5.5 SAMPLING PROGRAM

A summary of the sampling plan for this project is provided in Table 5, and the analytical program for these samples is summarized in Table 6. Collectively, this program generated data that provided sufficient understanding of contaminant distribution at each site. Note that to evaluate the data quality generated by modified (project-specific) methods, duplicate and/or split samples were also collected and analyzed using conventional techniques and methods (see Table 6). This rigorous evaluation is included as part of the performance objectives for the project.

5.6 SAMPLING RESULTS

Results of field characterization efforts and modeling are presented for the former Building 106 source area first, followed by the same set of results for the Building 780 source area. Also included in this section are a brief summary of the comparison of sampling and analysis methods, as well as source history modeling of other sites.

Building 106 Source Area: The first source area, the former Building 106 at OU3, was a dry cleaner that started operating in the early 1960s, with PCE as the primary contaminant that was released. MIP survey results suggested that the majority of contaminant mass was present within and immediately above a 5 to 15-ft thick lower permeability layer first identified (using the EC signals from MIP/HPT and the permeability (I_k) estimates from Waterloo$^{APS\ TM}$/HPT, later verified with inspection of soil cores) at a depth of 15 to 20 ft bgs.

CVOC concentration data collected at these locations confirmed that the majority of contaminant mass was present within the low permeability clays and in the transition zone immediately above the clay layer (Figure 8). At the near source location, OU3-3, the CVOC profile is dominated by PCE and TCE, with maximum total CVOC concentrations of approximately 30 mg/kg at 16 ft bgs. At least 80% of the total mass at this location was present between 15 and 21 ft bgs within the clay layer, with little indication of penetration through this layer and the shape of the profile indicative of diffusion-controlled transport. Moving downgradient, the maximum total CVOC concentrations gradually decreased but the relative contribution of cis-1,2-DCE was significantly higher. At these locations, the majority of the total CVOC mass (at least 80%) was encountered in these sand and transitional intervals above the clay layer. The furthest downgradient location, OU3-6, saw a significant shift to cis-1,2-DCE (~90% of the observed mass), and the maximum CVOC concentration (~15 mg/kg) was in the shallow sands at 13 ft bgs).

Table 5. Summary of sampling plan for field demonstration.

Project Component	Matrix	Collection Method	Number of Samples	Analyte(s)	Location
Screening-Level Characterization					
MIP	Groundwater/ Vapor	Downhole tooling using membrane/probe	Continuous to a total depth of at least 34 ft bgs per location	EC (indicator of soil type); gas chromatography (GC) detector response (indicator of contaminant presence)	Six locations at former Building 106 source area; (including all locations where high-resolution soil sub-sampling was completed)
Waterloo profiling (Waterloo$^{\text{APS TM}}$)	Groundwater	Downhole tooling using positive displacement pump	Continuous to a total depth of at least 34 ft bgs per location	Index of hydraulic conductivity (I_k)	Six locations at former Building 106 source area; 4 locations at Building 780 source area (including all locations where high-resolution soil sub-sampling was completed)
Hydraulic profiling tool (Geoprobe HPT)	Groundwater	Downhole tooling using positive displacement pump	Continuous to total depth of at least 34 ft bgs per location	EC (indicator of soil type); Estimated hydraulic conductivity	Five locations at former Building 106 source area (including all locations where high-resolution soil sub-sampling was completed)
High-Resolution Soil Sub-Sampling					
Soil coring	Soil	Geoprobe w/ liner for core; UG soil sub-sampling device; field preservation with methanol	374 (approximately 50 per location from multiple depths; includes 29 duplicate samples collected at multiple locations/depths	CVOCs (analysis at UG lab)	Four locations at former Building 106 source area; 3 locations at Building 780 source area (combination of source and downgradient areas)
			33 (9 to 13 per location from multiple depths)	Organic carbon	Four locations at former Building 106 source area
			178 (28 to 52 per location from multiple depths)	Physical properties: particle size distribution, porosity	Three locations at former Building 106 source area; 1 location at Building 780 source area
	Soil	Geoprobe w/ liner for core; UG soil sub-sampling device; field preservation with methanol and rapid extraction	27	CVOCs (analysis of methanol split samples at commercial lab)	Same locations where high-resolution soil sub-sampling/analyses completed

Table 5. Summary of sampling plan for field demonstration (continued).

Project Component	Matrix	Collection Method	Number of Samples	Analyte(s)	Location
High-Resolution Soil Sub-Sampling (continued)					
Soil coring	Soil	Geoprobe w/ liner for core; EnCore samplers for soil samples (no field preservation)	26	CVOCs (analysis of field duplicates at commercial lab)	Same locations where high-resolution soil sampling/analyses completed
	Soil	Geoprobe w/ liner for core; EnCore samplers for soil samples; preservation upon arrival at lab	32	CVOCs (analysis of field duplicates following delayed preservation)	Same locations where high-resolution soil sampling/analyses completed
	Soil	Geoprobe w/ liner for core; UG soil sub-sampling device; field preservation w/ methanol	29 (duplicate dataset)	CVOCs (analysis of field duplicates at UG lab)	One location at former Building 106 source area as duplicate dataset (OU3-5)
	Soil	Geoprobe w/ linear for core; UG soil sub-sampling device	18 (8 to 10 per location from multiple depths)	*Dehalococcoides* (DHC), vinyl chloride reductase (VCR)	Two locations at former Building 106 source area
Groundwater Sampling					
Waterloo profiling (Waterloo$^{\text{APS TM}}$)	Groundwater	Downhole tooling using positive displacement pump	93 (6 to 12 per location from multiple depths)	CVOCs, field parameters[1]	Six locations at former Building 106 source area; four locations per site (including all locations where high-resolution soil sub-sampling was completed)
Temporary piezometers	Groundwater	Peristaltic pump	19 (6 to 7 per location from multiple depths	CVOCs, dissolved gases (ethene, ethane, methane), sulfate, chloride, carbon isotopes (^{13}C/^{12}C)	Three locations at former Building 106 source area; (including all locations where high-resolution soil sub-sampling was completed)
Geoprobe SP16	Groundwater	Tubing equipped with check valve		CVOCs, dissolved gases (ethene, ethane, methane), sulfate, chloride, carbon isotopes (^{13}C/^{12}C)	

Notes: (1) Field parameters for groundwater include temperature, pH, oxidation-reduction potential, electrical conductivity, and dissolved oxygen; (2) Represents number of samples collected; actual number of samples analyzed may be lower; (3) CVOCs = chlorinated volatile organic compounds; UG = University of Guelph.

Table 6. Summary of analytical methods for samples collected during field demonstration.

Matrix	Analyte	Method(s)	Container and Preservative	Laboratory
Soil	CVOCs	EPA 5035 and EPA 8260	EnCore samplers with no preservative; 48 hr holding time prior to preservation[1]	TestAmerica
	CVOCs	Proprietary preparation method (rapid field extraction of methanol-preserved soil) and EPA 8260	40-mL glass vial containing 15 mL methanol (only methanol extract is sent to lab in 5mL glass vials)[2]	Stone Environmental
	CVOCs	Proprietary (purge-and-trap method based on modified EPA 5035 and EPA 8260)	40-mL glass vial containing 15 mL methanol	UG
	Particle size distribution	Sieve for coarser fraction; Hydrometer for finer fraction as applicable	4-oz plastic sealable jar; no preservative	UG
	Hydraulic conductivity	Repacked Permeameter (modified EPA 9100) using similar methods as Sudicky (1986).	4-oz plastic sealable jar; no preservative	UG
	Field moisture content of soils	SM-2540 G	40 mL, glass vial, no preservative. Sample weighed in field immediately after sample collection and then dried in lab and reweighed.	UG
	Organic carbon	Proprietary (using either Walkley-Black wet chemical oxidation [USDA 90.3] or combustion methods)	40-mL glass vial (same sample as moisture content; post-drying)	UG
	Biomarkers (DHC, VCR)	Proprietary (quantitative polymerase chain reaction [qPCR]-based)	2 to 8-oz plastic or glass sealable jar; no preservative	SiREM
Groundwater	CVOCs	EPA 8260	Three 40-mL glass vials; HCl to pH < 2	UG
	Dissolved Gases	RSK-175	Three 40-mL glass vials; no preservative	TestAmerica
	Chloride, sulfate	EPA 300	One 500-mL plastic; no preservative	
	$^{13}C/^{12}C$	Proprietary (GC/IRMS method)	Three 40-mL glass vials; HCl to pH < 2	University of Waterloo
	Field parameters (dissolved oxygen, electrical conductivity, oxidation-reduction potential, pH, temperature)	YSI Mulitmeter	> 100 mL; no preservative	Not applicable (field measurement)

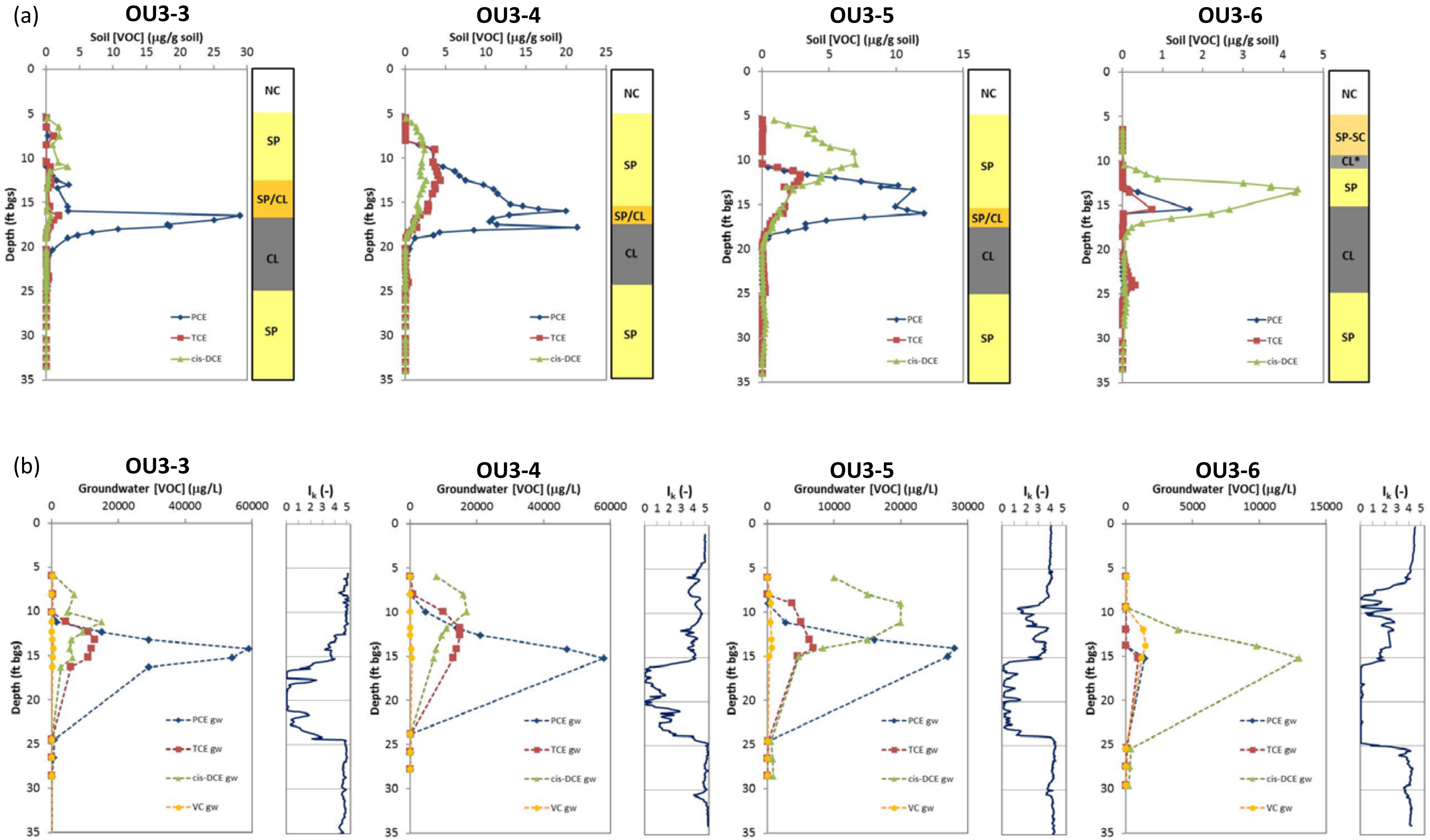
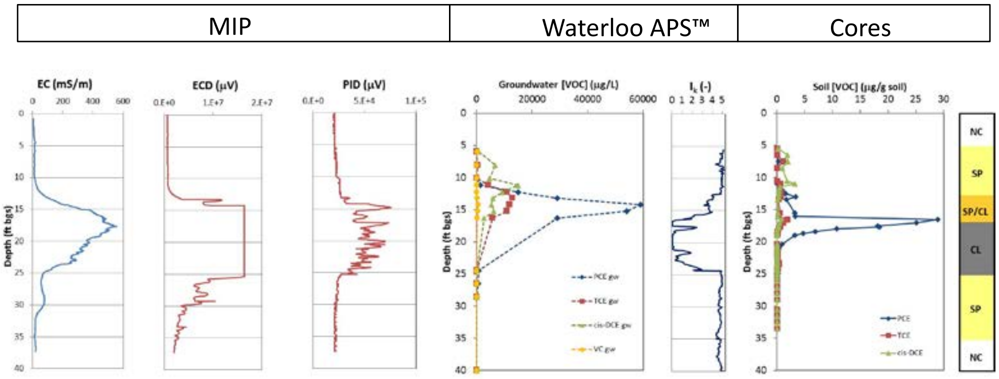


Figure 8. Soil and groundwater VOC concentrations from former Building 106 source area locations. Locations from left to right represent plume flowpath from near source (OU3-3) to downgradient plume (OU3-6). (a) Soil VOC concentrations and core logs; (b) Groundwater VOC concentrations and and I_k data from the Waterloo$^{APS\ TM}$.

