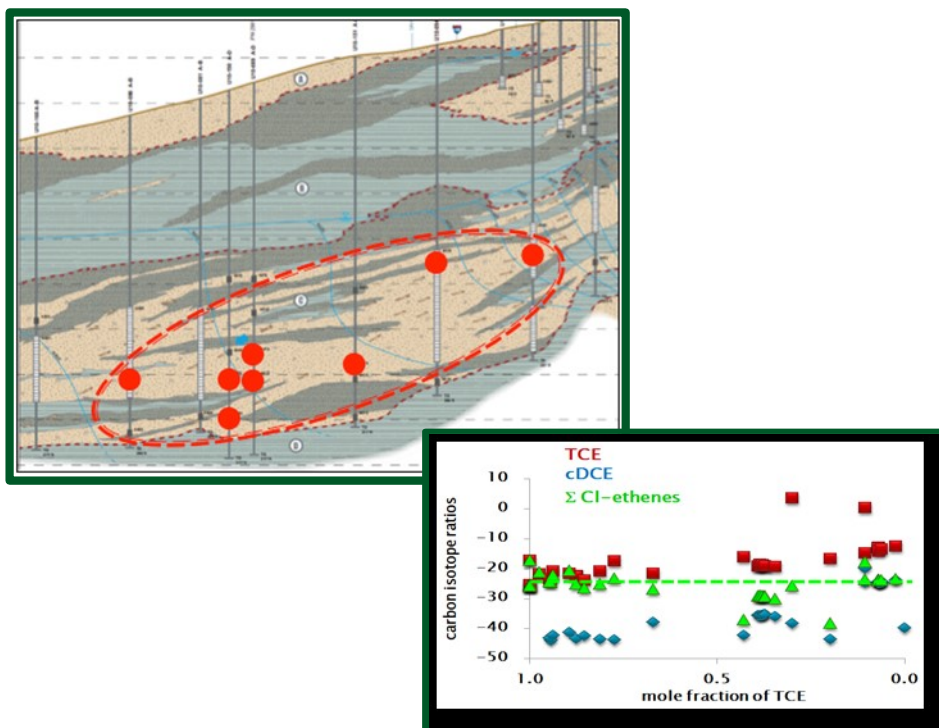


ESTCP Cost and Performance Report

(ER-201029)



Integrated Stable Isotope – Reactive Transport Model Approach for Assessment of Chlorinated Solvent Degradation

May 2016

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



ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

Page Intentionally Left Blank

This report was prepared under contract to the Department of Defense Environmental Security Technology Certification Program (ESTCP). The publication of this report does not indicate endorsement by the Department of Defense, nor should the contents be construed as reflecting the official policy or position of the Department of Defense. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the Department of Defense.

Page Intentionally Left Blank

REPORT DOCUMENTATION PAGE				Form Approved OMB No. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.					
1. REPORT DATE (DD-MM-YYYY) 16-05-2016		2. REPORT TYPE Cost and Performance Report		3. DATES COVERED (From - To) Jan. 2011 - Feb. 2016	
4. TITLE AND SUBTITLE Integrating Stable Isotope Analysis and Reactive Transport Modeling for Assessing Chlorinated Solvent Degradation Cost and Performance Report				5a. CONTRACT NUMBER W912HQ-10-C-0060	
				5b. GRANT NUMBER ER-201029	
				5c. PROGRAM ELEMENT NUMBER	
6. AUTHOR(S) Kuder, Tomasz; Philp, Richard, P.; vanBreukelen, Boris; Thouement, Heloise; Vanderford, Mindy				5d. PROJECT NUMBER ER-201029	
				5e. TASK NUMBER	
				5f. WORK UNIT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) University of Oklahoma, 100 E. Boyd St., SEC 810 Norman, OK 73019-2115 Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands VU University Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands GSI Environmental, Inc., 2211 Norfolk, Suite 1000 Houston, TX 77098				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) Environmental Security Certification Program (ESTCP) 4800 Mark Center Drive, Suite				10. SPONSOR/MONITOR'S ACRONYM(S) ESTCP	
				11. SPONSOR/MONITOR'S REPORT NUMBER(S) ER-201029	
12. DISTRIBUTION / AVAILABILITY STATEMENT					
13. SUPPLEMENTARY NOTES					
14. ABSTRACT This document presents the results of ESTCP Project ER-201029 Integrated Stable Isotope - Reactive Transport Model Approach for Assessment of Chlorinated Solvent Degradation. The objective of this guidance is to help site managers apply a Reactive Transport Modeling (RTM) approach for improved Compound-Specific Isotope Analysis (CSIA) data interpretation and to use models to estimate more accurate attenuation processes for chlorinated solvents. The quantification of various destructive and transport processes and how they contribute to plume size and longevity may help extend Monitored Natural Attenuation (MNA) remedies to sites that have, heretofore, not been able to apply this important technology. In comparison with traditional data interpretation, the approach presented has several important benefits: (1) improvement of a conceptual site models by identification and quantification of prevalent attenuation pathways and identification of secondary inputs from DNAPL dissolution or non-degradative sinks such as sorption or volatilization, diffusion or dispersion. (2) a more accurate assessment of degradation of the parent contaminant; (3) quantitative assessment of the net degradation/accumulation of the dechlorination intermediates.					
15. SUBJECT TERMS Compound-specific isotope analysis, reactive transport modeling, groundwater, chlorinated solvents					
16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT UU	18. NUMBER OF PAGES 36	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER (include area code)

Page Intentionally Left Blank

COST & PERFORMANCE REPORT

Project: ER-201029

TABLE OF CONTENTS

	Page
EXECUTIVE SUMMARY	ES-1
1.0 INTRODUCTION.....	1
1.1 BACKGROUND.....	1
1.2 OBJECTIVE OF THE DEMONSTRATION	2
1.3 REGULATORY DRIVERS.....	2
2.0 TECHNOLOGY.....	3
2.1 TECHNOLOGY DESCRIPTION.....	3
2.1.1 Compound-Specific Isotope Analysis (CSIA)	3
2.1.2 Reactive Transport Modeling (RTM).....	5
2.1.3 Technology Development	7
2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY	7
3.0 PERFORMANCE OBJECTIVES	9
4.0 SITE DESCRIPTION.....	11
4.1 SITE LOCATION	11
4.2 SITE GEOLOGY/HYDROGEOLOGY	11
4.3 CONTAMINANT DISTRIBUTION	12
5.0 TEST DESIGN.....	15
5.1 CONCEPTUAL EXPERIMENTAL DESIGN	15
5.2 BASELINE CHARACTERIZATION	16
5.3 LABORATORY STUDY RESULTS	16
5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS.....	16
5.5 FIELD TESTING	16
5.6 SAMPLING AND ANALYSIS METHODS.....	16
5.7 SAMPLING RESULTS	17
6.0 PERFORMANCE ASSESSMENT	21
6.1 SOFTWARE DEVELOPMENT.....	21
6.2 DEMONSTRATION OF CSIA-RTM FOR THE FIELD SITE ASSESSMENT	22
6.2.1 Classic Evaluation of CSIA Data	22
6.2.2 Model Approach.....	25
6.2.3 Modeling Results.....	27
6.3 CSIA-RTM TO IMPROVE CSM OF THE STUDY SITE	31
6.3.1 The Value of CSIA/RTM to Resolve Complex Attenuation Pathways	31
6.3.2 Degradation Constants	32
6.3.3 Summary of the Refined CSM for Demonstration Site.....	34

TABLE OF CONTENTS (Continued)

	Page
7.0 COST ASSESSMENT	37
7.1 COST MODEL.....	37
7.2 COST DRIVERS.....	37
7.3 COST ANALYSIS	38
8.0 IMPLEMENTATION ISSUES.....	39
9.0 REFERENCES	41
APPENDIX A POINTS OF CONTACT.....	A-1

LIST OF FIGURES

	Page
Figure 2.1. Isotope Ratios for a CE Subjected to Dilution Versus Degradation Processes.....	3
Figure 2.2. Spatial Dimensions of RTM.....	5
Figure 4.1. Hill AFB OU10 Site Location.....	11
Figure 4.2. Cross-Section of the Aquifer, NE-SW Transect (CH2MHILL, 2009).....	12
Figure 4.3. Map of the Operable Unit (OU) 10.	13
Figure 5.1. CEs Concentration and C Isotope Ratios, Cross-Section View	18
Figure 6.1. Calibration Results for the C, Cl, and H isotope Fractionation Model.	21
Figure 6.2. 2D-CSIA Plots, TCE in the Shallow Plume.....	24
Figure 6.3. 2D-Element CSIA Plots, TCE in the Deep Plume.	25
Figure 6.4. C Isotope Ratios for TCE (red circles), cDCE (light blue squares) and tDCE (dark blue squares), Versus the Groundwater Age.....	26
Figure 6.5AB. Scenario 1 (Table 6.1): Model for TCE Reductive Dechlorination only, cis-DCE Stall.....	29
Figure 6.6AB. Scenario 2 (Table 6.1): DCE Oxidation Model (blue dashed, $k_{DCE} = 0.2 \times k_{TCE}$; blue solid, $k_{DCE} = 1 \times k_{TCE}$) versus DCE Reductive Dechlorination Followed by Quick VC Oxidation Model (red dashed, $k_{DCE} = 0.2 \times k_{TCE}$; red solid, $k_{DCE} = 1 \times k_{TCE}$).....	30
Figure 6.7. First-Order Integral Degradation Rate Constants for TCE (circles), DCE (grey bars), and CEs Mineralization (black bars).	33
Figure 6.8. Estimation of Cumulative CEs Mineralization, Comparing Observed Values (markers) with the Modeled Contour Lines of the Percentage of Total CEs Mineralization. ...	34

LIST OF TABLES

	Page
Table 2.1. Information Required to Construct a Reactive Transport Model	6
Table 2.2. Calibration Process for Various Models.....	7
Table 3.1. Performance Objectives.....	9
Table 5.1. Analytical Methods for Sample Analysis	17
Table 5.2. Project Sampling Program, Analytes and Analyses	17
Table 6.1. Description of the Simulation Scenarios	26
Table 7.1. Cost Model for a CSIA/Model Application.....	37
Table 7.2. Cost Analysis: CSIA/RTM vs. MNA	38

ACRONYMS AND ABBREVIATIONS

δ	Delta
AFB	Air Force Base
C	Carbon
CE	Chlorinated Ethenes
C-IMB	Carbon Isotope Mass Balance
Cl	Chlorine
CSIA	Compound-Specific Isotope Analysis
CSM	Conceptual Site Model
cVOC	chlorinated Volatile Organic Compounds
DCE	Dichloroethene
DNAPL	Dense Non-aqueous Phase Liquid
DO	Dissolved Oxygen
DoD	Department of Defense
ESTCP	Environmental Security Technology Certification Program
ETH	Ethene
GC	Gas Chromatography
GC-IRMS	Gas Chromatography Isotope Ratio Mass Spectroscopy
H	Hydrogen
IRMS	Isotope Ratio Mass Spectrometry
LCS	Laboratory Control Samples
MNA	Monitored Natural Attenuation
OU	Operable Unit
PCE	Tetrachloroethene (Perchloroethene)
PT	Purge and Trap
QAQC	Quality Assurance Quality Control
RD	Reductive Dechlorination
RTM	Reactive Transport Modeling
TCE	Trichloroethene
USEPA	U.S. Environmental Protection Agency

VC	Vinyl Chloride
VOA	Volatile Organic Analyte
VOC	Volatile Organic Compound

ACKNOWLEDGEMENTS

This report presents the results and conclusions from a collaborative project between researchers at University of Oklahoma (OU), VU University Amsterdam (Vrije Universiteit Amsterdam in Dutch) and Delft University of Technology, the Netherlands, and GSI Environmental, Inc. (GSI). This demonstration project was funded by the Environmental Security Technology Certification Program (ESTCP), with the main goal of demonstrating the utility of combining Compound-Specific Isotope Analysis (CSIA) and Reactive Transport Modeling (RTM) to quantify and strengthen support for Monitored Natural Attenuation (MNA) remedies for groundwater contaminated with chlorinated ethene (CEs) constituents.