For each location at the former Building 106 source area, high-resolution characterization data were compiled as composite plots that show method-specific depth-discrete data side-by-side (or in some cases, as data overlays) (Figure 9). These plots provide the most complete picture of the datasets, and demonstrate that the various stratigraphic characterization methods generated data that was consistent with those obtained by soil coring and classification. They successfully identified the critical low permeability zones for further characterization efforts using soil and groundwater sampling. CVOC trends (in terms of magnitude and distribution of contaminants) were largely similar regardless of the sampling matrix or approach. Examples for location OU3-3 are shown in Figure 9b (including CVOC concentration data) and Figure 9b (focusing on hydrostratigraphic information).

(a) **OU3-3**



(a) **OU3-3**

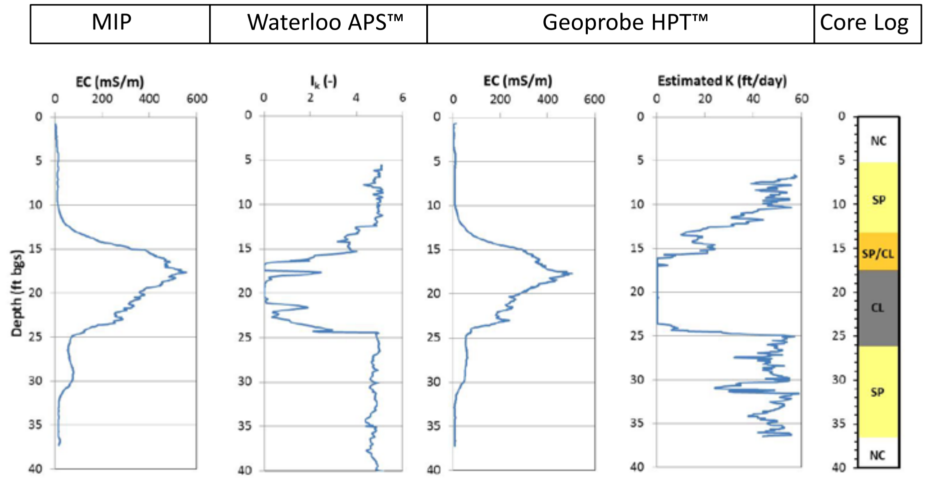


Figure 9. Composite plots of characterization data collected at location OU3-3 at former Building 106 source area.

(a) Composite plot with VOC concentration data; Shown from left to right are results from MIP, Waterloo$^{\text{APS TM}}$ (groundwater VOC concentrations and I_k data, and soil cores [soil VOC concentrations and geologic log]); (b) Composite plot of stratigraphic data. EC = electrical conductivity; ECD = electron capture detector and PID = photoionization detector; VOC = volatile organic compound; I_k = index of hydraulic conductivity.

Multiple potential lines of evidence for contaminant degradation were evaluated in an effort to determine if degradation in the low-k zone impacted the current soil concentrations, and as a consequence, the source history estimates. These included the presence/absence of parent compounds, the presence/absence of degradation products, the relative distribution of parent and compounds in the high-k versus low-k zones, concentration versus distance trends, geochemical conditions, biomarker data, and carbon isotope data. Collectively, these data supported a hypothesis that the majority of the degradation activity (which contributed the formation of significant amounts of by-products at downgradient locations) was occurring in the high-k zones and not the low-k zones. The carbon isotope data were particularly illustrative. At each location, the δ13C values for a particular constituent were generally higher (indicative of degradation) within the high-k zones than the values associated with the low k zone. This is true regardless of whether the shallow high-k zone (above the clay layer) or the deeper low-k zone (below the clay layer) is considered. The pattern also holds true for each of the constituents (PCE, TCE, cis-1,2-DCE, and VC). Because this means that the majority of the degradation products originated in the high-k zones before diffusing into the low-k zones, the consequence is that source history modeling can neglect low-k zone degradation for this site.

Source histories were generated for both PCE separately and PCE plus its degradation products at four distinct coring locations (plus a duplicate) using the Source History Tool. The modeling demonstrated that the locations at this source area were characterized by relatively constant source histories (see example for OU3-3 in Figure 10, see summary in Table 7). This was consistent with soil profiles that exhibited decreasing concentration with depth into the low-k zone, which is a distinguishing characteristic of continued loading over these low-k zones by a source strength at the interface that remains high relative to historical values. This constant source history trend held regardless of whether the parent compound (PCE) or parent compound plus degradation products were modeled.

The location-specific starting dates for contaminant loading (i.e., time zero for the source history estimate) matched expectations regarding plume arrival. The date of arrival increased moving downgradient, from 1962 at the near source location OU3-3 to 1992 at the far downgradient location OU3-6 (Figure 11). The modeling confirmed that while the source strength was constant at individual locations, the PCE concentration and the total CVOC concentration declined moving downgradient as a result contaminant degradation within the plume. This caused a stronger decline in concentrations than would be expected from physical processes (e.g., dispersion) only, as evidenced by the decreasing percentage of mass represented by the parent compound. The pattern is consistent with the increased contribution of degradation products to the total CVOC concentration moving away from the source. These results suggest that while an appreciable decline in the source strength cannot be verified, significant attenuation along the plume flowpath has occurred. Consequently, MNA may not an appropriate site remedy if source control is a requirement, but attenuation processes are clearly helping to maintain plume stability and reduce risk.

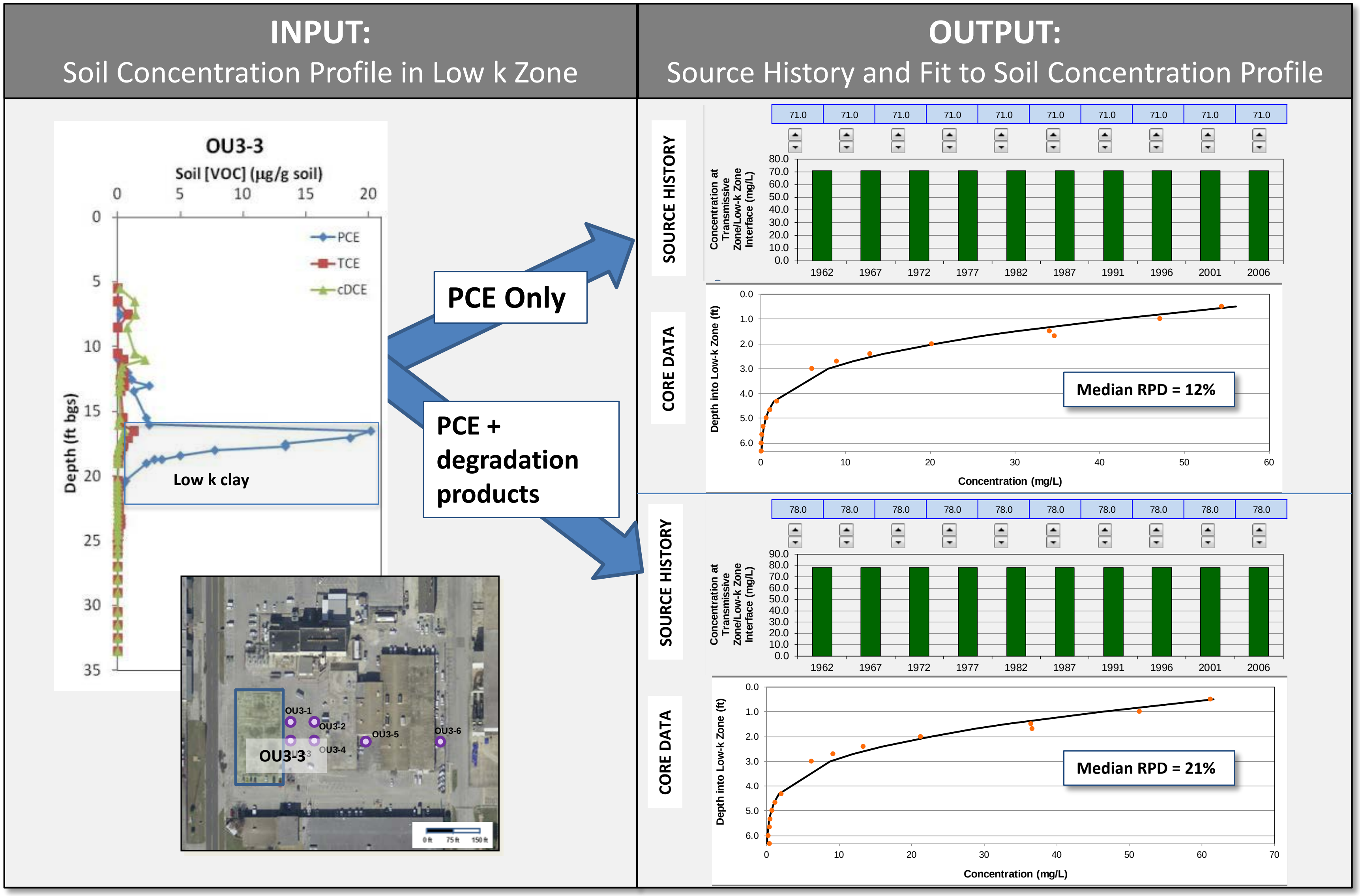


Figure 10. Source history modeling results for location OU3-3 at former Building 106 source area: chlorinated ethenes.

Table 7. Summary of source history trends for former Building 106 and Building 780 source areas.

Location	Compound(s)	Trend/Style of Source History	Median RPD (non-directional)	RMS Error (mg/L)	Ratio of RMS Error to Max Measured Concentration
Former Building 106 Source Area					
OU3-3	PCE	Constant	12%	2.9	5.3%
	PCE + Degradation Products	Constant	21%	2.3	4.7%
OU3-4	PCE	Constant	39%	7.5	19%
	PCE + Degradation Products	Constant	34%	7.9	17%
OU3-5	PCE	Constant	97%	1.2	5.3%
	PCE + Degradation Products	Constant	44%	1.7	5.5%
OU3-5-Duplicate	PCE	Constant	170%	3.2	18%
	PCE + Degradation Products	Constant	123%	1.9	6.5%
OU3-6	PCE	Constant	200%	0.45	14%
	PCE + Degradation Products	Constant	200%	0.68	5.1%
Building 780 Source Area					
OU3-9	TCE	Decreasing (Step/Exponential)	20%	1.27	30%
	TCE + Degradation Products	Decreasing (Step/Exponential)	7%	5.49	20%
	1,1,1-TCA + Degradation Products	Constant (for 1,1-DCA)	33%	0.075	8.3%
	1,2-DCA	Decreasing (Exponential)	15%	0.99	23%
OU3-10	TCE	Decreasing (Step/Exponential)	86%	3.25	30%
	TCE + Degradation Products	Decreasing (Step/Exponential)	28%	3.5	28%
OU3-11	TCE + Degradation Products	Decreasing (Exponential)	21%	0.036	16%

Notes: (1) For cases where degradation products were included, the concentration of each degradation product was converted to equivalent parent compound concentration on a molar basis; (2) RMS error = relative means square error; (3) Max measured concentration is the maximum measured soil concentration after converting to equivalent porewater concentration (mg/L).

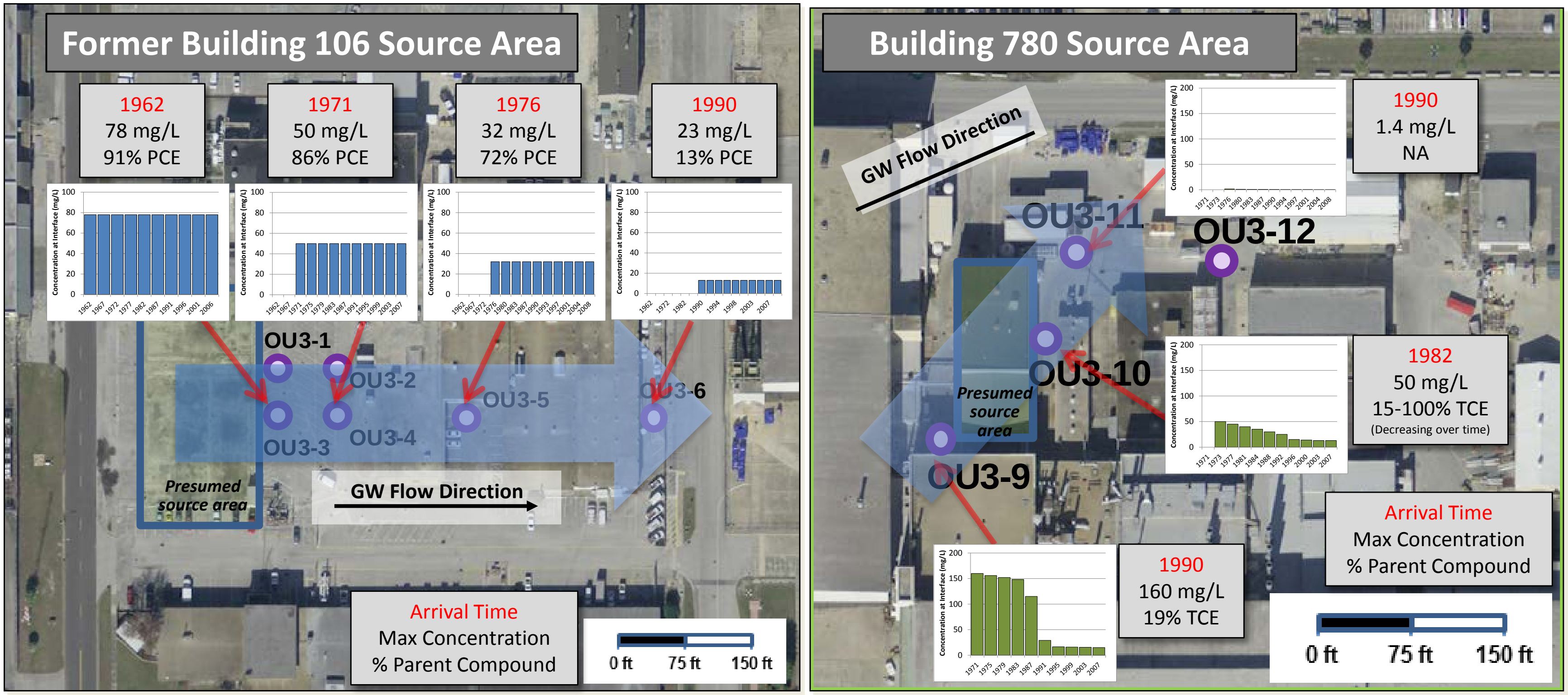


Figure 11. Overview of source history modeling results at former Building 106 source area (left panel) and Building 780 source area (right panel).

Dates reflect plumes arrival, concentrations reflect total chlorinated ethenes in the transmissive zone, and percentages reflect contribution of parent compound (PCE or TCE) to total chlorinated ethene concentration (at the specified date).

As a further evaluation of the representativeness of the source history estimates, a comparison was made to the available historical data from the site. Several monitoring locations in the area—primarily temporary piezometers—were sampled regularly during a several-year long period in early 2000s when interim remedial measures were being implemented. Three of these locations are within 20 ft or less of locations that were characterized as part of this project and screened in the aquifer above the interface with the clay layer (Figure 12). The predicted groundwater concentrations from these locations (i.e., the source history estimates) were then compared to the actual historical records. There was a reasonable level of consistency between the predicted and actual datasets. The source history modeling indicated that the source loading (groundwater concentration) was constant at each location. The actual groundwater data exhibit some fluctuation but demonstrated no clear temporal trends, and the median concentration values were within a factor of two of the (constant) values predicted from source history modeling at all locations (Table 8). The finding that the piezometer-based monitoring data are slightly lower than the predicted values may reflect the fact that piezometers were screened above the interface with the clay layer (typically from 9 to 14 ft bgs).

Table 8. Comparison of actual and predicted groundwater concentrations in the former Building 106 source area.

Location (temporary piezometer)	**Groundwater Concentration**	
	Actual (median over entire monitoring period)	**Predicted** (from nearest source history estimate)
PZ-1062	43 mg/L	71 mg/L
PZ-1066	29 mg/L	43 mg/L
PZ-1068	28 mg/L	32 mg/L

Notes: (1) Concentration is sum of constituents that were included in both datasets (PCE, TCE and cDCE); (2) Source history estimates from OU3-3, OU3-4, and OU3-5 were used to compare to data from PZ-1062, PZ-1066, and PZ-1068, respectively (see Figure 5.31); (3) Monitoring period was 2000-2004; (4) Source history modeling predicted constant source concentrations over time.

Building 780 Source Area: The second source area, Building 780 at OU3, housed a paint stripping and solvent recycling facility that reportedly operated in the 1970s and 1980s. Both chlorinated ethenes (primarily TCE) and chlorinated ethanes (1,1,1-TCA) were known to be have been used there. The only screening-level tool that was employed at this source area was Waterloo$^{APS\ TM}$, such that the data generated during the initial stage was limited to an I_k profile from four locations. The profiles suggested that a relatively distinct lower permeability interval was present starting at ~20 ft bgs at most locations, and extended to approximately 27 ft bgs. Below this interval, additional low-k zones of varying thickness were evident. The I_k data suggest that the Building 780 soils were generally more heterogeneous than those of the former Building 106 source area.

Similar to the other OU3 source area, CVOC concentration data collected at these locations confirmed that the majority of contaminant mass was present within the low permeability clays and in the transition zone immediately above (Figure 13). The primary differences at this source area are: (1) the presence of chlorinated ethanes in addition to chlorinated ethenes; (2) the maximum total CVOC concentrations are generally lower (10 mg/kg or less); and (3) peak concentrations of TCE and other compounds are frequently encountered within the low-k layer and not at the interface (consistent with source decay and back diffusion). At the farthest upgradient location, OU3-9, the concentration profile is characterized by significant levels of

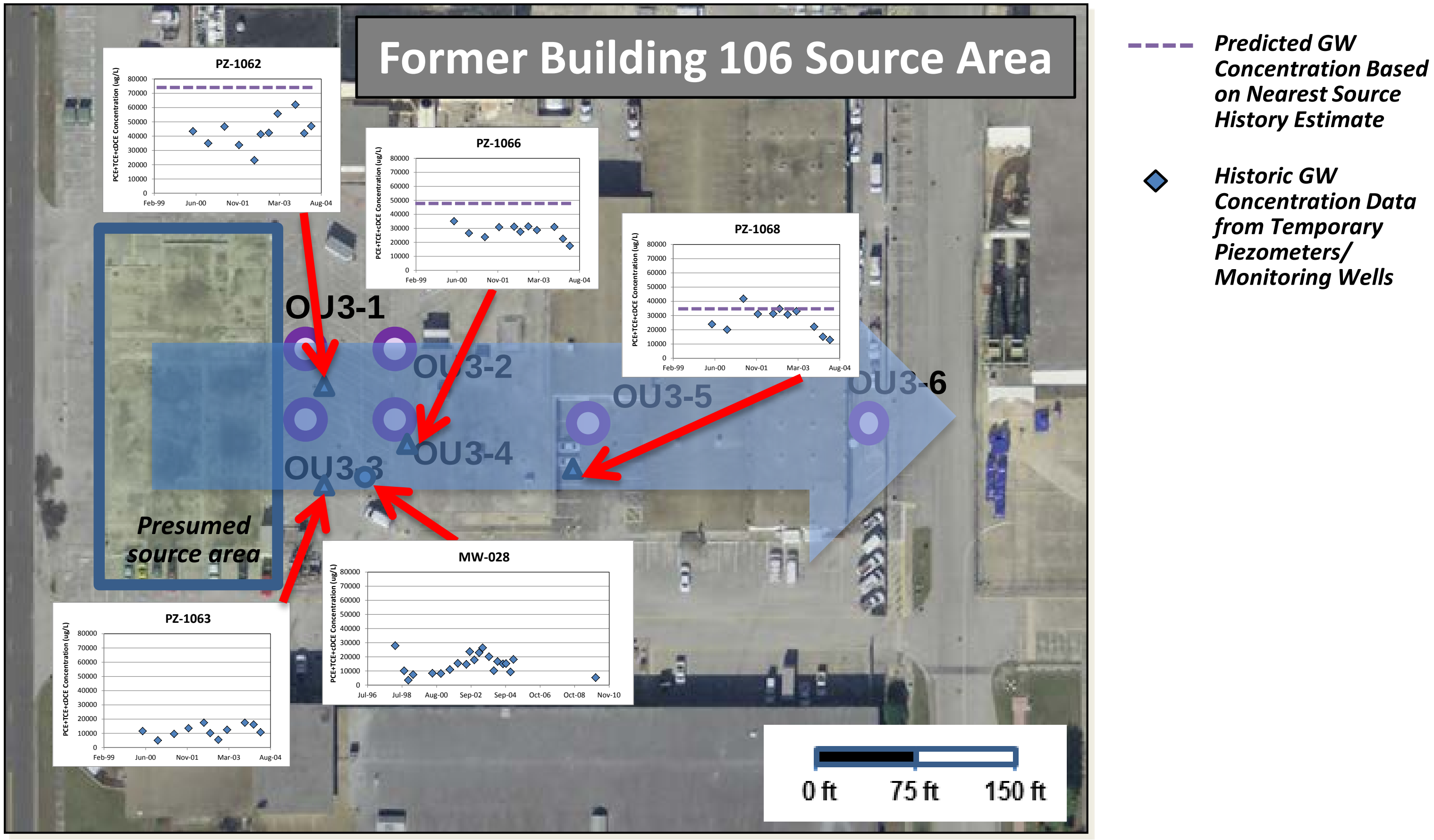


Figure 12. Comparison of source history modeling results at former Building 106 source area relative to historic data. Plots show historic concentration record, from monitoring points in the area, primarily temporary piezometers that were monitored during 2000 to 2004, as part of interim remedial measures. The dashed purple lines overlaid on the plots show the predicted groundwater concentrations based on the nearest source history estimates generated as part of this project. Data for PZ-1063 and MW-028 are included to illustrate that concentrations were generally moving perpendicular to the direction of groundwater flow; source history estimates were not overlaid on the plots for these locations because they are at least 30 ft from the nearest location where a source history estimate was generated.

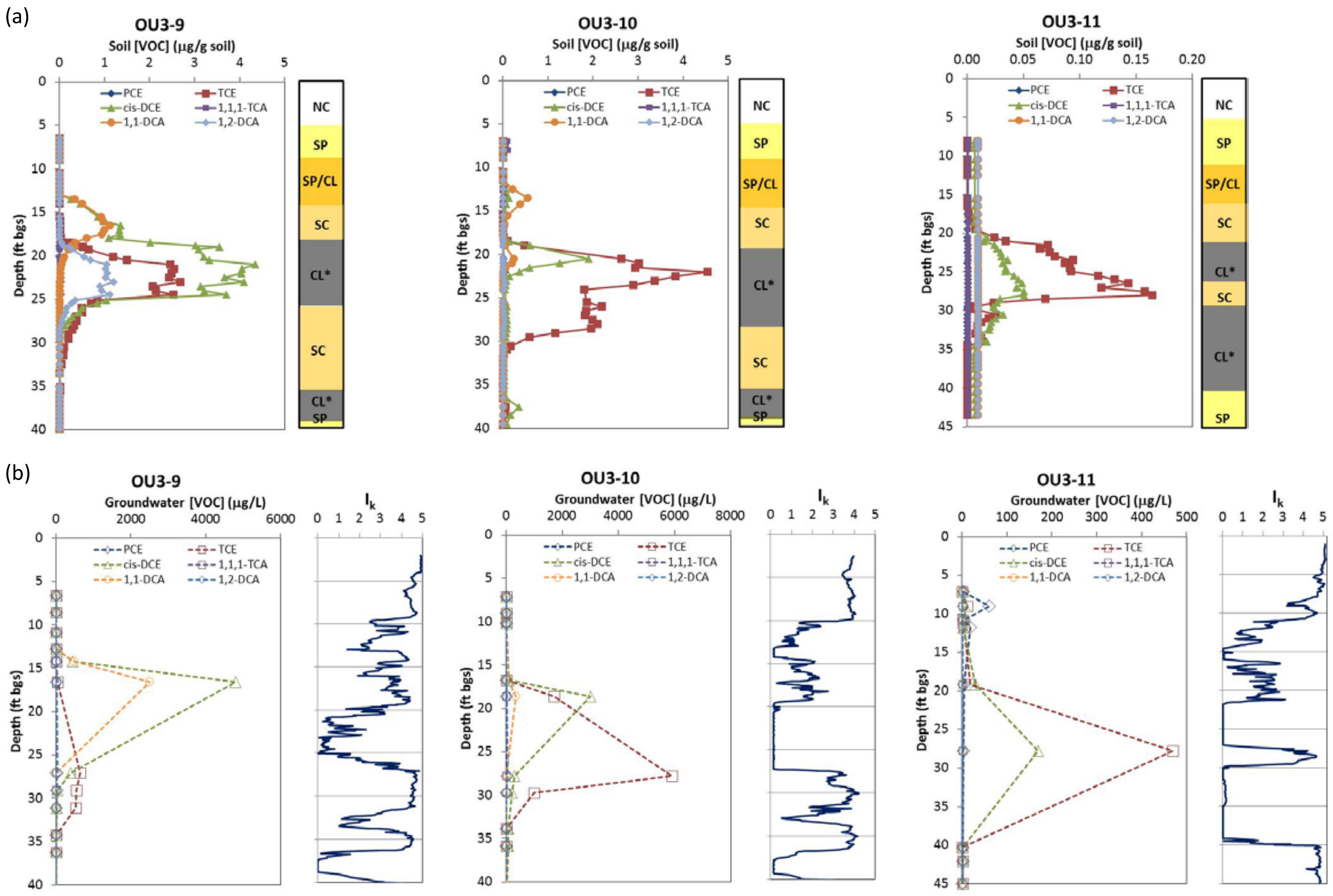


Figure 13. Soil and groundwater VOC concentrations from Building 780 source area locations.
Locations from left to right represent plume flowpath from near source (OU3-9) to downgradient plume (OU3-11). (a) Soil VOC concentrations and core logs; (b) Groundwater VOC concentrations and and I_k data from the Waterloo$^{APS\ TM}$.

TCE, DCE, and 1,2-DCA in the lower permeability zones. The overlying sandy layers contain much lower levels of DCE and negligible DCE and 1,2-DCA, but 1,1-DCA is present at a peak concentration of ~1 mg/kg. No 1,1,1-TCA was found. At the next location, OU3-10, 1,2-DCA is absent, but the vast majority of contaminant mass (primarily TCE with lower levels of DCE) is associated with the low permeability clay. 1,2-DCA is mostly confined to narrow clay-rich subintervals at 13 ft bgs and 21 ft bgs. The farthest downgradient location, OU3-11, is characterized by much lower concentrations (maximum total CVOC concentration of less than 0.3 mg/kg) and a lack of chlorinated ethanes. TCE is the primary contaminant and the peak concentration coincides with a depth below that of the primary clay unit where a thin sand layer (3 ft) was encountered. Again, 1,1,1-TCA was not encountered at these downgradient locations.

A comprehensive sampling and analysis program to evaluate low-k zone degradation was not completed at this site. However, based on the available lines of evidence (primarily the contaminant distribution and the lack of low-k degradation activity at the nearby Building 106 source area), it was assumed that degradation in the low-k zone at Building 780 was relatively negligible for the purposes of source history modeling.

The modeling demonstrated that the locations at this source area were characterized by declining source histories for TCE, i.e., source loading that changed gradually over time (see example in Figure 14, see summary in Table 7). At the near source location, OU3-9, a declining source history was also observed for 1,2-DCA, while a relatively constant source history was observed for 1,1-DCA. No 1,1,1-TCA (the parent compound for 1,1-DCA) was observed at OU3-9. Further, none of the chlorinated ethanes (1,1,1-TCA, 1,1-DCA, or 1,2-DCA) were observed at the other coring locations at this source area. Reasonable fits between simulated and measured soil concentration data were obtained at all locations, though there was a generally higher level of uncertainty when compared to the source history estimates from the other source area due to site heterogeneity.

With the exception of 1,1-DCA at OU3-9, soil profiles generally exhibited a maximum concentration at some distance (between 1 to 4 ft) into the low-k clay unit, with lower concentrations measured near the interface. This pattern is a distinguishing characteristic of a declining source strength over time, such that concentrations near the near the low-k interface have declined, changing the concentration gradient and causing diffusion out of the low-k zone, with higher remnant concentrations occurring deeper into the low-k zone and lower concentrations at the interface. These source history trends held regardless of whether the parent compound or parent compound plus degradation products were modeled.