Investigators for this project included Dr. Paul Philp (Principal Investigator, OU), Dr. Tomasz Kuder (Co-Principal Investigator, OU), Dr. Boris van Breukelen (VU), and Dr. Mindy Vanderford and Dr. Charles Newell (GSI). The modeling tool that was generated as part of this project was developed by Boris van Breukelen, Philip Stack, and Héloïse Thouement. The microcosm experiment was modeled as part of a research project of Philip Stack. The Hill Air Force Base (AFB) Operable Unit (OU) 10 site case study was evaluated as part of the dissertation of Héloïse Thouement.

We gratefully acknowledge Kyle Gorder (US Air Force) for his help in identifying potential demonstration sites and coordinating the field work at Hill AFB, OU10. We also acknowledge the support of AECC in conducting the field sampling at Hill OU10.

Finally, the project team wishes to thank Dr. Andrea Leeson, Dr. Jeff Marqusee, and the support staff from the ESTCP program office for their help and guidance throughout the demonstration.

Page Intentionally Left Blank

EXECUTIVE SUMMARY

OBJECTIVES OF DEMONSTRATION

Monitored Natural Attenuation (MNA) is an important groundwater remediation technology based on a carefully controlled and monitored demonstration of contaminant attenuation. However, demonstrating contaminant mass destruction can be challenging. Compound-specific isotope analysis (CSIA) is a specialized laboratory method that can provide a direct signal of biological or abiotic degradation and support assessment of the strength of physical attenuation processes. The popularity of CSIA has risen rapidly among project managers as one line of evidence supporting MNA remedies. While CSIA results help to refine conceptual site models (CSM), CSIA data can be difficult to interpret, especially at sites with complex hydrogeology or with competing degradation pathways. The overall goal of the project is to present methods for quantitative assessment of natural attenuation processes, including mass destruction, for chlorinated solvents, using a combination of CSIA with modeling-assisted data interpretation.

TECHNOLOGY DESCRIPTION

Many elements, such as carbon or chlorine, occur as different isotope species, differing in their atomic mass. CSIA permits to determine the isotopic makeup of the contaminants present in environmental samples and the information obtained can be used as a line of evidence in contaminant studies. The majority of CSIA applications concern the assessment of Volatile Organic Compound (VOC) contaminants degradation in groundwater. The principle of the approach is that isotope ratios of a contaminant, for example $^{13}\text{C}/^{12}\text{C}$, remain constant as the groundwater is diluted, while the fraction of the heavy isotope, ^{13}C , typically increases with degradation. The difference between ^{12}C and ^{13}C behavior originates from energetically favored reactions for the molecules containing the lower atomic mass isotope (e.g., ^{12}C). On the other hand, the rates of non-degradative processes tend to have no or little selectivity in respect to the isotope composition of the contaminant. The benefit of the CSIA approach for contaminant studies lies in its ability to distinguish mass destruction (by biodegradation and/or abiotic degradation) from other types of mass attenuation. However, interpretation of field CSIA data can be difficult due to competing degradation pathways and/or complex transport conditions in the aquifer. The value added to contaminated site assessment by the use of CSIA ultimately depends on the specificity of the interpretation. This study centers on demonstration of numerical modeling to improve the capabilities for attenuation pathway identification and quantitative assessment of CSIA data.

Reactive transport modeling (RTM) simulates transport and contaminant degradation, using a simplified numerical representation of the features of the modeled site. RTMs enable to simulate complex reaction networks (e.g., sequential reductive dechlorination together with oxidative degradation) together with isotope fractionation (C, H, Cl), while accounting for physical processes that may influence isotope ratios such as hydrodynamic dispersion. However, as discussed below, RTMs also enable sound data interpretation through simulating fewer dimensions like 2-D cross-sections, 1-D flow paths, or even 0-D batch degradation.

DEMONSTRATION RESULTS

The demonstration followed two main tracks, a development and initial calibration of the modeling software and a demonstration of the combined CSIA/RTM approach through an assessment of a contaminated site (Hill Air Force Base [AFB], Operable Unit [OU] 10, consisting of Shallow Trichloroethene [TCE] Plume and Deep TCE Plume). The success of the technology demonstration was defined in terms of producing site assessment results that are useful for development/improvement of Conceptual Site Model and are superior to those obtained by the “classic” CSIA alone.

The performance objectives for the software development and validation were met successfully: (i) 0/1-D PHREEQC model templates for simulation of isotope fractionation in reductive dechlorination, for carbon, chlorine, and hydrogen were developed and calibrated using a data set from a microcosm experiment (dechlorination of trichloroethylene by a *Dehalococcoides* culture); (ii) two 2/3-D model platforms, PHAST and PHT3D were then adopted to simulate the same set of reactions as PHREEQC.

The performance objectives for evaluation of the Demonstration Site had to be revised, after initial evaluation of the data collected at the Demonstration Site. Observed trends of isotope enrichment did not correlate to the distance from the plume source, the distance across the plume fringe, or to the groundwater age. Instead, degradation in the Shallow Plume was localized in disconnected zones of the plume. Degradation in the Deep Plume was occurring primarily in an irregular area in the proximity to the plume source zone. Since no meaningful trends of isotope fractionation could be identified along 1-D flow lines, the exercise of 1/2/3-D modeling would be meaningless. Instead, the modeling was conducted using the batch (0-D) mode of the 0/1-D PHREEQC software. Spatial and temporal dimensions were thus not explicitly simulated. Even so, in comparison with the “classical” CSIA evidence, the combined CSIA/modeling approach (using the model to test alternative attenuation scenarios; the scenarios are defined using the “classical” CSIA evidence) permitted: (i) a reduction of uncertainties in identification of specific degradation pathways; and (ii) more accurate identification of the range of isotope enrichment factors, leading to more accurate quantitation of contaminant mass destruction.

IMPLEMENTATION ISSUES

The proposed methodology is cost-effective: (i) the cost added by basic 0-D modeling of CSIA data is low in comparison to the complete cost of sample collection and CSIA analytical work; and (ii) the only requirement for implementation of CSIA/modeling is a reasonable CSIA and contaminant concentrations data completeness. End users can choose that line data interpretation after the “classical” CSIA indicates a need eliminating question marks by modeling various attenuation scenarios.

As indicated above, site heterogeneity complicates implementation of the modeling in data interpretation. Even after the model dimensions downgrade to 0-D, simulation of the degradation processes in the Deep Plume using the existing model template was difficult and less successful than in the case of the Shallow Plume. In the Deep Plume, it is likely that the problems were caused by the proportionally more significant role of diffusion/back-diffusion.

1.0 INTRODUCTION

Monitored Natural Attenuation (MNA) is an important groundwater remediation technology based on a carefully controlled and monitored demonstration of contaminant attenuation from natural subsurface processes (USEPA, 1998). MNA remedies have several advantages over active remedies in terms of cost, effort, carbon footprint, and energy savings. However, demonstrating contaminant mass destruction can be challenging. Conventional MNA analyses rely on “*lines of evidence*” such as concentration vs. distance or concentration vs. time plots and other simple data visualization techniques to demonstrate contaminant destruction.

Compound-specific isotope analysis (CSIA) can provide a direct signal of biological or abiotic degradation through analysis of groundwater samples collected at the contaminated site. However, CSIA data can be difficult to interpret, especially at sites with complex hydrogeology or release histories. In this project, CSIA data and simple reactive transport models (RTMs) are combined, to strengthen interpretation of both CSIA and conventional analytical data. The overall goal of the project is to present methods for quantitative assessment of natural attenuation processes, including mass destruction, for chlorinated solvents, using a combined CSIA and RTM approach.

1.1 BACKGROUND

Management of sites impacted by chlorinated solvent contaminants presents an on-going challenge for the Department of Defense (DoD) (SERDP-ESTCP 2006). The microbial degradation of chlorinated solvents in aquifers has been demonstrated in both laboratory and in situ over the past 25 years. However, a number of aspects of the mechanisms and rates of in-situ degradation have yet to be determined. For example, while the potential for aerobic oxidation of chlorinated volatile organic compounds (cVOCs) in subsurface has been recently recognized, little empirical evidence is available to demonstrate this process in situ. Over the last decade, Compound-Specific Isotope Analysis (CSIA) has been applied to environmental samples to demonstrate the occurrence of biological degradation and chemical transformation processes for a variety of contaminants, with most studies focusing on chlorinated ethene solvents (Tetrachloroethene (Perchloroethene) [PCE] and Trichloroethene [TCE]) (USEPA, 2008). The principle of the application of this technology is that stable isotope ratios (e.g., $^{13}\text{C}/^{12}\text{C}$) of contaminant molecules change as degradation proceeds, providing direct evidence for contaminant degradation.

CSIA is a potentially powerful tool to refine conceptual site models (CSMs) by identifying the sources and fate of contaminants released to groundwater. The application of the CSIA technology can potentially help to refine a number of aspects of CSMs, including the following: (i) Identifying prevalent degradation pathways; (ii) Identifying non-destructive contaminant sinks such as sorption, dilution, or volatilization; (iii) Delineating the areas of strong degradation processes within the plume; (iv) Providing more accurate assessment of the rate and extent of degradation of the parent contaminant and of the net degradation/accumulation of the dechlorination intermediates.

On the most basic level, CSIA can simply provide qualitative evidence of contaminant mass destruction. More detailed results, including quantitative estimates of the contaminant mass degraded and identification of degradation pathways can also be obtained at certain sites, as demonstrated in the past. However, interpretation of field CSIA data can be difficult due to competing degradation pathways and/or complex transport conditions in the aquifer.

The value added to contaminated site assessment by the use of CSIA ultimately depends on the specificity of the interpretation. This study centers on demonstration of numerical modeling to improve the capabilities for attenuation pathway identification and quantitative assessment of CSIA data.

1.2 OBJECTIVE OF THE DEMONSTRATION

The overall objective of the project was to validate a combined CSIA and numerical RTM approach as an advanced assessment tool for attenuation of chlorinated solvents. The Demonstration Site was Operable Unit 10 at Hill AFB, Utah, a site where groundwater is impacted by spills of TCE and PCE. The data set collected at the demonstration site serves as a **Case Study** for the RTM-CSIA approach.

The project deliverables include freeware RTM templates applicable to the assessment of Chlorinated Ethenes (CE) degradation in the User's Guide document, describing the applications of classic CSIA and the CSIA/RTM for chlorinated solvents sites (ESTCP ER-201029, User's Guide) and the Final Project Report (all deliverables are available online at <https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-201029>).

1.3 REGULATORY DRIVERS

For the majority of DoD sites with chlorinated solvent contamination, the primary regulatory driver is attainment of relevant cleanup goals in the affected media. Until cleanup goals are met, site managers must establish and demonstrate conditions protective of potential receptors. For sites regulated under CERCLA (Superfund), demonstration of protective conditions must be made every five years. Part of the demonstration of protectiveness can include showing that plumes are well controlled and that remedial systems are making progress toward site cleanup goals. MNA remedies can be very cost effective, but require regulatory approval. Use of MNA as a treatment and/or control strategy requires evidence of intrinsic degradation. CSIA may supply the type of information to support regulatory approval of MNA.

2.0 TECHNOLOGY

2.1 TECHNOLOGY DESCRIPTION

2.1.1 Compound-Specific Isotope Analysis (CSIA)

Molecules of chlorinated ethenes are composed of carbon, chlorine and hydrogen (C, Cl, and H). Isotopes of an element differ in the number of neutrons in their atomic nuclei (isotopes have identical atomic number, but different atomic mass). CSIA measures the ratios of isotopes for chemical compounds present in the samples.