For TCE, the starting dates for contaminant loading at each location (i.e., time zero for the source history estimate) were again consistent with expectations regarding plume arrival (Figure 11). The date of arrival increased moving downgradient, from 1971 at the near source location OU3-9 to 1976 at the far downgradient location OU3-11. The date for OU3-9 (1971) falls at the beginning of the presumed release period based on the solvent use at this site (1970s to 1980s).

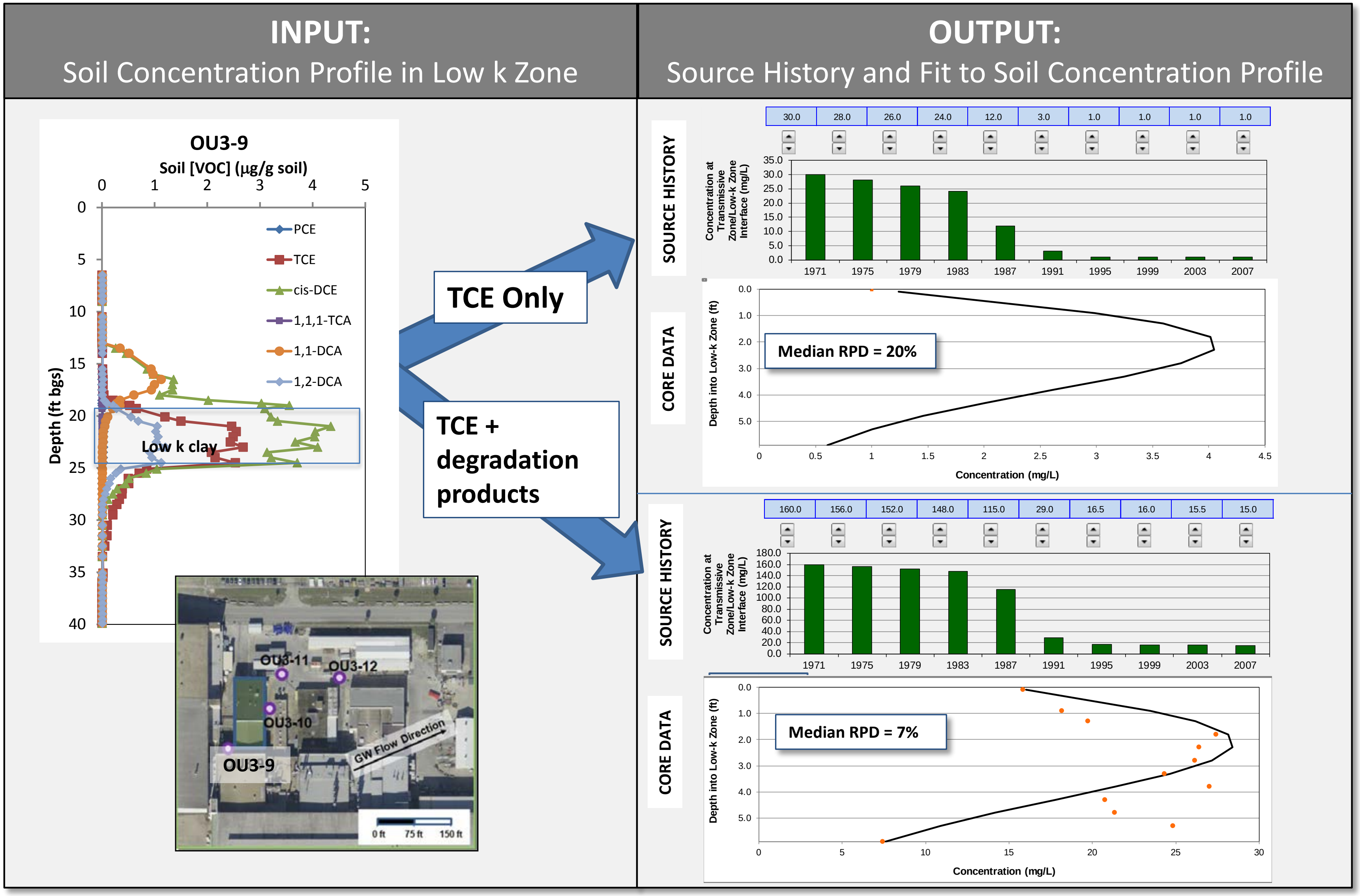


Figure 14. Source history modeling results for location OU3-9 at Building 780 source area: chlorinated ethenes.

Collectively, the results obtained at this source area suggest that significant source strength attenuation has occurred over time for TCE and 1,2-DCA. Potential contributing factors to this decline are active degradation process (particularly at the upgradient location) and interim remedial measures that were implemented at this site. 1,1,-DCA did not show a similar decline in source strength, but the lack of detection of the parent compound (1,1,1-TCA) combined with the lack of detection of any chlorinated ethanes at downgradient locations confirm that significant chlorinated ethane attenuation is occurring. Consequently, MNA may be an appropriate remedy for this site because the source history estimates provide evidence that these attenuation processes are controlling the source(s).

Model Sensitivity Analysis: To support the performance objectives, a comprehensive sensitivity analysis was performed using the datasets from one location at each of the two source areas. This was accomplished using the Monte Carlo sensitivity analysis that is a built-in component of the spreadsheet model.

Essentially, there are no changes to the source history trends that result from small changes (+/- 10%) to the input parameters. These changes may shift the soil VOC profile slightly, but do not significantly change the shapes of these profiles. As a result, there is no need to use a different source history trend to match the data that result from a small adjustment to a single parameter. Instead, improvements to the fit of the soil data can be achieved by slightly modifying other parameters to compensate. For example, a slightly higher porosity value can be compensated for by decreasing the concentration associated with the source history estimate. The main point is that the source history *trend* at a particular site is not—in and of itself—particularly sensitive to these parameters.

The Monte Carlo simulations provided another way of evaluating sensitivity by showing the impact of larger changes (+/- 50%) to one or more of these same parameters on the fits to the soil data (Figure 15). For the locations from both of the source areas, the style of the data remained the same regardless of the parameter changes. Of the parameters tested, porosity had the most significant influence. This is because the porosity has a direct effect on the conversion of soil concentrations to equivalent porewater concentrations, but also because it impacts transport calculations (as part of the retardation factor). The results also proved moderately sensitive to tortuosity (in the form of the apparent tortuosity factor exponent), particularly the depth of penetration. Neither the fraction of organic carbon nor the degradation half-life in the low-k zone had significant impacts on the results for these compounds. Larger changes in both of these parameters would be required to see any meaningful influence on the fits to the soil data. In particular, the results were not sensitive to the half-life until values fell below approximately 10 years. When degradation occurs at this magnitude (or greater), the result is lower concentrations throughout the soil profile and more limited penetration into the low-k layer.

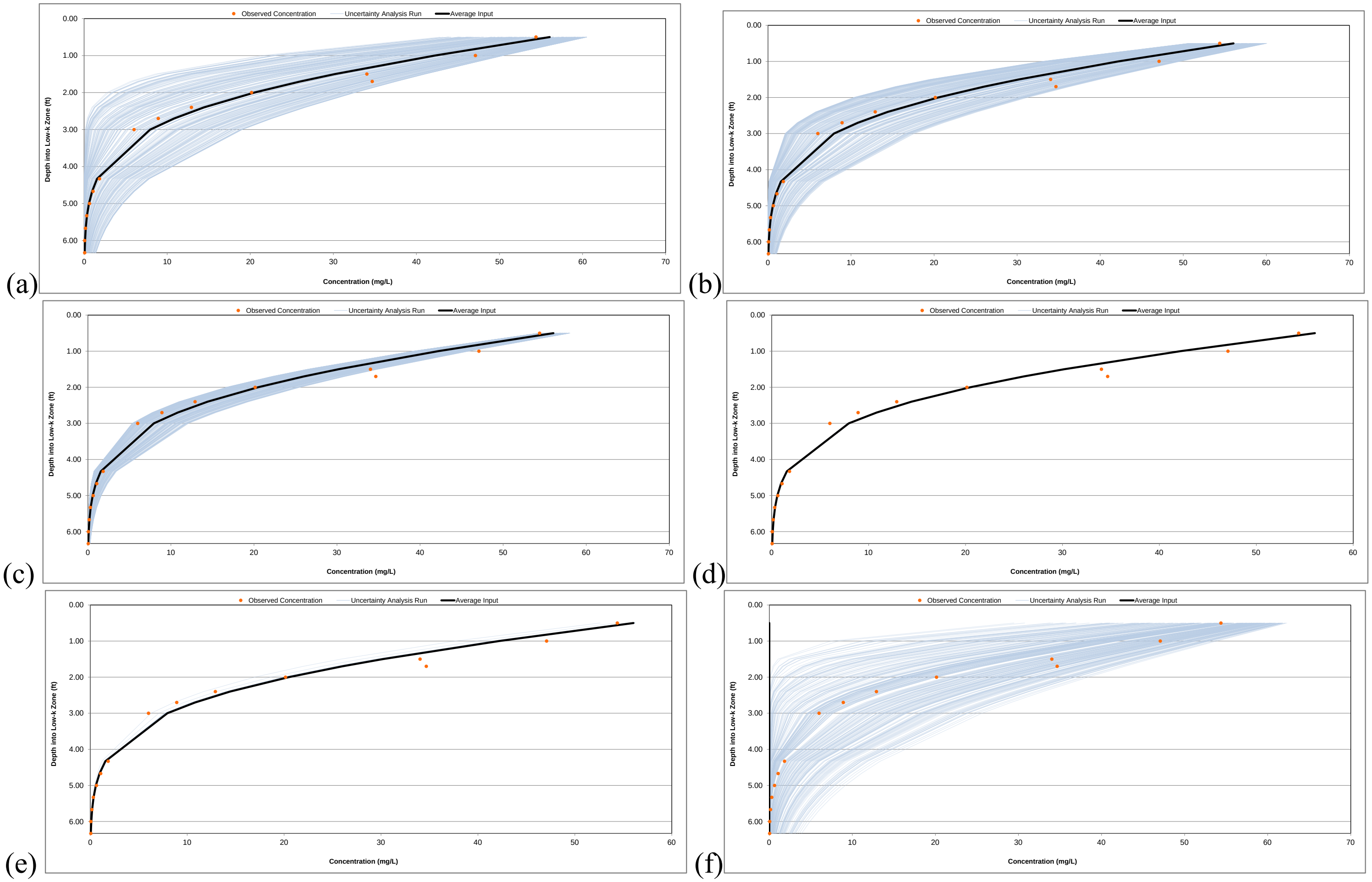


Figure 15. Monte Carlo sensitivity analysis for various input parameters for source history model at location OU3-3 at former Building 106 source area.

The following input parameters were adjusted using a lower limit of 50% and an upper limit of 150% (except where otherwise noted) to show the impact of these adjustments on the fit of the soil VOC concentration data versus depth: (a) porosity; (b) apparent tortuosity factor exponent; (c) fraction of organic carbon; (d) constituent half-life in low-k zone (lower limit 50%, upper limit 150%) (e) constituent half-life in low-k zone (lower limit 1%, upper limit 1000%); (f) all four parameters.

Source History Modeling for Other Sites: A review was completed to identify additional sites where high-resolution soil concentration datasets in low permeability zones were available for source history modeling using the project-generated Source History Tool ("Toolkit"). This included two different areas at a Connecticut site, a test site at Dover Air Force Base, a Florida site, and an Ontario site. For most of these sites, an estimate of the source history had already been generated using numerical modeling approaches. The objective of the evaluation described here was to compare whether these estimates are reasonably consistent with those generated with the Toolkit. For sites where there is no existing source history estimate, the objective was simply to evaluate whether the Toolkit-generated estimate was consistent with known site conditions.

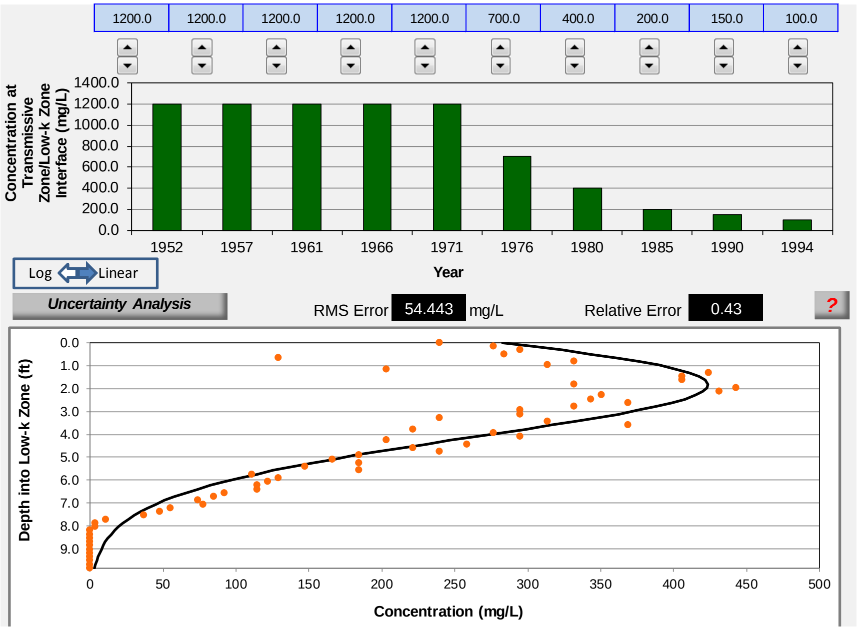
At all sites, modeling using the project Toolkit was able to consistently match available source history estimates and provide strong fits between measured and model-predicted soil data using the site-specific values for input parameters. In general, only minor improvements could be obtained by varying input parameters or modifying the assumed source histories.

An example is shown in Figure 16 for WCP-87 located within the source area of the Connecticut site described in Parker et al., 2004 and Chapman and Parker, 2005. Increasing the input value for the groundwater velocity from 1.5 cm/yr to 2.1 cm/yr slightly improved the source history estimate (based on the RMS error for each case), and the Toolkit used a more gradual decline in the source strength to produce a better fit than the step-decline in source strength that was presented in Parker et al (2004).

The results from this exercise: (1) demonstrated that the ability to incorporate a vertical advection into the 1-D model is a valuable component of the Toolkit; and (2) the fact that similarly good fits can be obtained with slightly different concentration versus time patterns illustrate the non-uniqueness of these solutions. For example, good fits were obtained using the Tool and simple two-step source strength patterns for the Dover Air Force Base locations (similar to those in Liu and Ball, 1999), but the Tool is not well-equipped to predict bi-modal patterns, such as those presented in other literature studies for this site (e.g., Liu and Ball, 2002). However, there is some question as to whether these more complex source history estimates are any more representative than the simpler ones; identifying which is more accurate would require site knowledge that is not available. Identifying the overall pattern (increasing versus decreasing source strength) should remain the priority.

Sampling and Analysis Methods Comparison: In support of the performance objectives for this project, soil concentration data were collected using several different methods to demonstrate their relative influence on data quality. This included methods that focused on sample collection/storage and sample extraction and analyses. The objective was to demonstrate the importance of certain steps in the data collection process, including those associated with the "UG methods" used extensively during this project (Gorecka et al., 2001).

WCP-87 Source History Estimate and Fit to Soil Data Using Project Specific Toolkit
(vertical groundwater velocity = 2.1 cm/yr)

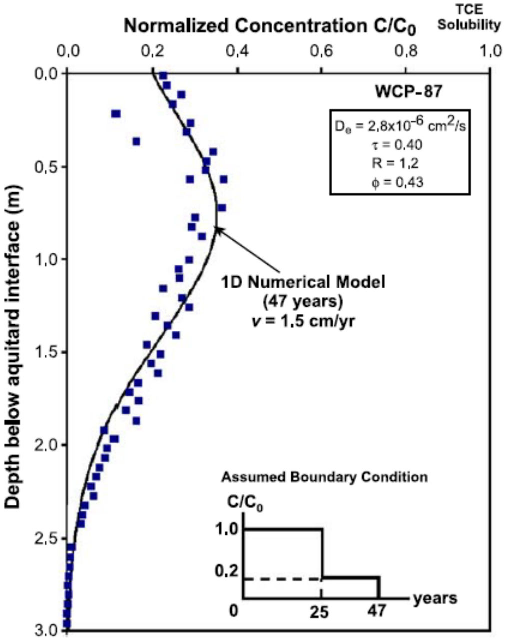


1952	1957	1961	1966	1971	1976	1980	1985	1990	1994
1200.0	1200.0	1200.0	1200.0	1200.0	700.0	400.0	200.0	150.0	100.0

RMS Error 54.443 mg/L

Relative Error 0.43

Fit to Soil Data in Parker et al (2004) Using Step-Decline Source History (shown in inset)



KEY FINDING: *Strong match achieved for WCP-87 using decreasing-style source history and input parameters described in Parker et al (2004). Slight improvement in fit was achieved by using higher gradual vertical groundwater velocity and more gradual decline in source strength as opposed to step decline used in Parker et al (2004).*

Figure 16. Source history estimate for location WCP-87 at Connecticut site (source area).
Site described in Parker et al. (2004).

All success criteria were met with the exception of the correlation between data collected using field-preserved soil samples analyzed at the UG lab and unpreserved Encore-sampled soils analyzed at a commercial lab. The latter data were negatively impacted by contaminant losses due to the lack of preservation and incomplete extraction, resulting in significant variability in the data (Figure 17). While this ultimately prevented the success criterion from being achieved, it more importantly highlighted that standard sample collection, handling, and analysis methods can lead to lower quality data. These results confirmed that the project-specific methods, including methanol preservation in the field, generate high-quality data and should be adopted when possible. A promising technique for "rapid field extraction" of soil samples (based on methods described in Dincutoiu et al., 2003) was also successfully validated by showing that similar data quality (relative to the baseline approach was obtained) (Figure 18).

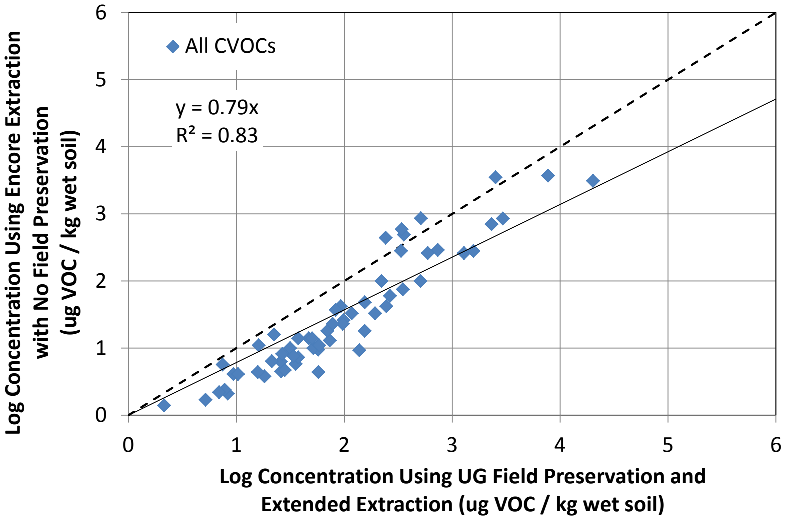


Figure 17. Comparison between CVOC concentration data collected with UG method and other methods: unpreserved encore samplers analyzed at commercial laboratory.
UG method (x-axis) involved collection using a UG metal coring device immediate field preservation in methanol, followed by extended "shake flask" extraction and analysis at UG laboratory. Solid line represents the best-fit regression line; dashed line represents 1:1 line through the origin.

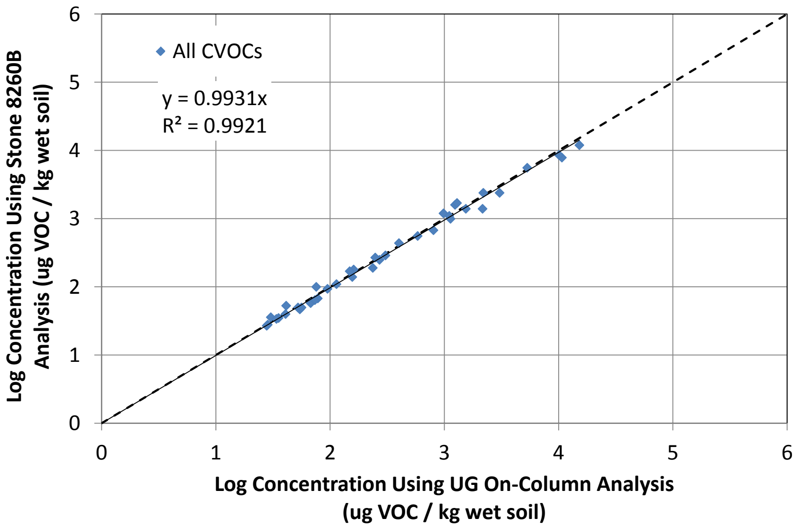


Figure 18. Comparison between CVOC concentration data collected with UG method and other methods: field duplicates at different analytical laboratories.

Both datasets generated using similar methods involving sample collection using UG metal coring device and rapid field extraction in methanol. Analyses completed at either a commercial laboratory (y-axis) or UG laboratory (x-axis). Solid line represents the best-fit regression line; dashed line represents 1:1 line through the origin.

This page left blank intentionally.

6.0 PERFORMANCE ASSESSMENT

A summary of the performance objectives for this demonstration, along with an overview of technology performance, was presented in Section 3. This section includes a detailed assessment of technology performance based on the quantitative data presented in Section 5. Following completion of the sampling and analysis program, the data were reviewed to determine whether the success criteria for each performance objective have been met. The evaluation of each individual performance objective is discussed below with references to relevant supporting results in Section 5.

6.1 RECONSTRUCT SOURCE HISTORIES – ACCURACY

Success Criteria Achieved? **PARTIALLY**

This performance objective was developed as a way to demonstrate the level of confidence that the Source History Tool ("Toolkit") was providing representative results. The assessment was based on the fit of the modeled soil concentration versus the measured field data for soil concentration. This was used because the source history results (C versus time data) cannot be compared to real site data in the absence of extended temporal monitoring records. Instead the comparison between the soil results (C versus depth data) was used as a surrogate for assessing accuracy or "goodness of fit."

Using the soil cores collected as part of this project, 17 different source history estimates were generated for the locations investigated using the project Toolkit. This included separate source histories for different parent compounds, as well as additional source histories for parent compounds alone and parent compounds plus degradation products. Only 7 of the 17 soil concentration profiles (measured and simulated) associated with these source histories met the criterion (median RPD $\leq$ 30%). This means that the performance objective was not met. The range of median RPD values was 10 to 200%. In addition to the seven that met the 30% limit, an additional four estimates had a median RPD of < 66% (i.e., measured and simulated values differed by a factor of two).

Based on a visual inspection of the data comparisons, it was clear that they passed a simple "eyeball test." For all of the cases, the simulated and measured soil data often appeared very similar in style throughout the entire low permeability interval. In particular, the shape of the curve was always captured, and concentrations near the interface and at the depth of maximum concentration were successfully representative. The poorer visual fits typically occurred deeper into the low permeability layers where concentrations approached zero.

The results of the RPD-based evaluation were not consistent with the visual inspection of the fits, in part because RPD is a limited metric in this case and in part because of the strictness of the criterion. Selecting a criterion that mandated that all of the source histories had to exhibit an RPD of $\leq$ 30% was unlikely to meet with success. This rigid criterion did not account for outliers. Even more importantly, it did not account for the inadequacies of RPD as a goodness of fit metric. This is particularly true when the concentration values approach zero, where even small absolute differences in concentration can result in very high RPD values. This is what occurred at deeper penetration depths into the low permeability layers, where the fits did appear poorer in many cases, but the actual magnitude of the differences (frequently much less than 1 mg/L) was relatively small.

To overcome these limitations, a secondary metric was developed to aid in the evaluation of this performance objective. The RMS error, which was generated during modeling runs to optimize the results, was well suited for these purposes. The RMS error represents the average error for the datasets, i.e., the average concentration difference between the measured and simulated data over the entire low permeability interval. This makes it a better representation of the error associated with a source history estimate, primarily because it is a single value that accounts for errors throughout the entire interval. Outliers will still impact the error calculation, but the error will be better distributed. The limitation in using the RMS error is that its magnitude is dependent on the magnitude of the datasets being compared, which limits its comparative value across datasets. However, simple normalization procedures can be used to improve its utility. For this project, the RMS error associated with each source history estimate was simply normalized by the maximum soil-based concentration measured throughout the entire depth interval at that location. To be consistent with the RPD-based metric, a limit of 0.3 (i.e., 30%) was set as the criterion for the RMS-based ratio, with success based on at least 75% of the ratios being below this criterion.

For the 17 source history estimates, the RMS error was generally low (0 to 8 mg/L, expressed as equivalent porewater concentration after converting soil concentration data). At any given location, the RMS value was generally an order of magnitude smaller than the maximum measured concentration. When the ratio of RMS error to maximum concentration was calculated, the value for 17 of 17 source history estimates were equal to or below the 30% limit. Consequently, the secondary criterion for this performance was successfully achieved. Using this more representative metric confirmed that the modeling results demonstrated reasonable accuracy, which matches the expectations based on simple "eyeball tests."

Additional source history modeling was completed for cores collected from several other sites that were not part of this demonstration project. For the 18 source history estimates generated using the Toolkit from these other sites, 12 of 18 met the criterion that the median RPD is ≤ 30%. Further, 18 of 18 estimates met the criterion that the ratio of RMS error to maximum measured concentration is ≤ 30%.

6.2 RECONSTRUCT SOURCE HISTORIES – PRECISION

Success Criteria Achieved? **YES**

To demonstrate that the source history method can generate precise and reproducible results, duplicate cores were collected at locations spaced approximately 1 m apart (OU3-5 within the Former Building 106 source area). Sub-samples were analyzed to establish the soil concentration profiles with the low permeability intervals, and then source history estimates were generated for each soil core profile. The goal was to achieve an RPD between paired data points for the two source histories (i.e., modeled source concentration at single time point versus source concentration at same time point using duplicate datasets) that was less than 30% for at least 70% of the paired data points. A second objective established the same trend for both source histories using a non-parametric statistical test (Mann-Kendall).

Both of the sub-objectives were successfully achieved. The source histories from the duplicates cores collected at OU3-5 exhibit the same constant trend over time. The initial concentrations at the two locations were slightly different (30 versus 32 mg/L) but both remained unchanged from the initial to final timepoints. As a result, a constant RPD of 7% was achieved for all 10 of 10 datapoints. This easily met the goal of 70% of the points achieving an RPD of less than 30%.

The success criterion for the second sub-objective was also met. Specifically, the Mann-Kendall non-parametric test confirmed both source histories exhibited stable trends that were statistically significant. Due to the uniformity of the two source histories, the trend analyses yielded identical Mann-Kendall tests statistics (0), Coefficient of Variation (0), and Confidence Factor (45.6%). Note that this type of non-parameteric test is well-suited for datasets that are not expected to be normally distributed, and the Mann-Kendall method in particularly is widely used in analyzing environmental data.

The results from these duplicate cores support the assumption that both the high-resolution soil concentration profiles, as well as the source histories generated from these profiles, are reproducible. It is natural to expect some differences at certain sites due to spatial subsurface heterogeneities. At NAS Jacksonville, the similarity between the duplicate datasets suggests that there was little to no evidence of heterogeneity at the scale associated with their respective locations (i.e., < 1 m apart).

6.3 RECONSTRUCT SOURCE HISTORIES – SENSITIVITY

Success Criteria Achieved? **YES**

The purpose of this performance objective was to evaluate the impact of small and large changes to various input parameters on the modeling results. While the number of input parameters is relatively limited, several may be unfamiliar to end-users of the spreadsheet tool (e.g., tortuosity). The Toolkit provides guidance for cases when site-specific values are not available, but it is still valuable to demonstrate how uncertainty in these parameters may impact the results.

Both sub-objectives that were developed as part of this evaluation were met. Small changes in tested parameters (tortuosity, porosity, degradation rates/half-life, organic carbon, release date) did not necessitate changes to the source history trend to fit the adjusted data. Similarly, larger changes to these same parameters did not result in a shift in the “style” of the soil concentration versus depth results. The latter evaluation relied on a Monte Carlo analysis that is a built-in component of the Toolkit. This allows for a visually-compelling assessment of how sensitive the modeling results are to changes in the individual parameters. Of the parameters tested, porosity has the greatest impact, in part because it impacts concentration estimates (i.e., conversion of soil concentrations to equivalent porewater concentrations) and contaminant transport (i.e., as part of the retardation calculation). Contaminant half-life had little influence until relatively low values were selected (< 10 yr) supporting the use of conservative half-life values in the absence of site-specific evidence of degradation in low-k zones.