In the last decade, CSIA became a mainstream tool in the studies of groundwater contaminants (USEPA, 2008). The majority of CSIA applications concern the assessment of degradation (biodegradation and/or chemical abiotic degradation) of Volatile Organic Compounds (VOCs) in groundwater, including CEs, MTBE and benzene, and, to a lesser extent, source-contaminant correlation (USEPA, 2008 and Section 3.0 in ESTCP ER-201029 User's Guide).

CSIA data as evidence of contaminant degradation. The main benefit of CSIA in groundwater contaminant studies is the ability to distinguish mass destruction (biodegradation and/or abiotic degradation) from other types of attenuation. The principle of the approach is that isotope ratios of a contaminant (for example $^{13}\text{C}/^{12}\text{C}$) change as the result of contaminant degradation. Typically, degradation leads to an enrichment of the heavy isotope (e.g., ^{13}C) in the remaining contaminant residue. On the other hand, $^{13}\text{C}/^{12}\text{C}$ of the contaminant is not affected by dilution (Figure 2.1). The enrichment of ^{13}C in partially degraded contaminant residue is the result of lower activation energy in bond cleavage in the contaminant molecules with the lighter isotope, ^{12}C , at the reaction center. Consequently, the degradation product, e.g., Dichloroethene (DCE) produced by reductive dechlorination of TCE, is depleted in ^{13}C related to the parent compound.

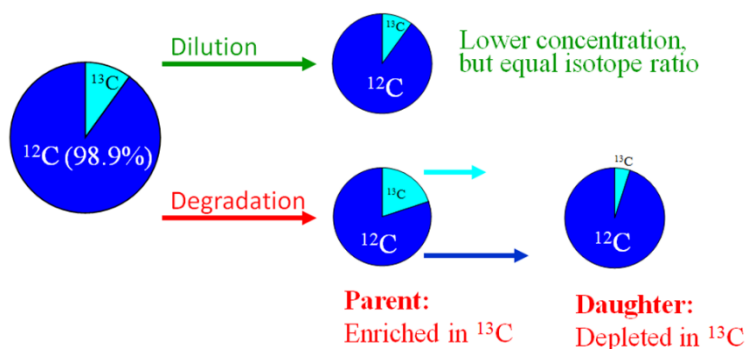


Figure 2.1. Isotope Ratios for a CE Subjected to Dilution Versus Degradation Processes.

Dilution results in no change in isotope ratios while biodegradation results in an increase in the proportion of the heavy isotope of the parent compound. A daughter product will have a depleted isotope ratio compared to the parent compound.

CSIA data as evidence of physical remediation. Recent CSIA studies of certain non-degradative processes indicate that physical attenuation can also be associated with isotope effects. In particular, diffusion of contaminants out of the mobile groundwater porosity (diffusion into adjacent clays or volatilization into vadose zone) could lead to measurable changes of isotope ratios.

While those effects tend to be small in comparison with the effects resulting from contaminant degradation (see User's Guide, Section 3.0 for additional information), evaluation of the field data from the present Demonstration Site detected the isotope effects from such physical attenuation as further discussed in Section 6. Isotope effects resulting from the non-degradative attenuation processes can complicate interpretation of CSIA data from field sites. However, such effects can also be used as a source of information in the assessment of non-degradative attenuation pathways.

Basic terminology. In environmental contaminant studies, isotope ratios (for carbon isotopes, $R = {}^{13}\text{C}/{}^{12}\text{C}$) are reported using the so-called delta (δ) notation (Equation 1). A δ value does not show the absolute isotope abundance but rather a difference vs. the international standard for the element (USEPA, 2008). The δ values are typically written with a ‰ (per mill) symbol to reduce the number of decimals (e.g., $\delta^{13}\text{C} = 0.0013$ is written as $\delta^{13}\text{C} = 1.3$ ‰).

$$\delta^{13}\text{C} = (R_{\text{sample}}/R_{\text{standard}} - 1) \quad (\text{Eq. 1})$$

A change of isotope ratios of a contaminant undergoing degradation can be described by the Rayleigh Model (Eq. 2 is written for the example of C isotopes). The model predicts $\delta^{13}\text{C}_t$ (an isotope ratio of the degraded contaminant at time t) as a function of the fraction of the contaminant mass remaining (f). The enrichment factor (ε) is a constant, a reaction-specific magnitude of the isotope effect; $\delta^{13}\text{C}_0$ is the pre-degradation isotope ratio of the contaminant; $\delta^{13}\text{C}_t$ is the isotope ratio of the contaminant in a groundwater sample, measured by CSIA.

$$\ln [(\delta^{13}\text{C}_t + 1000) / (\delta^{13}\text{C}_0 + 1000)] = \varepsilon \times \ln f \quad (\text{Eq. 2})$$

$$f = \exp\{\ln [(\delta^{13}\text{C}_t + 1000) / (\delta^{13}\text{C}_0 + 1000)] / \varepsilon\} \quad (\text{Eq. 3})$$

Eq. 2 can be rewritten to calculate the value of f , to assess the contaminant mass destruction (Eq. 3). The estimates obtained by Eq. 3 are usually very conservative because of uncertainty margins for the constants ε and δ_0 (f determination must be based on conservative end-member values ε and δ_0). Moreover, the Rayleigh Model is directly applicable when degradation is the only sink for the reactant, i.e., in batch reactors or in homogenous steady-state contaminant plumes. As the Rayleigh Model does not account for spatial heterogeneity of a contaminant plume, the obtained values of f are further masked by mixing of more or less degraded contaminant within the hydraulic radius of a monitoring point (Van Breukelen and Prommer 2008). Finally, the equation applies directly only to the parent contaminant (e.g., TCE) but not to the intermediates in reaction chains (e.g., cDCE).

Using 2D-CSIA in identification of attenuation pathways. 2D-CSIA combines two different isotope ratios, to obtain a signature of specific degradation/attenuation process. See User's Guide, Section 3.

Using Carbon Isotope Mass Balance (C-IMB) for validation of Reductive Dechlorination (RD) intermediate stall. C-IMB combines C isotope ratios of the parent and daughter CEs (and possibly ethene [ETH] and ethane, if present). If RD is the only degradation process occurring, C-IMB remains identical to the pre-degradation $\delta^{13}\text{C}$ of the parent CE. An enrichment of ${}^{13}\text{C}$ indicates a competing degradation process (e.g., oxidation). See User's Guide, Section 3.

Analytical techniques. The method involves extraction of the target compounds from environmental sample matrix, followed by separation of the compounds using gas chromatography (GC), and mass spectrometry to determine isotope ratios in individual compounds: (i) **Sample extraction** – typically, VOCs are extracted from samples using the Purge and Trap (PT) approach (USEPA 5030 method or similar); (ii) **Chromatography** – standard GC separation approach is used, similar to the approach in VOCs concentration analysis methods (USEPA 8260 method or similar); (iii) **Spectrometry, C CSIA** – The effluent from the GC column is passed through an in-line oxidation reactor, prior to isotope ratio determination by isotope ratio mass spectrometry (IRMS). C isotope ratios are determined after combustion of the target compounds to surrogate gas, CO₂; (iv) **Spectrometry, Cl CSIA** – Cl isotope ratios are determined by spectrometry of ionized molecules introduced into the spectrometer without thermal conversion. Cl CSIA methods utilize IRMS or standard quadrupole MS detectors. The latter option was used in the present project; (v) **Spectrometry, H CSIA** – The effluent from the GC column is passed through an in-line reduction reactor, prior to isotope ratio determination by isotope ratio mass spectrometry (IRMS). H isotope ratios are determined after reduction of the target compounds to surrogate gas, H₂.

2.1.2 Reactive Transport Modeling (RTM)

A model is a numerical representation of a site (in the present case, contaminant concentrations and isotope ratios in the space of an aquifer). *RTM can be an interpretive tool to simulate interactions between chemical and physical processes across space and time scales.*

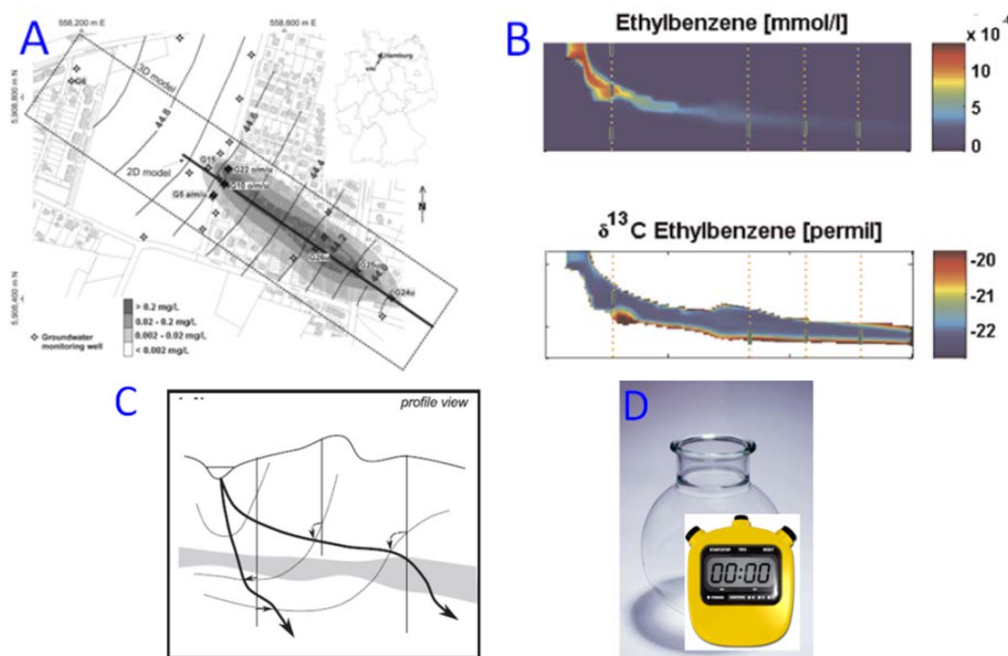


Figure 2.2. Spatial Dimensions of RTM.

A) 2-D plan view of 3-D pollution plume (D'Affonseca, 2011). The black line following the groundwater flow direction shows the position of a 2-D cross-section shown in B. B) 2-D cross-section of pollution plume depicted in A showing simulated ethylbenzene concentrations and carbon isotope ratios (D'Affonseca, 2011). C) 1-D flow paths simulating observations in 2-D space (Karlsen, 2012). D) A well-mixed closed 0-D batch system where the properties only change as function of time or reaction progress.

RTMs, in principle, enable users to simulate reaction networks (e.g., sequential reductive dechlorination together with oxidation) together with isotope fractionation (C, H, Cl), while accounting for physical processes that may influence isotope ratios such as hydrodynamic dispersion, diffusion, and sorption (Van Breukelen and Prommer, 2008; Jin et al, 2014 ;Van Breukelen and Rolle, 2012; Eckert, 2013).

RTM software platforms used as modeling tools for this project include:

1. **PHREEQC** – 0/1-D geochemical transport model.
2. **PHAST** – 2/3-D groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHAST couples PHREEQC to the groundwater flow and solute transport model HST3D.
3. **PHT3D** –2/3-D groundwater flow and transport model capable of simulating the same set of reactions as PHREEQC. PHT3D couples PHREEQC to the groundwater flow model MODFLOW and the solute transport model MT3DMS.

RTM Spatial Dimensions. Figure 2.2 illustrates the number of spatial dimensions that can be simulated using RTM techniques. Site data occur in 3-D space. However, this does not imply that RTMs in 3-D are required to interpret concentrations and CSIA data. Many relevant site characterization questions can be answered by models created in lower dimensions.

RTM Inputs and Calibration. Table 2.1 summarizes the information required for model setup. Detailed data on hydrogeological properties are needed to develop 2-D and 3-D models, whereas 1-D models only require information on the average groundwater flow velocity and trajectory of the flow path. 0-D models omit the transport and only the degradation processes are considered.

Table 2.1. Information Required to Construct a Reactive Transport Model

Conceptual Info	• Site history • Key contaminants • Base map	• A good conceptual site model • Source identity and history
Hydrogeologic Data	• Hydraulic conductivity at several locations • Effective porosity • Configuration of the transmissive zone (layers, location of any no-flow boundaries) • Confined vs. unconfined conditions	• Any recharge/discharge zones • Recharge rates to transmissive zone • Hydraulic gradient information • Location, pumping rate of any major wells
Transport Data	• Bulk density of soil in aquifer matrix • Total porosity of soils in aquifer matrix • Fraction organic carbon in aquifer matrix • Partition coefficients	• Estimates of longitudinal and transverse dispersivity • Diffusion coefficient estimates • Tortuosity or effective diffusion coefficients • General ranges of expected degradation coefficients
Reaction Data	• Reaction rates (k) for various CEs under different biogeochemical conditions	• Isotope enrichment factors (ϵ)
Contaminant Data	• Decay chain for the contaminants of interest • Parent compound concentration at multiple locations and multiple times • Daughter compound concentration at multiple locations and multiple times	• Carbon isotope data at multiple locations (probably 10 or more) for at least one sampling event. • Chlorine isotope data at multiple locations (probably 10 or more) for at least one sampling event. • Hydrogen isotope data

Model calibration is the adjustment of model input parameters to maximize the fit between the model and the field site. Calibration involves the values of field site-specific constants and parameters used in the model algorithms. All models require some level of calibration to be useful for a specific site. Table 2.2 provides a summary of calibration processes for the RTMs used to interpret CSIA data. After the trial-and-error process of model calibration, the model results can be presented as illustrated in the example 1-D and 2-D models described in Section 4.2 of the User's Guide (ESTCP ER-201029, User's Guide). 0-D model results are presented in Section 6 of this report.

Table 2.2. Calibration Process for Various Models

Model Name	Model Type	Calibration Process
PHREEQC	0-D	Adjusting degradation rate constants and isotope fractionation factors to fit isotope ratio versus molar concentration ratio plots
	1-D	Adjusting degradation rate constants, isotope fractionation factors, and the longitudinal dispersion coefficient to fit isotope ratio and molar concentration ratio versus travel distance plots
PHAST/ PHT3D	2-D	Assuming the flow field has been properly calibrated: Adjusting degradation rate constants, isotope fractionation factors, and the longitudinal and transverse vertical dispersion coefficients to fit CSIA and concentration data in the 2-D cross-section. Fitting should be regarded as approximately reproducing the observed concentration and CSIA patterns.
	3-D	The same as for 2-D. However, also the horizontal transverse dispersion coefficient should be fitted. The model-data comparison will be a considerably larger challenge than for a 2-D model. Fitting should be regarded as roughly reproducing the observed concentration and CSIA patterns.

2.1.3 Technology Development

The main item for CSIA technology development was the novel method permitting H CSIA of chlorinated compounds. The detailed description of the H CSIA method is given in a paper published in Environmental Science and Technology (Kuder and Philp, 2013). The modeling software development goals of this project were an extension of the PHREEQC model to complete (C, Cl, H) set of elements and adaptation of the PHREEQC to 2/3-D transport simulation, using PHAST and PHT3D.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

CSIA is the only technology that is currently available that has the power to directly identify the effects of in-situ degradation on contaminant plumes through analysis of groundwater samples collected at standard monitoring points. The primary advantages of CSIA for the assessment of chlorinated solvents sites can be summarized as follows: (i) CSIA provides a footprint of degradation (in the form of ^{13}C enrichment) which is specific of given contaminant of interest; (ii) CSIA evidence is independent from contaminant concentration data; (iii) CSIA evidence is not affected by contaminant dilution etc. so that the evidence of in-situ degradation is unequivocal; (iv) CSIA permits identification of degradation of a contaminant even in the absence of the specific degradation products; (v) Isotope ratios of the cDCE and/or Vinyl Chloride (VC) product can be used to determine if dechlorination stalls at those intermediates; (vi) CSIA may be able to distinguish different sources of parent material using isotopic signatures.

In comparison to “classic” interpretation of CSIA data, the combined use of CSIA-RTM approach has the potential to better quantify the extent of contaminant mass attenuation and to resolve the contributions from different mechanisms of attenuation. In summary, CSIA and CSIA-RTM data can potentially help in the MNA decision process.

Site heterogeneity may potentially limit the utility of the technology. It is possible degradation in certain sections of a plume never commenced or that degradation occurred only at limited scale. Monitoring wells intersecting heterogeneous aquifers can yield mixed samples dominated by undegraded contaminants. CSIA of such samples may produce average isotope ratio signatures dominated by the undegraded contaminants. Consequently, the decision on whether or not to implement CSIA should consider the site’s comprehensive hydrogeologic CSM. Complex hydrogeology can also be problematic for groundwater fate and transport modeling. Multiple source areas with original contaminants produced from multiple spills may produce isotope signatures that are difficult to interpret. Sites where basic groundwater modeling is not productive may not benefit from reactive transport modeling using CSIA data. The site heterogeneity limitations were indeed encountered in this project. As discussed in Section 6, the spatial patterns of isotope fractionation at the Demonstration Site suggested localized and irregular zones of reductive dechlorination, as opposed to 1-st order kinetics that is conducive to reactive transport modeling.

Applicability of the proposed technology can also be limited by the difficulties in obtaining the isotope data by CSIA. Two potential limitations are: (i) the analyte concentrations that are below detection limits of CSIA, and (ii) interferences from excessive content of non-target VOCs present in the same samples (e.g., CEs commingled with fuel hydrocarbons, leading to problems with GC resolution of the target CEs).

Finally, interpretation of the data can be hampered by the absence of published references, defining isotope effects to be expected for certain degradation mechanisms that can be relevant at the studied sites. For example, as of today, no reference data exist to benchmark hydrogen isotope fractionation observed in field samples. Therefore, the information potential of dual-element CSIA (C+H) remains unknown and unrealized in field studies.

3.0 PERFORMANCE OBJECTIVES

Table 3.1. Performance Objectives

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
1. Optimize CSIA method for C, H, Cl	Analyses for microcosm and field data	Isotope analysis results for concentrations of the CEs above the MCLs	The performance objective was met. C, Cl and H CSIA methods were developed for this project
2. Adapt 1-D PHREEQC Model for H isotope enrichment	Microcosm data of sufficient quality and quantity	The model fits H-CSIA observations and thereby gives information on isotope fractionation during the degradation steps and on the control of environmental conditions on the H-CSIA values.	The performance objective was met. The model of H isotope fractionation was developed and calibrated to experimental data.
3. Calibrate 0/1-D geochemical model for C, Cl and H enrichment	Microcosm data of sufficient quality and quantity to calibrate model	C and Cl data confirm earlier model assumptions H data sufficient to develop enrichment model (see above) Model functions as a baseline geochemical model for anaerobic sequential decay	The performance objective was met. The model was accurate in simulation of the experimental data. The validated model serves as a baseline for applications in field data assessment.
4. Adapt model to 3-D in PHAST and PHT3D	1-D Model and microcosm data	Comparison of PHAST and PHT3D models give similar results as kind of benchmark validation; mass balances of all isotopes are met.	The performance objective was met. The model outputs of PHAST and PHT3D were almost identical in simulation of RD of TCE with oxidative degradation at the plume fringe.
5. Calibrate 2/3 D model with site – specific data	Data from field demonstration site	The model fits (concentration and CSIA data are close to the observation values) in most (75%) of the monitoring points.	The original performance objective was not met. The spatial complexity of the degradation zones at the site was too great to permit 2/3-D simulation. The redefined performance objective (validation of 0-D model) was met. The 0-D model provides informative evidence for understanding contaminant transformations.
6. Use CSIA/ model technology to demonstrate the presence of multiple degradation pathways	Data from field demonstration site	As above; the model needs inclusion of multiple degradation pathways to explain field data.	The performance objective was met. Evidence of RD, oxidation and physical attenuation of CEs was identified.

Table 3.1. Performance Objectives (Continued)

Performance Objective	Data Requirements	Success Criteria	Results
7. Estimate degradation constants for COCs at demonstration site	CSIA/modeling results	Estimation of rate constants as result of model calibration. Comparison of model uncertainty with calibration using only concentration data vs. both concentration and CSIA data, to address the benefit of CSIA data.	The performance objective was met. The model permitted narrowing the uncertainty range of parameters used in rate determination, relative to the CSIA-only approach.
Qualitative Performance Objectives			
8. Develop a new framework for interpreting CSIA data	CSIA and modeling results	Develop a model that can be applied at different sites to visualize and interpret CSIA data, demonstrate the presence of degradation processes, predict future plume behavior and support remedial decision making.	The performance objective was met. The framework for the use of the CSIA/model approach was presented in the User's Guide deliverable (ER-201029), published online in 2014.
9. Refine CSM for demonstration site	CSIA and modeling results	Comparison of CSIA-RTM modeling with alternative data processing options (CSIA-conventional Rayleigh Model; RTM calibrated by concentrations only) Data sufficient to update CSM on the strength of attenuation mechanisms at various locations in the plume	The performance objective was met. Adding the model-based interpretation of CSIA data helped to identify degradation pathways and advanced the accuracy of the biodegradation assessment.

4.0 SITE DESCRIPTION

4.1 SITE LOCATION

The demonstration site is Hill Air Force Base Operable Unit 10 (OU10), located in northern Utah, approximately 25 miles north of Salt Lake City. Figure 4.1 illustrates the site location, the extent of groundwater contamination, and the monitoring well locations. OU10 encompasses the Building 1200 Area along the western boundary of Hill AFB and extends off-base into the cities of Clearfield, Sunset, and Clinton. Aircraft/vehicle maintenance activities at Building 1200 Area began in approximately 1940 and continued through 1959, at which point the building complex was converted to administrative offices. Chlorinated solvents were released in 1940-1959.

4.2 SITE GEOLOGY/HYDROGEOLOGY

The subsurface lithology is characterized by detailed cross-sections and soil profiles (Figure 4.2) (CH2MHILL, 2009). The subsurface consists of two saturated units (Unit A and Unit C) separated by an aquitard (Unit B). Below Unit C, a thick aquitard (Unit D) prevents further downwards migration of pollutants. Units A and C consist of sand (fine- to medium-grained) and silt, with moderate to high permeability. Groundwater velocities were determined previously, using slug or pump tests and groundwater dating (CH2MHILL, 2009). In Unit A, average groundwater flow velocity is about 0.15 m/d. The calculated retardation factors for PCE, TCE, c-DCE, and t-DCE, are relatively low (≤ 3.1 , 1.7, 1.6, and 2.0, respectively), due to the low organic carbon content (0.03 % in sand; 0.07 % in silty sand). In Unit C, the groundwater velocity decreases abruptly between the easternmost area (0.58 m/d), where the sand layers are thin and interbedded with clay layers, and the western area (0.18 m/d), where the sand packages are thicker. The organic carbon content of Unit C is higher (0.2 %), resulting with higher sorption and higher retardation factors (TCE migrates at half the rate of DCE).