Collectively, the results of this evaluation confirmed that the modeling results (source history trend and the style of the soil VOC profile) at a particular site are not particularly sensitive to these input parameters.

6.4 COMPARISON OF DATA COLLECTION METHODS

Success Criteria Achieved? **PARTIALLY**

The purpose of this performance objective was to confirm the high level of data quality obtained using the sampling and analysis procedures that were part of this project (i.e., the UG methods). Several sub-objectives were developed as part of this evaluation. Two of the three sub-objectives were successfully achieved.

For the split samples analyzed by different laboratories, the goal was that at least 70% of the sample pairs exhibited an RPD of 30% or less. Twenty-seven samples were included in this evaluation, resulting in 39 compound detections. For this set of 39 data pairs, 37 exhibited an RPD of less than 30%, meaning that the success criterion was achieved. The two that were above this limit represented marginal exceedences (30.03% and 42.6%). The median non-directional RPD of this dataset was 11.8%. A strong correlation was also obtained following linear regression of the split sample datasets (slope = 0.99, R2 = 0.99). These results confirm that there was a high level of precision between data generated at the UG laboratory and data generated at a standard commercial laboratory.

A total of 26 co-located soil samples were collected and analyzed using two different methods: (1) baseline method, consisting of Encore sample collection without preservation in the field followed by sample analysis at a commercial laboratory; and (2) the UG method, consisting of a metal soil sample with methanol preservation in the field followed by extended shake-flask extraction and analysis at the UG laboratory. The goal was to demonstrate limited variability between the two datasets (R2>0.9 based on linear regression). Linear regression of the datasets generated an R2 of 0.83, which was slightly lower than the objective of 0.9. It was clear based on the slope of the regression line (0.79) that the baseline method resulted in significant losses as a result of eliminating the field preservation step. This loss of volatiles was expected, but it appeared to also contribute to overall variability in the dataset comparison, as evidenced by the R2 value. These results provide a quantitative basis for the importance of preservation in reducing variability and limiting volatile losses. Because the split sampling results demonstrated the differences between lab analyses were minimal, it is clear that sample handling differences are a primary contributor to bias and variability in the data.

A final sub-objective was designed to show that the UG laboratories met standard acceptance criteria for precision. In this case, a limit of no more than 10% RSD between duplicate samples was chosen as the success criterion. Twenty-two field duplicates were collected and analyzed at the UG laboratory, with a resulting median RSD of 7% (covering 60 analyte detections). Therefore, the success criterion of a median RSD of 10% was achieved. For further evidence, the RSD of 95% of the sample pairs fell below this limit. The duplicate datasets also demonstrated strong correlation following linear regression.

6.5 EASE OF USE

Success Criteria Achieved? **PARTIALLY**

Success criteria for this objective were primarily evaluated qualitatively. As part of a larger objective to evaluate the time required to complete these methods, a specific criterion that was chosen involved completing all work at a site within a single mobilization. Due to project restrictions, the field work at NAS Jacksonville was completed in two separate mobilizations. In other words, screening-level characterization data (MIP, Waterloo$^{\text{APS TM}}$, Geoprobe HPT) were completed as part of an initial mobilization, and the coring was completed as part of a second mobilization. The reasons for this were logistical and not technical in nature:

a. The two source areas that were investigated are part of the same site (OU3 at NAS Jacksonville). This meant that the entire program was longer, and it was more logical to complete each characterization phase (e.g., Waterloo profiling) at both source areas before moving on to the next phase (e.g., soil coring).

b. Extra work was done in support of another project involving this PI group (SERDP ER-1740), specifically the inclusion of another screening-level characterization method (MIP).

As a result, multiple screening-level methods were used during the initial mobilization (including both MIP and Waterloo$^{\text{APS TM}}$). This made it too difficult to perform the soil coring during the same mobilization. Instead, the work was completed in two separate, shorter field programs.

Note that the all work related to this characterization approach was completed at two different source areas in approximately 3 weeks, or approximately 1.5 weeks per source area. For high-resolution characterization using multiple methods, this is a reasonable length. If these requirements had not existed and only a single site was being investigated, then it is certain that the field program could have been completed in a single mobilization. Therefore, the success criterion for this sub-objective would have been met under normal circumstances.

The bulk of the success criteria for this objective were met. Specifically, field personnel found the field characterization approach straightforward to implement. This included personnel who were relatively unfamiliar with specific methods. All were able to familiarize themselves rapidly and are confident that they could implement them again in future projects. Stone Environmental Inc. served as a technology specialist for the project, and they supplied and operate the Waterloo$^{\text{APS TM}}$, MIP, and Geoprobe HPT systems. However, a local contractor supplied the direct-push rig to used drive the tools and collect data. This drilling contractor had extensive experience with MIP but no experience in using some of the other data collection system. Regardless, the contractor had no problems successfully executing the work plan under the supervision of GSI Environmental, Inc. (GSI)/UG/Stone field personnel.

Collectively, the project demonstrated that the field characterization methods are easy to implement and can be completed in a timely manner.

6.6 SELECTION OF APPROPRIATE LOCATIONS

Success Criteria Achieved? **YES**

Success criteria for this objective were evaluated qualitatively. Of particular importance was evaluating whether site documentation was sufficient to select an appropriate test area at each site. At NAS Jacksonville, this was confirmed. While groundwater monitoring data was limited, extensive mapping of the sites with MIP had already been completed, and these data were useful in understanding site conditions and selecting locations for further investigation. For the purposes of this project, collecting additional characterization data was deemed unnecessary. Exact coring locations were based on screening-level characterization data that was a specific component of this project. This step is recommended for most sites, although there was an option to omit it at NAS Jacksonville OU3 given the availability of MIP data. However, the existing MIP data were approximately 5 years old and relying on these data could have resulted in some problems, including difficulty in calibrating model data (e.g., MIP provides no groundwater data) and potential inconsistencies between tool operating procedures.

The data generated for this project were consistent with existing site data, though the former (particularly the coring data) were purposely more quantitative.

The collection of soil concentration profiles at multiple locations per site also proved valuable in understanding source history and attenuation patterns. In particular, the selection of points along a downgradient flowpath provided confirmatory information about contaminant fate and transport (without having to rely on 2-dimensional modeling). Without multiple points per site, information may have been lost or subject to misinterpretation.

7.0 COST ASSESSMENT

A key objective of this project was to track costs associated with this technology demonstration in order to provide a basis for estimating costs of a full-scale implementation of the technology. Full-scale implementation costs were then incorporated into various scenarios and then compared to various alternatives. Specifically, an outcome-based cost comparison was made, using the data generated during this project to determine the viability of MNA versus more aggressive remedial options, and then determining the net cost difference between the various outcomes.

7.1 COST MODEL

As part of the demonstration, the cost of implementing the field program was carefully tracked and this cost data was used to estimate the cost that would be associated with implementing this methodology at a generic site. These are summarized in Table 9. Only those elements that are unique to this technology were included as part of the cost assessment and comparison. Other costs that are standard to characterization methods were tracked but not included in the cost assessment, along with costs that were incurred during this demonstration with the objective of obtaining a more comprehensive dataset than during a standard implementation.

Table 9. Cost model for field demonstration.

Cost Element	Tracked Data
Review of existing data and selection of locations	Costs are standard for site characterization but were tracked to demonstrate effort associated with typical application of this method • Personnel required and associated labor
Screening-level characterization (profiling)	Detailed stratigraphic pre-characterization is recommended • Unit costs for characterization per ft (including time for oversight, mobilization) Other costs are standard for baseline characterization
soil sampling and analysis	High-resolution soil sampling is required • Unit costs for sampling per ft (including time for oversight) • Unit costs for analysis per sample
well installation	Multi-level wells are optional (to track temporal trends in groundwater for comparison to model predictions) but were ultimately not used for this demonstration; no cost tracking
Data review and source history reconstruction (modeling)	Trained personnel for compiling and evaluating data • Personnel required and associated labor Use of publicly-available free software tool and guidance document
Material cost	No unique requirements anticipated; no cost tracking
Long-term monitoring	No unique requirements beyond option for additional monitoring wells; no additional cost tracking
Operations and maintenance costs	No unique requirements anticipated; no cost tracking
Waste disposal and decommissioning	No unique requirements; no cost tracking

7.1.1 Technology-Specific Cost Elements

The following descriptions focus on the cost elements that are specifically associated with the source history characterization approach. There are other cost elements associated with the various scenarios that were part of the scenario-based cost model, but these are not discussed separately here.

Review of Existing Data and Preliminary Selection of Locations: The approach developed as part of this project focuses on characterization of one or more locations at a chlorinated solvent site. In order to select generally favorable locations, a review of existing site data (to the extent that it is available) by experienced personnel is required prior to completing additional site work. The level of review is similar to that for conventional characterization efforts at a site, such that there are no unique requirements for the review proposed as part of the current project. Typical reviews would involve approximately 100 hours of labor and cost $10,000 to $20,000 depending on personnel used (mix of entry-level and mid-level engineers and/or geologists) and labor rates.

Screening-Level Characterization: The field demonstration included a comprehensive pre-characterization that incorporates Waterloo$^{\text{APS TM}}$ with groundwater sampling and analysis. In addition, MIP and HPT were completed at a number of locations to provide companion high-resolution characterization datasets as a basis for methods comparison (partially in support of SERDP ER-1740). Regardless of the type of characterization method that is selection, this step is important in fully understanding stratigraphic conditions at the test site, identifying locations for soil sub-sampling, and calibrating quantitative relationships between soil and groundwater concentrations. For the purposes of the cost comparison, Waterloo$^{\text{APS TM}}$ was used to provide a significant source zone characterization and detailed spatial information (particularly vertical) for permeability and target contaminants. For the demonstration, costs for labor (geologist/engineer for oversight) and implementation (subcontractor mobilization, day rate, sample analysis) were tracked and reported as total cost and included in the cost per vertical foot estimates that incorporated all steps in the characterization process (amortized over the number of locations characterized). The scale of the characterization efforts that are part of this project were similar to what would be proposed for full-scale implementation at other sites. As a result, there are no issues of scale.

Note that for this phase of the project, a higher number of personnel than would otherwise be used for a standard screening-level characterization, in part to orient various project team members to the site. Only those costs associated with a standard screening-level characterization were included for the scenario-based cost comparison.

Soil Sampling and Analysis: The proposed approach focuses on detailed soil sub-sampling, a task that is typically included as part of initial characterization efforts at impacted sites. However, the number of soil samples collected per location is higher than what would be typically collected during conventional soil characterization.

In terms of analytical requirements, the analyte list for this project included VOCs and organic carbon. The latter is infrequently included in analytical programs but is important for understanding sorption effects in low permeability zones. In addition, the project-specific analyte list included several parameters (carbon isotopes, biomarkers, geochemical indicators) that would not necessarily be part of a conventional application of this approach. These were added to provide more complete forensic information about contaminant degradation and were important for project objectives, but could be omitted from more general applications. As such, they were not included in the scenario-based cost comparison. Both the VOC analyses and organic carbon analyses were performed at UG using slightly modified techniques to improve extraction and detection limits. Note that UG operates in a manner similar to a commercial laboratory, charging on a per sample unit rate that depends on the analyses performed and the total number of samples anticipated. This facilitates cost tracking as well as cost comparisons to third-party commercial laboratories. In the end, the overall analytical unit costs for this project were similar to commercial labs.

The cost assessment tracked soil sampling and analyses costs on a per foot basis using real project costs. Costs also included labor (geologist/engineers for collecting samples and oversight), drilling subcontractors, and sample analyses. There are no issues of scale anticipated with these unit costs since the scale for this project is relatively close to what would be proposed for full-scale implementation at other sites.

Because this high-resolution soil sampling was considered a standalone or extra step in the scenario-based cost comparison, there was no direct comparison to costs associated with more conventional soil sampling and analyses, using a commercial laboratory and fewer samples per location. However, an estimate of unit costs associated with the project-specific method (for the scenario envisioned) was approximately $400 per vertical foot, while a rough estimate of the costs associated conventional soil sampling and analysis would be $100 to $200 per vertical foot (depending on the number of analytes).

Similar to the screening-level characterization step, this phase of the project utilized a higher number of personnel than would otherwise be used for a more typical implementation of this method. Only those costs associated with a typical high-resolution soil sampling program were included for the scenario-based cost comparison.

Well Installation: Multi-level monitoring wells are an option for the proposed characterization approach because they provide data for tracking temporal trends in groundwater and for checking/calibrating model predictions on source history. Installation of multi-level wells immediately after soil sub-sampling is more cost-effective because it can utilize the open borehole and available personnel. The number of sampling ports (i.e., number of discrete sampling depths) can be tailored to generate long-term groundwater data that compliment the soil/groundwater data obtained.

For the current demonstration, wells were not installed due to the short-term nature of the project. Consequently, costs were not included as part of the comparison. However, costs associated with well installation for the purposes of long-term monitoring were included in the scenario-based cost comparison.

Data Review and Source History Reconstruction (Modeling): The field data obtained as part of this approach must be reviewed and processed in order to generate source history estimates for sites involved. In terms of labor hours, the level of review is similar to what would be required for conventional characterization efforts, and thus will not be tracked separately. However, the actual reconstruction of source history will require personnel to use the spreadsheet tool ("Toolkit") that is one of the project deliverables. For the purposes of the cost assessment, real project costs were used though it was assumed that the individual did not need to undergo extra training (i.e., reading relevant sections of the guidance document and becoming familiar with how the model works). These trained personnel require several hours with the spreadsheet tool in order to generate the desired output data. As a result, the costs for this element were based on the labor required, and units reported on a per site basis. Note that both the guidance document and spreadsheet tool are intended to be publically available and thus free to all end-users, therefore will be no separate costs with their use beyond labor.

Material Cost: There are no additional material requirements for this characterization method. Therefore, there are no unique cost elements that were tracked.