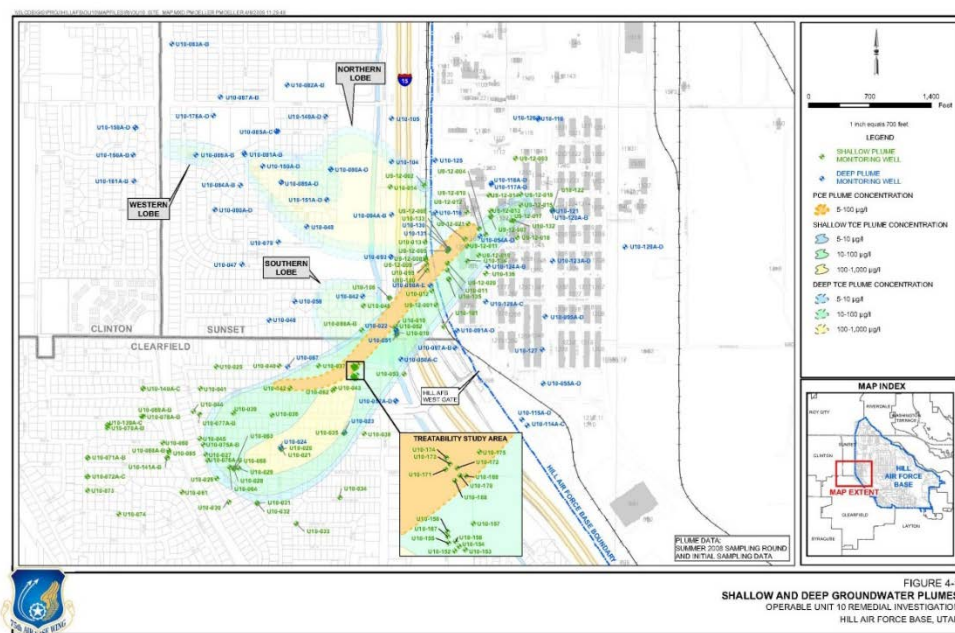


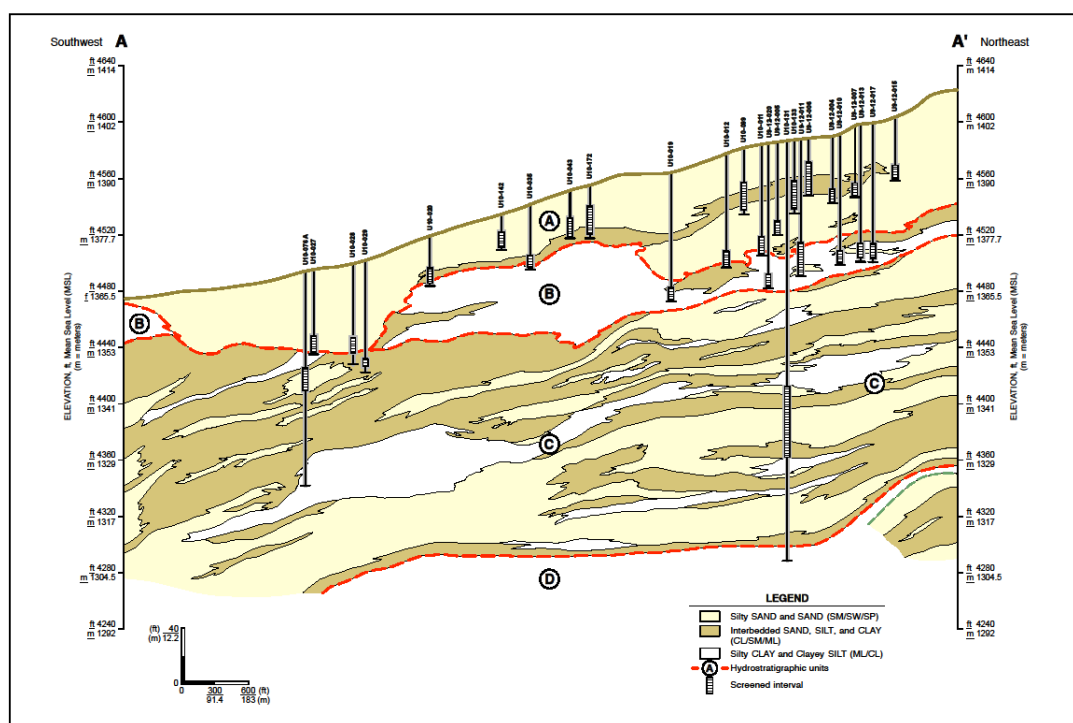
Figure 4.1. Hill AFB OU10 Site Location.

Redox Conditions and Microbiology. The site exhibits significant variability of redox conditions (CH2MHILL, 2009). Based on dissolved Oxygen (DO), nitrate, and sulfate levels, Unit A was classified as overall oxic, while Units B and C were classified as mildly reducing. Detections of methane in some wells in Unit C indicated methanogenic conditions, while other wells in Unit C showed high nitrate. In Unit A, aerobic cometabolic CEs degraders were identified. Aerobic methanotrophs (potentially capable of CEs comebolism) were also detected in the Lower Zone (CH2MHILL, 2009). In the Lower Zone, RD bacteria *Desulfuromonas* and *Dehalobacter* have been identified. On the other hand, DO and ORP levels in Units B and C were high, suggesting a potential for aerobic biodegradation, probably in the mobile porosity.

4.3 CONTAMINANT DISTRIBUTION

Two primary sources of contamination have been identified. TCE was spilled continuously over an extended period of time, from an oil/water separator (CH2MHILL, 2009). The resulting contaminant plume extends from the source area to the SW and off-base (Figure 4.1). PCE was probably spilled incidentally on the parking lot west of Building 1274, and the PCE occurrences are limited to the shallow Unit A.

In Unit A, the Shallow TCE Plume travels along the surface of the aquitard (Unit B). The plume is thin (6 - 12 m), 90-425 m wide, and has traveled approximately 1,500 m southwest from the source, across the Hill AFB boundary and underneath a residential area. PCE travels to the SW close to the groundwater surface and partially mixes with the Shallow TCE Plume.



The Unit B aquitard is entirely eroded in some areas and leakage from Unit A to Unit C leads to formation of the Deep TCE Plume in Unit C (Figure 4.3), moving to the northwest, between 53 m and 88 m BGS. Locally, TCE is also detected in wells screened within Unit B. The Deep TCE Plume includes Northern and Southern Lobes. The Northern Lobe is 425 m wide at its maximum, and 800 m long. The Southern Lobe is 245 m wide and 425 m long.

The original TCE source is likely exhausted, as Dense Non-aqueous Phase Liquid (DNAPL) was not detected in the probable source area during site investigations, and since the present CEs concentrations are low in the source zone. The highest TCE concentrations in the shallow plume are located 900-1300 m downgradient from the source zone, which also suggests that the source is depleted. Consequently, the water flowing into Unit C to form the upgradient part of the Deep Plume is less polluted today than in the past, as suggested by the decreasing concentrations in well U10-131, at the junction between the Shallow Plume and the northern lobe of the Deep Plume (CH2MHILL, 2009).

The observed RD products are mostly cis-DCE and, at lower concentrations, trans-DCE. DCE species are present locally in the Shallow Plume, mostly in wells screened in or near Unit B. DCE species are present in nearly all samples collected at the Deep Plume. Low concentrations of VC, ethene and ethane were observed historically and in the 2011 samples, in several wells screened in Units B and C (Figure 4.3).

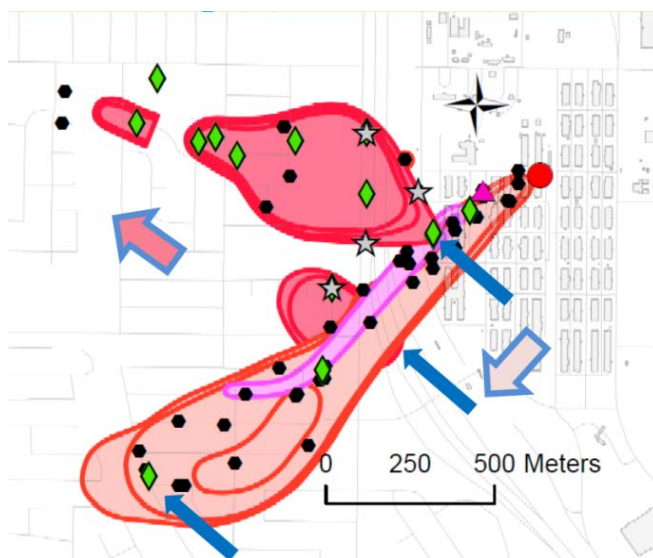


Figure 4.3. Map of the Operable Unit (OU) 10.

Shown are the shallow PCE plume (purple), the shallow TCE plume beneath (pink), and the deep TCE plume (red). The groundwater flow directions are indicated by large arrows. The black dots represent the wells sampled for CSIA. The estimated spill locations are indicated by a purple triangle (PCE) and a red circle (TCE). The blue arrows indicate the leakage areas connecting the shallow with the deep plume. The green diamonds indicate wells where either VC or ethene was detected at least once since 2004.

Page Intentionally Left Blank

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The broad objective of this project was to develop groundwater modeling tools and approaches to better interpret CSIA data collected from chlorinated solvent plumes, to assist site managers in integration of CSIA evidence into remediation efforts. The experimental design for this project combines three main components:

Software development and initial calibration

1. The PHREEQC model was extended and calibrated for simulation of C, Cl, and H isotope fractionation in reductive chlorination. The calibration used an experimental data obtained in a microcosm study, for reductive dechlorination of TCE to ethene.
2. The base model (0/1-D PHREEQC) was integrated into 2/3-D model software platforms, PHAST and PHT3D, adopted to simulate the same set of reactions as the PHREEQC.

Field-scale application of the model

1. Data collection. Groundwater samples for CSIA were collected at high spatial density from the Demonstration Site. CSIA and VOCs concentration analysis of the samples provided the data set for model validation.
2. The main data set was collected in 2011. A smaller data set was collected in 2014, to close gaps in the 2011 data.
3. The field data were evaluated (“classical” CSIA evaluation) in combination with existing CSM of the Demonstration Site, to identify alternative attenuation scenarios to be tested by the model. E.g., a scenario of cDCE stall was compared to a scenario where cDCE degrades in aerobic cometabolism.
4. The modeling approach was revised. The originally planned 2/3-D modeling was impossible due to the spatial heterogeneity of degradation at the site. The modeling exercise was conducted using the 0-D dimensionality.
5. Scenarios identified in the preliminary data assessment were tested using the 0-D approach. The output of the model (fit of the model to the field data) served to validate or disqualify the proposed scenarios.

Assessment of the added benefit of the CSIA/model approach

1. The information from the “classic” CSIA and from the CSIA/model approach was used to advance the existing CSM.
2. The information from the CSIA/model approach was compared to the following: (i) contaminant concentration model, assuming plume-wide first-order type of degradation; (ii) “classic” CSIA (no model-based scenario testing).

5.2 BASELINE CHARACTERIZATION

Selection of Demonstration Site was based on existing site characterization data (CH2MHILL, 2009). Since this project did not involve actual activities of contaminant remediation and comparison of before/after the treatment, baseline characterization *sensu stricto* was not required.

5.3 LABORATORY STUDY RESULTS

A laboratory study was conducted to facilitate the development and calibration of the modeling software. The complete results from the study have been published in the form of a peer-reviewed paper (Kuder, T.; van Breukelen, B. M.; Vanderford, M.; Philp, P., *3D-CSIA: Carbon, Chlorine, and Hydrogen Isotope Fractionation in Transformation of TCE to Ethene by a Dehalococcoides Culture*. *Environmental Science and Technology* 2013, 47, 9668–9677).

5.4 DESIGN AND LAYOUT OF TECHNOLOGY COMPONENTS

The project does not require extensive new design components. Setup and operation of the modeling software were described previously in the User's Guide (ESTCP ER-201029, User's Guide).

5.5 FIELD TESTING

The project did not involve field activities other than collection of groundwater samples for CSIA. The sampling techniques are identical to those applied in routine MNA application.

5.6 SAMPLING AND ANALYSIS METHODS

Groundwater sample collection. Groundwater was collected from existing monitoring wells, using a variety of sampling methods: BarCad, low flow, permeable diffusion bags. Sample volumes required for CSIA are higher than those collected in routine MNA work. For this project, approximately 500 mL of groundwater was collected in Volatile Organic Analyte (VOA) vials from each location to allow enough material to potentially determine isotope ratios of C, Cl, and H in several target compounds. Samples were preserved with H₂SO₄ and refrigerated.

Laboratory analytical methods. See Table 5.1.

CSIA Quality Assurance. Quality Assurance/Quality Control (QA/QC) for CSIA has been described in more detail in Section 3 of the User's Guide for this project (ESTCP ER-201029). QA/QC samples are required to control the analytical precision and accuracy of isotope ratio determination. The main QA/QC evidence is obtained from Laboratory Control Samples (LCS), prepared in identical matrix to that of the field samples (e.g., water) and analyzed under identical conditions as the environmental samples.

Table 5.1. Analytical Methods for Sample Analysis

Matrix	Analyte	Method	Container	Preservative	Holding Time
Groundwater	Chlorinated ethenes	8260 ¹	VOA	H ₂ SO ₄ , 4°C	2 weeks
	C Isotope ratios	C CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³
	Cl Isotope ratios	Cl CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³
	H Isotope ratios	Cl CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³
Microcosm water	Chlorinated ethenes	8260 ¹			Analyzed immediately
	C Isotope ratios	C CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³
	Cl Isotope ratios	Cl CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³
	H Isotope ratios	Cl CSIA ²	VOA	H ₂ SO ₄ , 4°C	n/a ³

¹ Modified analytical protocol described in Section 5.6 of the Final Report

² In-house analytical CSIA protocols described in Section 5.6 of the Final Report

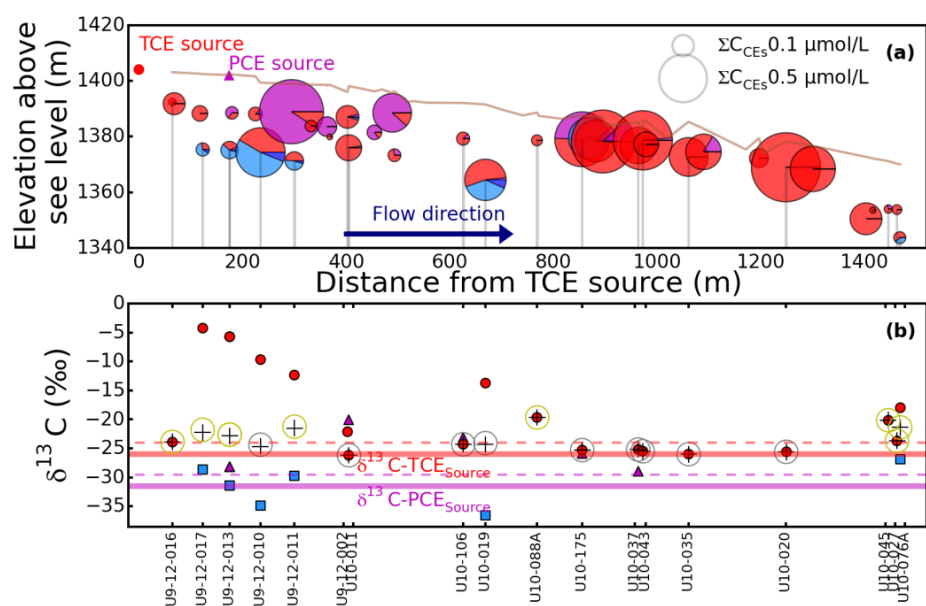
³ Preserved (pH <2, 4°C) CE samples can be analyzed for their isotope ratios after as much as several months of storage.

5.7 SAMPLING RESULTS

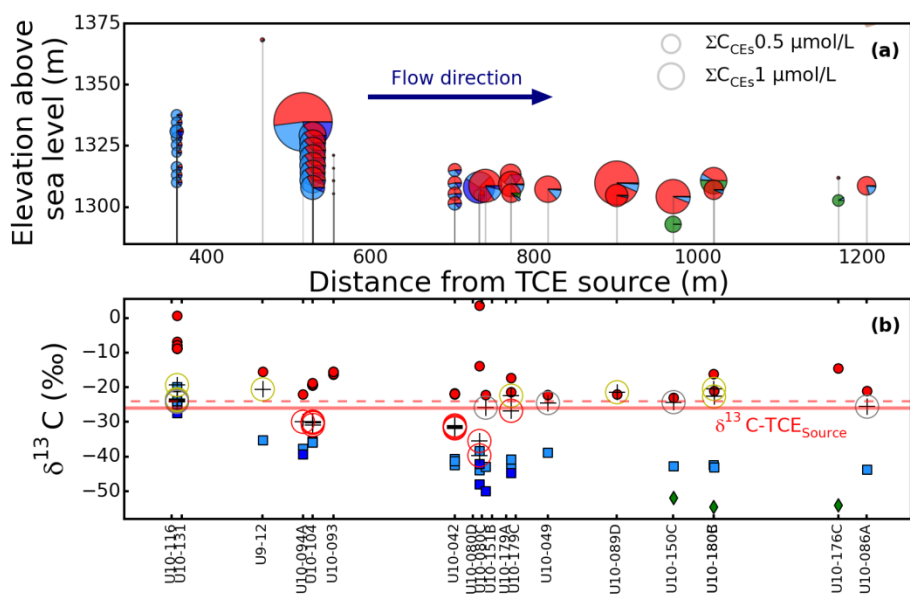
Table 5.2 provides a summary of the sampling program. Figure 5.1 shows the analytical data (CEs concentrations and C isotope ratios) plotted using a topographic cross-section format.

Table 5.2. Project Sampling Program, Analytes and Analyses

Task	Matrix	Number of Samples	Analytes	Analyses	Location
Microcosm Study	Microcosm water medium	Time series samples from microcosms	PCE, TCE, cDCE, tDCE, VC, ethylene	Concentration by GC CSIA by Isotope Ratio GCMS	Laboratory experiment
Field Program (2011)	Groundwater	83 Locations	PCE, TCE, cDCE, tDCE, VC, ethylene	Concentration by GC; CSIA by Isotope Ratio GCMS	See Fig. 5.2 (map of the well locations); Table D1 identifies all sampling points.
	Groundwater	83 Locations	Field Parameters	T, pH, groundwater elevation, DO, conductivity, turbidity	See Fig. 5.2 (map of the well locations); Table D1 identifies all sampling points.
Field Program (2014)	Groundwater	22 Locations	PCE, TCE, cDCE, tDCE	Concentration by GC; CSIA by Isotope Ratio GCMS	See Fig. 5.2 (map of the well locations); Table D2 identifies all sampling points.



**Figure 5.1A. CEs Concentration and C Isotope Ratios, Cross-Section View
Shallow Plume, 2011 Sample Set.**



**Figure 5.1B. CEs Concentration and C Isotope Ratios, Cross-Section View,
Deep Plume, 2011 Sample Set.**

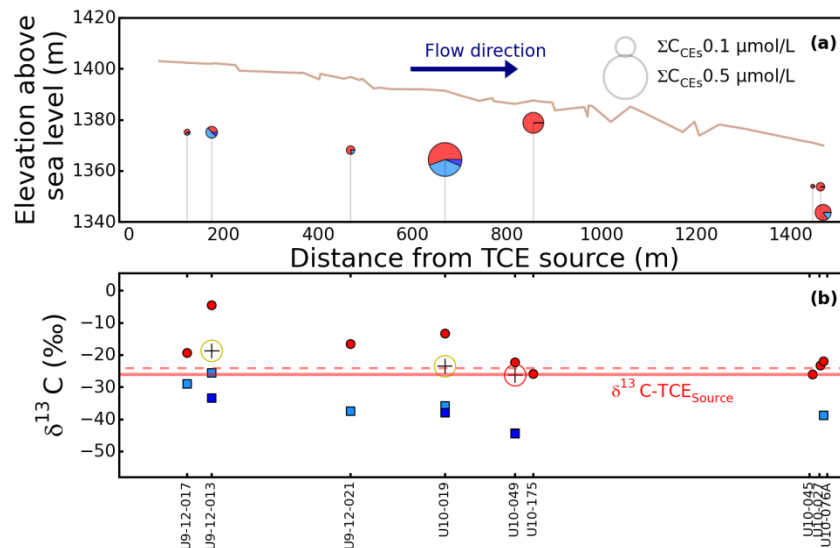


Figure 5.1C. CEs Concentration and C isotope Ratios, Cross-Section View, Shallow Plume, 2014 Sample Set.

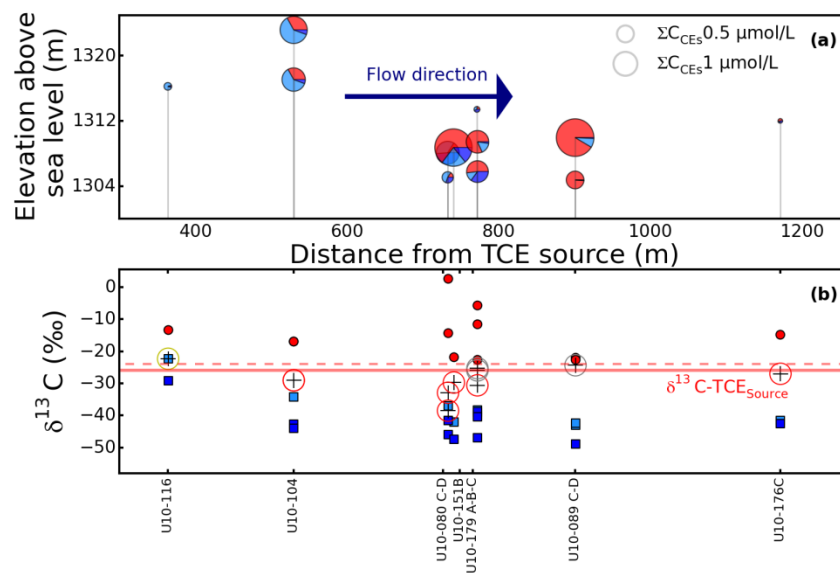


Figure 5.1D. CEs Concentration and C isotope Ratios, Cross-Section View, Deep Plume, 2014 Sample Set.

Page Intentionally Left Blank

6.0 PERFORMANCE ASSESSMENT

This summary of the project performance is organized into three sections: (i) Software development (Objectives 2-4, Table 3.1.); (ii) Demonstration of the CSIA-model approach in the field site assessment (Objective 5, Table 3.1.); and (iii) Discussion of the benefits of CSIA-RTM to improve CSM of the Demo Site (Objectives 6-9, Table 3.1.).

6.1 SOFTWARE DEVELOPMENT

Model for C-Cl-H isotope fractionation in reductive dechlorination. The model employed for this study includes C, Cl, and H isotope fractionation, through both RD ($\text{PCE} \rightarrow \text{TCE} \rightarrow \text{c-DCE/t-DCE} \rightarrow \text{VC} \rightarrow \text{ETH}$) and oxidation ($\text{c-DCE/t-DCE} \rightarrow \text{CO}_2$, $\text{VC} \rightarrow \text{CO}_2$). The three-isotope model of reductive dechlorination was validated using data from the anaerobic microcosm experiment for reductive dechlorination processes. Figure 6.1 shows the results for the 0-D PHREEQC model calibration. The 2-D model templates discussed below are based on this model. A good agreement between the calibrated model and the microcosm observations confirms that the model can be used for realistic simulation reductive dechlorination, for C, Cl, and H isotope ratios. Further details of the model calibration will be published by van Breukelen et al. (2016, manuscript submitted).