Long-Term Monitoring: Additional long-term monitoring requirements are a potential cost depending on the option to install monitoring wells as part of characterization efforts or to confirm assumed trends over longer periods. Wells were not installed as part of this project, and therefore long-term monitoring was not a relevant cost element for the standalone application of this approach (i.e., Scenario 1). However, it was included as part of Scenarios 2 and 3, which consider for longer project lifetimes.

Operations and Maintenance: Because there are no permanent installations that are associated with the proposed technology, there are no additional operations and maintenance costs. Therefore, costs were not tracked as a unique element.

Waste Disposal and Decommissioning: For the technology, there were no additional costs associated with either waste disposal or decommissioning. These were not considered unique cost elements and, as a result, were not tracked separately.

7.1.2 Cost Scenarios

The cost elements described above were incorporated into several scenarios for comparing the costs associated with various uses of the source history approach.

- ***Scenario 1: Implementation of Source History approach as a standalone characterization method.*** In this case, it was assumed that the source history method was used to improve the conceptual site model but was not necessarily included as part of remedy selection process. As such, there is no comparison to alternative outcomes (e.g., MNA versus source remediation) and simply represents the costs associated with implementing the approach itself. This means it also represents a situation where the method was implemented but did not ultimately change the remedy selection.
- ***Scenario 2: Source History Leading to MNA versus Source Treatment.*** In this case, the source history method was implemented and resulted in a strong line of evidence for source attenuation over time. Consequently, MNA was approved as a site remedy moving forward. The alternative outcome was that source treatment

was required as an initial step. For the purposes of this cost assessment, in situ bioremediation was used as a representative in situ treatment technology, followed by MNA as a long-term management strategy.

- ***Scenario 3: Source History Leading to MNA versus Pump-and-Treat.*** This case also involves the use of the source history method as a strong line of evidence that supports the selection of MNA as a long-term management strategy to ultimately achieve site closure. The alternative outcome was that pump-and-treat was required as part of the long-term management strategy for the site.

7.1.3 Assumptions

The various assumptions used to develop the cost model and generate cost estimates for the various scenarios are described below:

- Site characteristics for the generic site used in this assessment were assumed to be similar to those at the former Building 106 source area at NAS Jacksonville. This ensured that the cost tracking performed for the project would be useful and representative. Consequently, the site was assumed to be contaminated with chlorinated solvents to depths of ~35 ft bgs. A low-k layer was present within the impacted zone and a high percentage of the low to moderate degradation activity observed near the source. The size of the source area and near downgradient plume was assumed to be 0.5 acre. The total volume requiring treatment was assumed to be 11,100 cubic yards.
- The source history characterization approach was assumed to include six locations for screening-level characterization (using Waterloo$^{\text{APS TM}}$) and four locations for high-resolution coring. These locations would be focused in the source area and near downgradient plume. Soil subsampling occurred within a 35-ft interval at a frequency of approximately one sample every 0.7 ft (averaged over low and high permeability zones).
- For those scenarios that involve comparison of outcomes (2 and 3), the costs associated with additional characterization efforts during the post-remedy selection period were not considered. For example, additional characterization may occur immediately prior to the start of in situ bioremediation to optimize the design. These costs can vary widely based on site-specific considerations and thus were not included in this cost assessment.
- MNA and pump-and-treat were tracked over a 30-year timeframe. This was based on normal expectations for site management rather than any assumptions about the actual remediation timeframe associated with these remedies. In part, this is because there are no specific remedial goals for the site used during this demonstration project at this time.
- Source treatment was assumed to reduce the remediation timeframe by 33% relative to MNA or pump-and-treat. This is based on the reduction of mass of approximately 90% following implementation of the treatment technology. This is a conservative estimate—in many cases, the impact of source treatment on

remediation timeframe can be minimal (Newell and Adamson, 2005). Further, the majority of mass is assumed to be present in the lower-k zones, such that it would be hard to target using conventional amendment delivery strategies.

- The treatment area for in situ bioremediation was assumed to focus on only the source (and not the downgradient plume). This area was estimated to be approximately 15,000 ft^2 (150 x 100 ft) with a 20 ft treatment thickness and require 150 injection points installed using direct-push rig (using 10 ft center spacing). Two direct-push rigs working in parallel were assumed. The design was assumed to rely on a two injections of a slow-release substrate (2 years apart), using an injection rate of 1 to 10 gpm to estimate the time required for injecting substrate and chase water (assuming manifold with ability to inject up to 10 wells at a time). Note that the labor requirements are based on an extended pumping period (45 days per event) due to the slow delivery rate assumed for the lower permeability layers, There are other delivery strategies that could be used, which may result in slightly different cost estimates. However, the design used for this model resulted in a unit cost of $38 per cubic yard (based on a treatment volume of approximately 11,000 cubic yards), which is consistent with typical unit costs for in situ bioremediation as a source zone depletion technology (McDade et al., 2005). It is our experience that higher unit costs are appropriate for settings with significant portions of the contaminants present in low permeability zones.
- The treatment area for a groundwater extraction system (i.e., pump-and-treat) was assumed to be similar to that for the in situ bioremediation option. A design pumping rate of 2 gpm was selected based on a similar rate that was targeted as part of the interim remedy for the Building 780 site from the late 1990s through the mid 2000s. Due to the low hydraulic gradient at the site, this pumping rate should be sufficient to capture the plume using 2 extraction wells (with only one operating at a time and the second as backup). Ex situ treatment using granular activated carbon (GAC) or air stripping was assumed, with discharge to the storm sewer at no additional cost (due to the low rates). The capital ($245,000) and operation and maintenance (O&M) costs (~$40,000 annually) were consistent with published values (USEPA, 2001) for small-scale systems.
- Long-term monitoring involved bi-annual (twice yearly) monitoring of eight wells for CVOCs. The monitoring period for MNA and pump-and-treat options were assumed to be 30 years, while the period for the in situ source treatment option was assumed to be 20 years.

7.2 COST ANALYSIS

This section provides a cost comparison for each of the three scenarios described above. The costs were compiled using a combination of the demonstration data, information from similar projects, vendor quotes, literature values, and the Remedial Action Cost Engineering and Requirements (RACER) software. Drillers and analytical laboratories that were part of the demonstration were used where applicable. The cost breakdown for each scenario is presented in Table 10 and summarized below.

Table 10. Summary of results of cost modeling.

	Scenario 1	**Scenario 2**		**Scenario 3**	
Cost Element	Source history characterization only (duration = 3 months)	Source history characterization followed by MNA (duration = 30 years)	In situ source treatment followed by MNA (duration = 15 years)	Characterization followed by MNA (duration = 30 years)	Pump-and-treat as sole remedy (duration = 30 years)
Task 1. Review of available data and location section	$8650	$8650	$0	$8650	$0
Task 2. Screening-level characterization	$35,100	$35,100	$0	$35,100	$0
Task 3. High-resolution soil coring and sampling	$49,300	$49,300	$0	$49,300	$0
Task 4. Modeling	$10,900	$20,400	$0	$20,400	$0
Task 5. Other characterization/ reporting in support of remedy selection/ design	$0	$0	$0	$0	$0
Task 6. Well installation (monitoring wells, injection wells, extraction wells)	$0	$29,450	$29,450	$29,450	$33,950
Task 7. Treatment system design and installation	$0	$0	$422,800	$0	$245,300
Task 8. Treatment system operations and maintenance	$0	$0	$0	$0	$1,235,000
Task 9. Long-term monitoring	$0	$387,000	$250,000	$387,000	$657,000
Task 10. Closeout and decommissioning	$0	$0	$0	$0	$30,000
Task 11. Final reporting	$35,800	$35,800	$35,800	$35,800	$35,800
Contingency (15%)	$20,963	$84,855	$110,708	$84,855	$335,558
Total cost	$160,713	$650,555	$848,758	$650,555	$2,572,608
Cost per location (4)	$40,178	NA	NA	NA	NA
Cost per foot	$1148	NA	NA	NA	NA
Life-cycle cost per cubic yard treated	NA	$59	$76	$59	$232

Notes: (1) See Section 7.1.2 for description of scenarios; (2) See Appendix S in the Final Report for full list of all cost input and output data; (3) Costs per location and per foot include only those locations that were cored; (4) Treatment volume is approximately 30,000 cubic yards.

Scenario 1: For the case when the source history method was applied at a single site at a scale similar to that used for this project, the standalone costs were approximately $161,000, or $1150 per vertical foot (cored). Essentially, this represents the approximate costs that were associated with implementing the method at former Building 106 source area in a standard manner (i.e., if the costs of extra project-specific analyses and personnel were excluded). Note that this method includes $35,800 related to the project-specific report, a cost that could likely be reduced from a generic application since reporting would be included as part of the modeling-focused data analysis step. This would reduce the unit costs to approximately $950 per vertical foot. Regardless of whether or not the results are used to support MNA as a remedy, the information can prove valuable for developing and/or refining the conceptual site model.

Scenario 2: For the case when the source history method was implemented (at a single site at a scale similar to that used for this project) to support MNA, the total life-cycle cost was $651,000 (or $59/cy). Approximately 26% of this was associated with the supplemental source history characterization method, while the remaining cost was associated with long-term monitoring and reporting. The total life-cycle cost associated with the alternative source treatment option was estimated to be $849,000 (or $76/cy) with ~50% of this cost related to the treatment itself and the remaining cost attributable to long-term monitoring and reporting. Therefore, the source history approach resulted in a total cost that was 23% lower than the source treatment option.

The primary benefit of the in situ treatment option is that it could result in a shorter remediation timeframe (and thus allows the land or groundwater resources to return to beneficial uses more quickly). However, there is considerable uncertainty regarding the performance of in situ bioremediation at a site where much of the mass is present in low permeability zones. Amendment delivery within these zones is challenging, and even if effective, may not significantly reduce the remediation timeframe relative to MNA. The MNA-based option has the advantage of lower cost, but it is also significantly less material-intensive and energy-intensive. Because there is a reduced labor requirement, it is also preferable from a health and safety perspective (i.e., lower risk of on-site accidents). Finally, the potential impacts on secondary water quality that are associated with in situ bioremediation are avoided with MNA.

Scenario 3: This scenario compared the case when the source history method was implemented (at a single site at a scale similar to that used for this project) to support MNA versus a site where pump-and-treat was required as a source control measure. For the MNA option, the total life-cycle cost was again $651,000 (or $59/cy) with approximately 26% related to the supplemental source history characterization method. The total life-cycle cost associated with the alternative pump-and-treat option was estimated to be $2,570,000 (or $232/cy) with approximately 50% of this cost related to long-term (30 year) o&m of the system. Therefore, the source history approach resulted in a total cost that was 75% less than the pump-and-treat option.

The MNA-based option represents a significant cost savings and has the advantage of demonstrating that a source is attenuating (and thus more likely to result in a stable or shrinking plume). In many cases, pump-and-treat is unlikely to change the remediation endpoint relative to MNA, so its costs will naturally increase the total costs associated with site management. Even in cases where the source history method indicates that the source loading has been relatively constant over time (i.e., as indicated for the former Building 106 area), the method can be used to confirm significant attenuation along the plume flowpath. Additional benefits of the MNA-based approach were described for Scenario 2, many of which are related to sustainability and safety issues. A final consideration is that once a pump-and-treat system is operating, it can be difficult to shut off from a political perspective. Because the costs of pump-and-treat accrue at a higher rate than MNA, this can result in much higher lifecycle costs if the project extends beyond the 30-year timeframe that was assumed for this simple model.

7.3 COST DRIVERS

The total costs of implementing this technology are primarily associated with the level of characterization performed at a site. The goal should be to collect sufficient data to meet site-specific objectives (i.e., line of evidence for MNA, improve conceptual site model). The key cost drivers are the number of locations characterized per site and the number of soil samples collected per location. These parameters were included in the following sensitivity analysis.

7.3.1 Sensitivity to Number of Locations Cored Per Site

The baseline scenario in the cost model used four locations for a relatively modest-sized source area where extensive characterization data were already available. At larger sites, additional investigation points may be necessary. Assuming all other inputs remained unchanged, the estimated costs associated with the number of cored locations are shown in Figure 19.

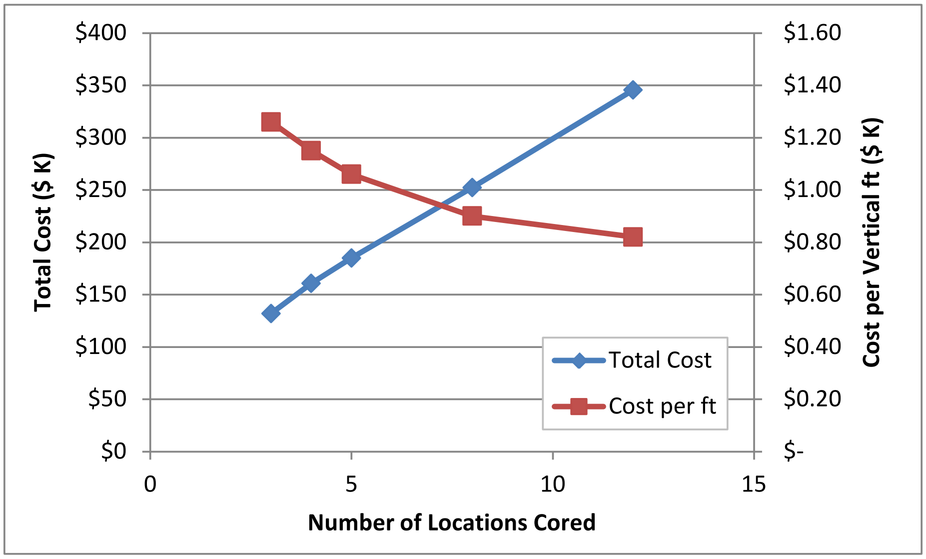


Figure 19. Sensitivity of cost of source history characterization approach to number of locations cored.

While total costs understandably increase if the number of locations is increased, there is an economy of scale that results in a decrease in the cost per vertical foot. Note that this sensitivity analysis assumed that there was also an increase in the number of locations where a screening-level characterization method was used (allowing for amortizing of mobilization fees). It also includes modeling and reporting costs, which increase modestly when additional locations are added to the characterization program.

7.3.2 Sensitivity to Number of Soil Samples Characterized Per Site

The baseline scenario in the cost model assumed that 50 soil samples were collected and analyzed per location, over a vertical interval of 35 ft. In addition, duplicates were collected at a frequency of one per 10 samples. This represents one sample per 0.7 ft of characterized soil (not including duplicates). For an interval containing low-k and high-k intervals of similar thickness, this is approximately equivalent to a 1-ft sampling frequency within the high-k interval(s) and a 0.5-ft sampling frequency within the low-k interval(s). Higher sampling frequencies may be desirable, especially in heterogeneous formations, and the sensitivity of the cost estimates to this parameter is shown in Figure 20.

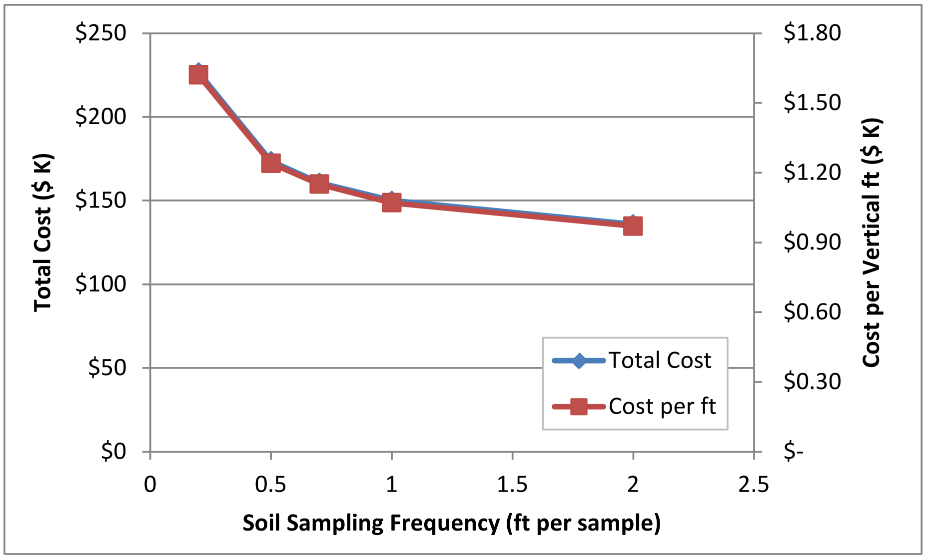


Figure 20. Sensitivity of cost of source history characterization approach to soil sampling frequency.

Both total costs and costs per foot increase at the same rate as the sampling frequency is increased. However, the curves in Figure 20 show that the rate of change is relatively flat. The most significant cost increase that results from increasing the number of samples per location is associated with sample analyses. Field labor costs increase slightly because it requires more time to process cores. However, the number of cores collected does not change, and thus drilling costs exhibit only marginal increases. Labor costs for modeling and reporting also change little.

Increasing the number of samples per location essentially increases the level of confidence that an accurate soil VOC profile is obtained, and thus the style of the source history can be estimated using the model. Because the incremental costs of higher sampling frequencies are relatively modest, it is recommended that sampling programs should use as high of frequency as project budget reasonably permit. Because diffusion-dominated penetration into low permeability units generally occurs within the first 5 to 10 ft, it is recommended that sampling frequencies of no more than 1 sample per ft are used to implement this approach. Further, sampling frequencies of 1 sample per 0.2 to 0.5 ft are highly preferable within the low permeability zones.

8.0 IMPLEMENTATION ISSUES

Key implementation issues are summarized below:

- Methods for collecting data to support this approach are already familiar and are unlikely to be subject to additional regulatory oversight. Implementation of this technology has no permitting concerns beyond what are already associated with subsurface drilling at a contaminated site (e.g., digging clearance, proper disposal of investigation-derived waste).
- High-resolution site characterizations of this nature are typically regulated the same way as other site investigations. Specifically, work plans would need to be approved in advance by the appropriate regulatory entity.
- The primary end-user concerns are associated with understanding how to collect site data and apply the source history model in an appropriate way, as well as understanding how to use results.
- The User's Manual generated from this project provides detailed guidance on both data collection and how to apply the software model. In terms of how to use these results, they should be considered a "line of evidence" for supporting MNA decision-making. For example, the output graphs from the source history model (concentration versus time in the high-k zone) are intended to be directly transferrable to any type of site report. This would include feasibility studies or remedy selection documents that would be submitted to a regulatory agency in support of MNA. The results are likely to be unfamiliar to a regulator, so a certain level of educating by the end-user may be necessary, as is the case with any line of evidence for MNA. The format for the model results, as well as the input parameters, were kept as simple as possible to help smooth this education process.
- However, it should be understood that the source history results from the model are not "unique," meaning that they are aimed at capturing the style of the source history as opposed to matching the "true" source history. The latter, understandably, cannot be established with 100% certainty regardless of the methods employed. First-time users of the software will appreciate that a certain level of knowledge about conditions at the site will be helpful in determining reasonable starting values for the input parameters. The demonstration project completed a sensitivity analysis to show the importance of many of these parameters. The model is relatively transparent, so it is easy for the user to see how changes in any one parameter can impact the results. It also should be understood that the model does not perform unconstrained guesses at the source history. In other words, the user must provide an initial guess at the release date, and then adjust accordingly based on the initial results. This trial-and-error approach is normal with this type of modeling effort and can lead to a better appreciation for how the input data affect the results.
- Finally, while not necessarily providing a unique solution, it can be equally valuable to use the model to understand what are not reasonable estimates of the source history for a particular location. This can be very useful for building a

proper conceptual site model, as well as for evaluating whether certain preconceived notions about a site are.

9.0 REFERENCES

Adamson, D.T., Chapman, S.C., Mahler, N., Newell, C., Parker, B., Pitkin, S., Rossi, M., and Singletary, M., 2013. Membrane Interface Probe Protocol for Contaminants in Low-Permeability Zones. Groundwater, DOI: 10.111/gwat.12085.

AFCEC, 2007. AFCEC Source Zone Initiative: Final Report. Prepared by Colorado State University and the Colorado School of Mines for the Air Force Center for Environmental Excellence, May 2007.

Chapman, S.W., and Parker, B.L., 2005. Plume persistence due to aquitard back diffusion following dense nonaqueous phase liquid source removal or isolation. *Water Resources Research*, 41, W12411, doi:10.1029/2005WR004224.

Dincutoiu, I, T. Górecki and B.L. Parker, 2003. A novel technique for rapid extraction of volatile organohalogen compounds from low permeability media. *Environmental Science & Technology*, 37(17): 3978-3984.

EPA, 2001. Cost Analysis for Selected Groundwater Cleanup Projects: Pump and Treat Systems and Permeable Reactive Barriers. Solid Waste and Emergency Response, US Environmental Protection Agency, EPA 542-R-00-013.

Górecka, M., T. Górecki and B.L. Parker, 2001. Automated cool on-column injection for highly sensitive determination of chlorinated solvents in soils and rocks. International Containment & Remediation Technology Conference and Exhibition. Orlando, Florida, June 10-13.

Liu, C., and Ball, W.P., 1998a. Analytical modeling of diffusion-limited contamination and decontamination in a two-layer porous medium. *Advances in Water Resources*, 21(4): 297-313.

Liu, C., Ball, W.P., and Ellis, J.H., 1998b. An analytical solution to one-dimensional solute advection-dispersion equation in multi-layer porous media. *Transport in Porous Media*, 30(1): 25-43.

Liu, C., and Ball, W.P., 1999. Application of inverse methods to contaminant source identification from aquitard diffusion profiles at Dover AFB, Delaware. *Water Resources Research*, 35(7): 1975-1985.

Liu, C., and Ball, W.P., 2002. Back Diffusion of Chorinated Solvent Contaminants from a Natural Aquitard to a Remediated Aquifer Under Well-Controlled Field Conditions: Predictions and Measurements. *Groundwater*, 40(2): 175-184.

Mackay, D.M., Wilson, R.D., Brown, M.J., Ball, W.P., Xia, G., and Durfree, D.P., 2000. A controlled field evaluation of continuous versus pulsed pump-and-treat remediation of a

VOC-contaminated aquifer: site characterization, experimental setup, and overview of results. *Journal of Contaminant Hydrology*, 41(1-2): 81-131.

McDade, J.M., McGuire, T.M., and Newell, C.J., 2005. Analysis of DNAPL source depletion costs at 36 field sites. *Remediation*, 15(2): 9-18.

McGuire, T.M., Newell, C.J., Looney, B.B., Vangelas, K.M., and Sink, C.H., 2004. Historical analysis of monitored natural attenuation: A survey of 191 chlorinated solvent sites and 45 solvent plumes. *Remediation*, 15(1): 99-112.

Newell, C.J., and Adamson, D.T., 2005. Planning-level source decay models to evaluate the impact of source depletion on remediation timeframe. *Remediation*, 15(4): 27-47.

Newell, C.J., Cowie, I., McGuire, T.M., and McNab Jr., W.W., 2006. Multiyear temporal changes in chlorinated solvent concentrations at 23 monitored natural attenuation sites. *Journal of Environmental Engineering*, 132(6): 653-663.

Parker, B.L, Cherry, J.A., and Gilham, R.W., 1994. Diffusive disappearance of immiscible-phase organic liquids in fractured geologic media. *Ground Water*, 32: 805-820.

Parker, B.L. and J.A. Cherry, 1995. Age-dating DNAPL source zones from diffusion profiles in low permeability layers. Session 141: Innovative Characterization of DNAPL Impacted Aquifers, Geological Society of America Abstracts and Program, p. A-403. New Orleans, LA, November 6-9.

Parker, B.L., Cherry, J.A., and Gilham, R.W., 1996. The effect of molecular diffusion on DNAPL behavior in fractured porous media. Chapter 12 in Dense Chlorinated Solvents and Other DNAPLs in Groundwater, J.F. Pankow and J.A. Cherry, Editors. Waterloo Press, pp. 355-393.

Parker, B.L., McWhorter, D.B., and Cherry, J.A., 1997. Diffusive loss of non-aqueous phase organic solvents from idealized fracture networks in geologic media. *Ground Water*, 35(6): 1077-1088.

Parker, B.L., Cherry, J.A., Chapman, S.W., and Guilbeault, M.A., 2003. Review and Analysis of Chlorinated Solvent Dense Nonaqueous Phase Liquid Distribution in Five Sandy Aquifers. *Vadose Zone Journal*, 2(2): 116-137.

Parker, B.L, Cherry, J.A., and Chapman, S.W., 2004. Field study of TCE diffusion profiles below DNAPL to assess aquitard integrity. *Journal of Contaminant Hydrology*, 74: 197-230.

Parker, B.L, Chapman, S.W., and Guilbeault, M.A., 2008. Plume persistence caused by back diffusion from thin clay layers in a sand aquifer following TCE source-zone hydraulic isolation. *Journal of Contaminant Hydrology*, 102: 86-104.

Pitkin, S. E., J.A. Cherry, R.A. Ingleton and M. Broholm (1999), Field Demonstration Using the Waterloo Groundwater Profiler. Groundwater Monitoring & Remediation, 19: 122-131. doi: 10.111/j.1745-6592.1999.tb00213.x

Sale, T., Newell, C., Stroo, H., Hinchee, R., and Johnson, P., 2008. Frequently-asked questions regarding management of chlorinated solvents in soils and groundwater. Developed for ESTCP (Project No. ER-0530).

Schwille, F., 1988. *Dense chlorinated solvents in porous media: model experiments*. Translated from German by J. F. Pankow, Lewis Publishers, Boca Raton, Florida, 146 pages.

Seyedabbasi, M.A., Newell, C.J., Adamson, D.T., and Sale, T.C., 2012. Relative contribution of DNAPL dissolution and matrix diffusion to the long-term persistence of chlorinated solvent source zones. *Journal of Contaminant Hydrology*, 134-135: 69-81.

Sudicky, E.A., Gilham, R.W., and Frind, E.O., 1985. Experimental investigations of solute transport in stratified porous media: 1) the non-reactive case. *Water Resources Research*, 21(7): 1035-1041.

Sudicky, E.A., 1986. A natural gradient experiment on solute transport in a sand aquifer; spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research*, 22(13): 2069-2082.

USGS, 1998. Ground-water hydrology and simulation of ground-water flow at Operable Unit 3 and surrounding region, U.S. Naval Air Station, Jacksonville, Florida. U.S. Geological Survey, Open File Report 9 8-68, 1998.

USGS, 2000. Fate and transport modeling of selected chlorinated organic compounds at Operable Unit 3 and surrounding region, U.S. Naval Air Station, Jacksonville, Florida. U.S. Geological Survey, Open File Report 00-255, 2000.

This page left blank intentionally.

APPENDIX A

POINTS OF CONTACT

Point of Contact	Organization	Phone Fax Email	Role In Project
Charles Newell	GSI Environmental Inc. 2211 Norfolk Suite 1000 Houston, TX 77098	Phone: (713) 522-6300 Fax: (713) 522-8010 Email: cjnewell@gsi-net.com	GSI PI
David Adamson	GSI Environmental Inc. 2211 Norfolk Suite 1000 Houston, TX 77098	Phone: (713)522-6300 Fax: (713) 522-8010 Email: dtadamson@gsi-net.com	GSI Co-PI/PM
Beth Parker	University of Guelph 50 Stone Road East School of Engineering Guelph, Ontario N1G 2W1, Canada	Phone: (518) 824 4120 Email: bparker@uoguelph	UG Co-PI
Steven Chapman	University of Guelph 50 Stone Road East School of Engineering Guelph, Ontario N1G 2W1, Canada	Phone: (506) 454-2173 Email: schapman@uoguelph	UG Co-PI
Tom Sale	Colorado State University B001 Engineering Research Center Fort Collins, CO 80523	Phone: (970) 491-8413 Fax: (970) 491-8224 Email: tsale@engr.colostate.edu	CSU Co-PI
Andrea Leeson	ESTCP Office 4800 Mark Center Drive, Suite 17D08 Alexandria, VA 22350	Phone: (571) 372-6398 Email: andrea.leeson.civ@mail.mil	ESTCP Program Manager Environmental Restoration

This page left blank intentionally.

ESTCP

ESTCP Office
4800 Mark Center Drive
Suite 17D08
Alexandria, VA 22350-3605

(571) 372-6565 (Phone)

E-mail: estcp@estcp.org
www.serdp-estcp.org