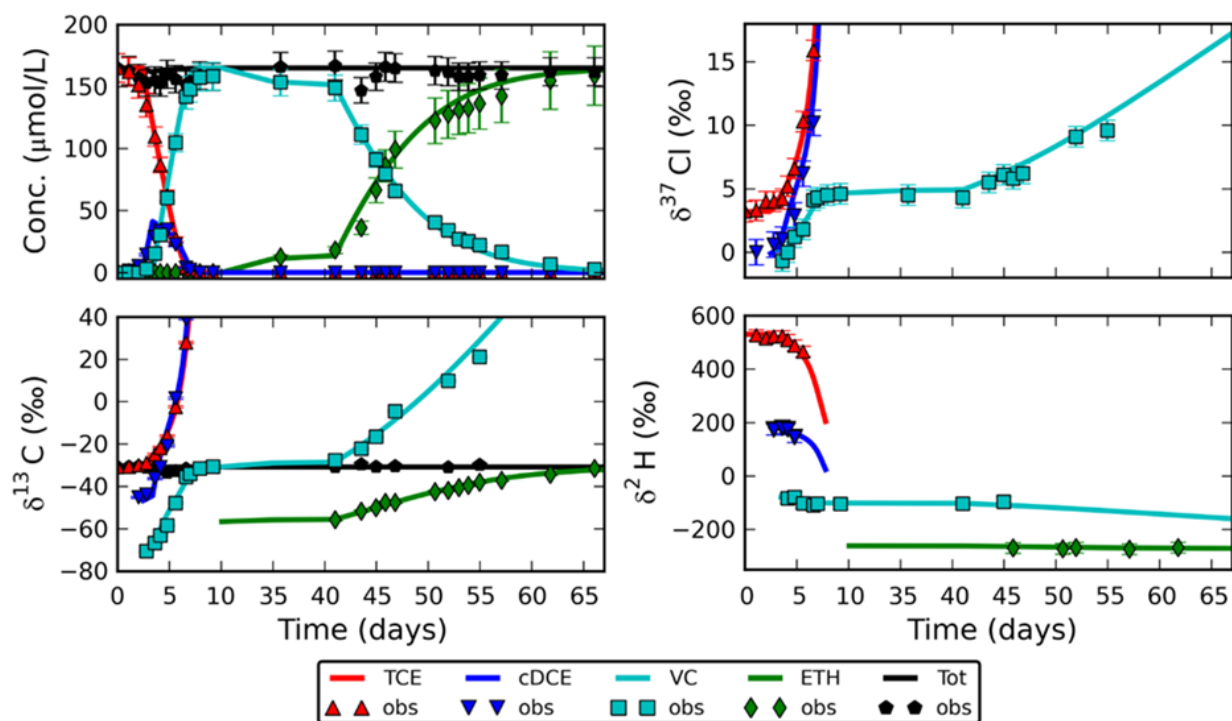


Figure 6.1. Calibration Results for the C, Cl, and H isotope Fractionation Model.

The model accurately simulates concentrations, and C, Cl, and H isotope ratios of CEs and ETH over the course of sequential dechlorination.

Adaptation of the model to 2/3-D reactive transport. This performance objective has been addressed as Case 3 in the User's Guide prepared for this project (cf. section 4.2.3 in the User's Guide). Case 3 is a simulation of a 2-D cross-section of a TCE plume degrading through reductive dechlorination in the anoxic plume core and through oxidative transformation at the plume fringes where the pollution plume mixes with clean aerobic water. Simulations were made using PHAST and PHT3D, and the results obtained were nearly identical for both types of software. In principle, the developed models are capable to simulate complex situations (core and fringe degradation) in 2-D. The model input files needed to run the model are explained in detail in Section 7.3 of the ER-201029 User's Guide. The developed model can simulate complete dechlorination of PCE to ETH together with oxidative transformation of DCE and VC under aerobic conditions.

6.2 DEMONSTRATION OF CSIA-RTM FOR THE FIELD SITE ASSESSMENT

In this section, we summarize the application of the model to help in interpretation of the CSIA data from the Shallow and Deep TCE Plumes. The discussion is limited to the fate of the TCE plumes and to the C and Cl isotope data. Due to limited number of wells with PCE and even fewer wells with evidence of PCE degradation, modeling of PCE plume was not conducted. The present discussion of the model application is restricted to the lines of evidence that were informative in field site data evaluation. E.g., in this section, we do not discuss the model simulating Cl isotope composition of cDCE, since that model's output was not providing added benefit to the field site evaluation. Similarly, H data are not discussed in this section. The anticipated target for H isotope ratio modeling (a line of evidence for detection of TCE produced by reductive dechlorination of PCE) turned out to be not applicable at the Demonstration Site.

The summary of the existing CSM of the site. The following paragraph summarizes the existing CSM for OU10 (CH2MHill, 2009). TCE in the Shallow Plume was proposed to degrade via aerobic cometabolism. In addition to aerobic cometabolism, reductive dechlorination evidence was reported from the toe of the plume. The CSM of the Deep Plume proposed that the contaminants reside in mobile (sand) and immobile (clay and silt) porosities. Geochemical conditions likely range from highly anaerobic and reducing in the immobile porosity, conducive to reductive dechlorination, to aerobic in the mobile porosity, conducive to aerobic cometabolism and contaminant oxidation. The CSM postulated reductive dechlorination as the primary mechanism for degradation of TCE within the immobile porosity, followed by diffusion of partially degraded TCE and the degradation products into the mobile porosity. On the other hand, reductive dechlorination rates in the mobile porosity of the Lower Zone were suggested to be slow. Degradation of TCE and the daughter products of reductive dechlorination present within the mobile porosity may also occur through cometabolic oxidation.

The conclusion from the CSM is that contaminant attenuation at the site likely involves multiple degradation pathways, potentially both reductive dechlorination and aerobic cometabolic biodegradation.

6.2.1 Classic Evaluation of CSIA Data

Initially, CSIA data were evaluated for evidence of attenuation processes, without the application of modeling. The following conclusions could be obtained:

1. C and Cl isotope enrichment suggested degradation of TCE at 11 out of 38 wells at the Shallow Plume and nearly at all sampling points of the Deep Plume. Most of those wells showed detections of DCEs alongside TCE (Figure 5.1A-D). In the Shallow Plume, the isotope enrichment was observed near the contact with Unit B. In the Deep Plume, the samples in the E/NE area showed largest net values of enrichment.
2. The dual-element CSIA of TCE of the Shallow Plume showed a bimodal separation of the data (Figure 6.2). One group of samples followed a trend consistent with reductive dechlorination (that trend included all samples where RD products were detected plus additional samples, where only TCE was present). Remaining wells followed a trend consistent with TCE attenuation by diffusion out of the mobile porosity of the dissolved plume.
3. In the Shallow Plume, one possible outlier was well U9-12-021 (Figure 6.2). In that sample, TCE and cDCE and fractionation of carbon isotopes of TCE (+10 ‰ enrichment vs. the source TCE) were detected, but no fractionation of chlorine isotopes (the signature was identical to the source, within the analytical uncertainty margin).
4. The dual-element CSIA of TCE from the Deep Plume site showed a trend that was generally consistent with the range of values reported from reductive dechlorination (Figure 6.3). However, the apparent slope of the trend was poorly defined and the observed dual-element CSIA slope could be rationalized by at least three different degradation/attenuation scenarios, always involving RD of TCE, but with possible contributions of isotope fractionation caused by TCE diffusion or TCE undergoing aerobic degradation.
5. For the Shallow Plume, the samples with RD evidence (as well as U9-12-021) displayed enriched values of C-IMB (Fig. 5.1A and 5.1C), suggesting that additional degradation process, not simply TCE to DCE transformation, was involved.
6. For the Deep Plume, the values of C-IMB varied from those with enriched values to those depleted relatively to the primary source signature of TCE. The depleted signatures were observed in the E/NE area. Depleted C-IMB cannot be explained by degradation.

Questions remaining after “Classic” CSIA

While the evidence for RD occurring in certain Shallow Plume wells and in the Deep Plume was strong, uncertainties remained:

1. The role of oxidation and physical attenuation of TCE (compare cases A and B in Figure 6.2; compare cases A, B, and C in Figure 6.3).
2. Can the enriched C-IMB values (Figure 5.1A-D) also be explained by differences in sorption or diffusion/back-diffusion of DCE vs. TCE, which separates the depleted daughter products from the enriched parent compound, rather than by degradation proceeding beyond DCE?
3. How to explain the depleted C-IMB values?

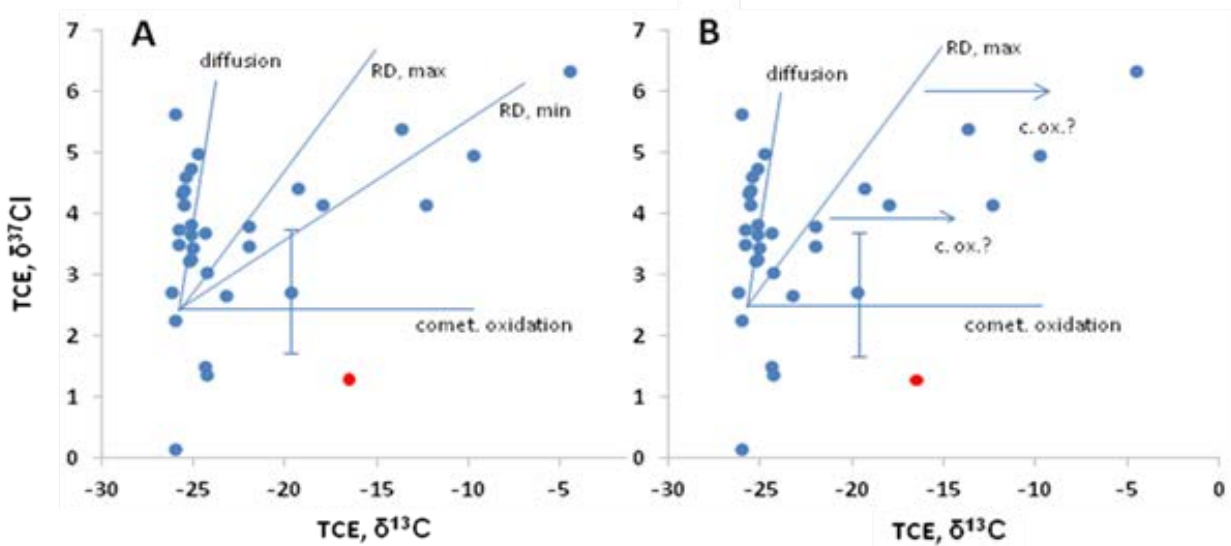


Figure 6.2. 2D-CSIA Plots, TCE in the Shallow Plume.

The red marker indicates well U9-12-021. The 2D-CSIA reference trends are shown for RD (minimum and maximum range) and diffusion based on published experimental data (see the summary of isotope effect in TCE biodegradation, Appendix B of the User's Guide, ER-201029, see Wanner and Hunkeler, 2015 for the isotope effects in TCE diffusion). The reference for cometabolic oxidation is theoretical (the absence of Cl fractionation accounting for the known reaction mechanism with formation epoxide intermediate). A) Rationalization with RD and diffusion accounting for isotope fractionation (except for well U9-12-021). B) Rationalization by TCE oxidation following RD.

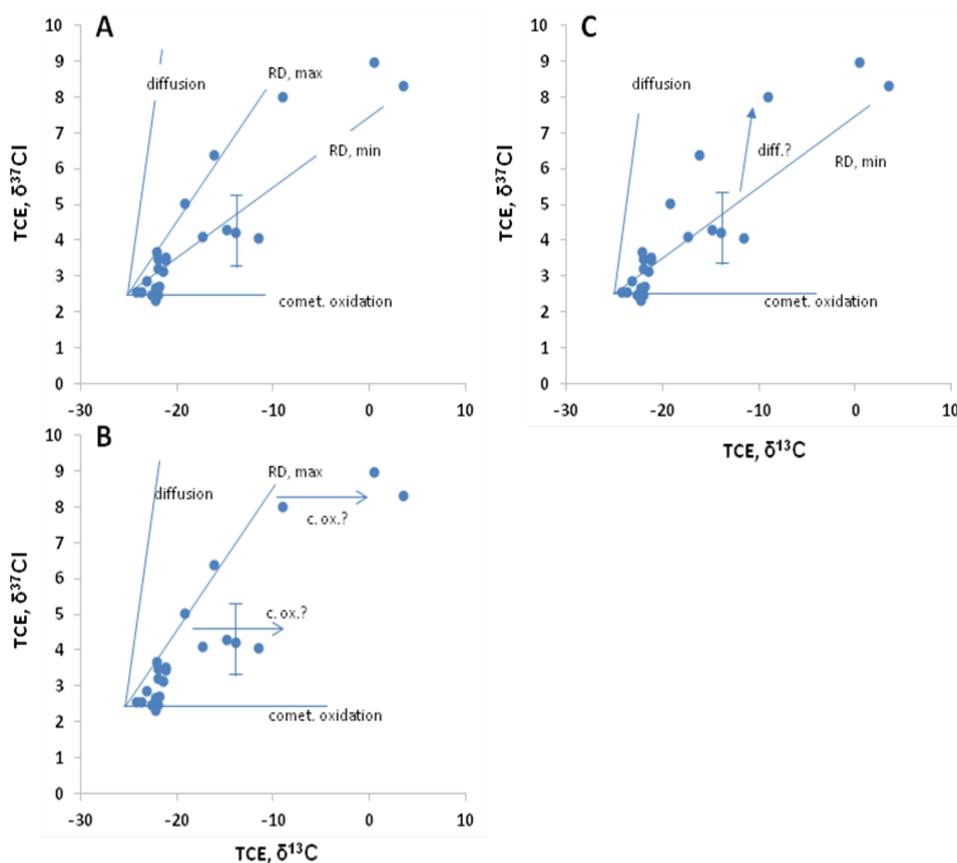


Figure 6.3. 2D-Element CSIA Plots, TCE in the Deep Plume.

The 2D-CSIA reference trends are shown for RD (minimum and maximum range) and diffusion based on published experimental data (see the summary of isotope effect in TCE biodegradation, Appendix B of the User's Guide, ER-201029, see Wanner and Hunkeler, 2015 for the isotope effects in TCE diffusion). The reference line for cometabolic oxidation is theoretical (the absence of CL fractionation accounting for the known reaction mechanism with formation epoxide intermediate). A) Rationalization with RD only; B) Rationalization by TCE oxidation following RD; C) Rationalization RD, with additional Cl fractionation resulting from TCE diffusion.

6.2.2 Model Approach

Based on the existing CSM and the “classic” CSIA interpretation (Section 6.2.1), tentative attenuation scenarios were proposed (Table 6.1), combining reductive dechlorination of TCE with other degradation pathways. Those scenarios were then tested using the 0-D PHREEQC model. Model inputs (isotope enrichment factors, source isotope ratios, and rates of individual reactions) are detailed in the Final Report (Tables 6.3 and 6.4).

Given the limitations of the 0-D approach, only the wells with evidence of degradation qualified for evaluation. This was because the model addresses the contaminant concentration through calculation of the molar fraction of individual contaminants. If no degradation products are present ($x = 100\%$) and the isotope ratio of the contaminant is identical to the source value, the data point cannot be interpreted beyond stating the lack of evidence of degradation.

Table 6.1. Description of the Simulation Scenarios

#	Simulation	Variables	Figure
1	Scenario 1. Reductive dechlorination only, end product c-DCE	none	6.5
2	Scenario 2. Simultaneous (TCE,DCE) RD and (DCE, VC) OX.	Variations in relative DCE degradation rate constant	6.6
3	Scenario 3. Sequential (TCE, DCE) RD and (TCE, DCE, VC) OX.	Rate constants, eC-TCE (oxidation) enrichment factor	not shown ¹
4	Scenario 4. Simultaneous RD and OX.	Rate constants, eC-TCE (oxidation) enrichment factor	not shown ¹
5	Scenario 1. Reductive dechlorination only, end product c-DCE – alternative ϵ C-TCE value	none	not shown ¹

¹ See Final Report for the complete set of model output figures (Figures. 6.9-6.13)

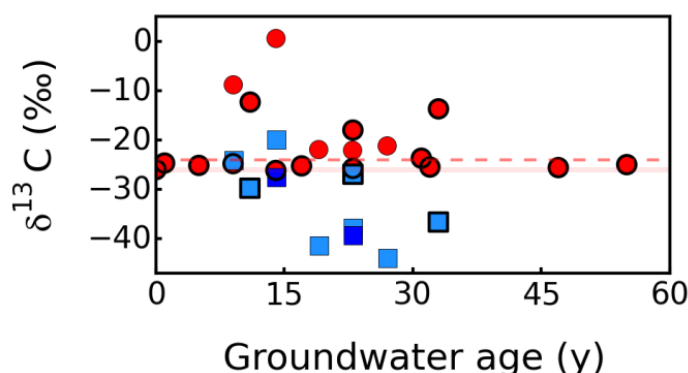


Figure 6.4. C Isotope Ratios for TCE (red circles), cDCE (light blue squares) and tDCE (dark blue squares), Versus the Groundwater Age.

Shallow wells are identified with a black edge. The red line corresponds to the uncertainty of the TCE source signature, the dashed parallel line correspond to the minimum $\delta^{13}\text{C}$ signal indicative of degradation of 2 ‰ (US EPA, 2008).

The rationale for the revision of the spatial dimensionality of the model to 0-D. We applied the 0-D batch model where a plume was considered a reaction vessel where concentrations and isotope ratios change in a logical fashion but where spatial locations of the individual samples and the transport are not considered. That decision was motivated as follows:

1. The patterns of isotope ratios of TCE vs. distance (Figures 5.1A-D) and vs. groundwater age (tritium-helium data, Figure 6.6) were irregular, not matching the assumed homogeneous first-order degradation rate constant postulated by the CSM.
2. CEs degradation appears to be unevenly spread across the shallow plume, while occurring predominantly near the former source of the deep plume (and with significant element of diffusion and back diffusion, see discussion below).

3. A solution could be to simulate multiple flow paths covering multiple areas in the aquifer. However, we could not find areas like shallow/middle/deep parts of the aquifer where downgradient wells are hydraulically connected and the CSIA enrichment shows a steady pattern over the flow line.

The 0-D model approach is still informative, through validation of field isotope enrichment factors and by proving/disproving various degradation scenarios (Table 6.1). The obtained enrichment factors can subsequently be used in Rayleigh-type equation (Eq. 3) to calculate the extent of transformation (Section 6.3.2).

6.2.3 Modeling Results

Shallow Plume: Scenario test results

RD of TCE was confirmed as a significant degradation process. All scenarios without TCE oxidation yielded good fit of the simulated TCE isotope ratios and concentrations to the field data (Figures 6.5 and 6.6). As already suggested in the preceding section, sample U9-12-021 was an exception in that a better fit was obtained for the scenario involving TCE oxidation (see Final Report, Figures 6.11 and 6.12).

The RD-only model (Scenario 1, Figure 6.5) showed a poor fit to the field data, in particular, in regards to the C isotope ratios of DCE (Fig. 6.5B). Scenario 1 overpredicted the production of DCE and/or underpredicted the isotope ratios of DCE. That result was not unexpected, since C-IMB data evaluation has also suggested the possibility of CEs mineralization proceeding past DCE. Scenario 2 (Figure 6.6) confirmed that hypothesis. Introduction of a sink for DCE (either through direct oxidation or through production of VC which is subsequently oxidized) produced a much better data fit, for DCE, without significant worsening of the fit for TCE. In that model, there was a clear effect of the relative rates of cDCE production and degradation. The model required that the rate of DCE degradation was low in comparison to the rate of TCE degradation through reductive dechlorination. Clear identification of the sink for DCE was not possible, but based on existing site data (relatively high content of DO and the presence of aerobic bacteria capable of CEs degradation), oxidation of the RD products appears the most likely option.

Finally, potential of TCE oxidation was assessed by testing Scenarios 3 and 4 (see Final Report, Figures 6.11 and 6.12). Both scenarios can be forced (by adjusting model inputs) to match the dual-element field data for the RD and oxidation of TCE for individual data points, however, such an outcome is not very realistic, since it would require hand-picked input parameters for each well to maintain the appearance of a dual-element trend for a group of wells.

Conclusions

- The model combining RD of TCE and relatively slower degradation of the RD products yields a good fit to the field TCE and DCE data collected from the Shallow Plume.
- Model results confirm that DCE is degrading (most likely, by cometabolic oxidation).
- Introduction of TCE oxidation into the model helps to explain the CSIA results for U9-12-021. That sample's isotope ratios and the observed concentrations appear to be consistent with the effects of combined reductive dechlorination of TCE and aerobic degradation of both TCE and DCE.

- For most wells, there is no clear evidence of TCE oxidation.
- Oxidation of TCE cannot be excluded, but the present results imply that (i) the process would have to be associated with minimal isotope fractionation (such as reported for cometabolic sMMO organisms, but not the organisms utilizing toluene oxygenases that were identified at the Hill site); and (ii) the rates of TCE and DCE oxidation would have to be precisely balanced to maintain the observed RD-like data patterns.
- Note that the model omits the wells that were not exhibiting C isotope fractionation. TCE in those wells was not affected by RD. If TCE oxidation occurred, it must have been limited or the degradation pathway did not involve isotope fractionation (the enrichment factor of the aerobic degradation would be near zero).
- In addition to TCE degradation, the Shallow Plume shows isotope signature of significant TCE mass attenuation by diffusion out of the mobile porosity (Fig. 6.2).

Deep Plume: Scenario test results

Figures 6.5A and 6.6A show that the wells in the W section of the deep plume (green data points) are consistent with the RD model that also successfully simulated the data from the Shallow Plume. On the other hand, the model showed significant fit deviations vs. the majority of samples from the E/NE area. The model (all scenarios tested) significantly overpredicted the molar fractions of TCE and/or the isotope ratios of TCE if the applied enrichment factor was the same as in the Shallow Plume (-20 ‰). While the applied TCE isotope enrichment factor seems too large compared to the observations, the model using a smaller enrichment factor to fit $\delta^{13}\text{C}$ of TCE would not reproduce the depleted $\delta^{13}\text{C}$ of DCE in the same samples.

Apparently, the present model does not address the attenuation mechanisms in the Deep Plume. The model accounts for chemical reactions, but not for contaminant transport. Note that the Deep Plume is situated in heterogeneous lithology, with dominant element of fine-grained sediment. According to the CSM, diffusion and back-diffusion of contaminants may be significant at the Deep Zone, in particularly in the E/NE area. Accordingly, diffusion and back-diffusion may be responsible for the observed anomalies of TCE and DCE molar fractions and isotope ratios. For example, if TCE degradation occurs in clay but not in mobile porosity, the excess of (isotopically depleted) DCE product in the clay compartment leads to preferential back-diffusion of DCE vs. TCE. The same process might also explain the C-IMB depletions observed in certain samples. While no perfectly satisfying explanation could be suggested, we expect transport processes to considerably influence the molar ratios and the distribution of the pollutants at this site.

Conclusions

- Model results are consistent with a major role of RD of TCE.
- The model results concerning the fate of degradation products and potential oxidation of TCE are inconclusive.
- Significant problems with fitting the simulation results for various reaction chain scenarios to the field data suggest that the concentrations and isotope ratios of the contaminants in the mobile porosity are largely controlled by back-diffusion.

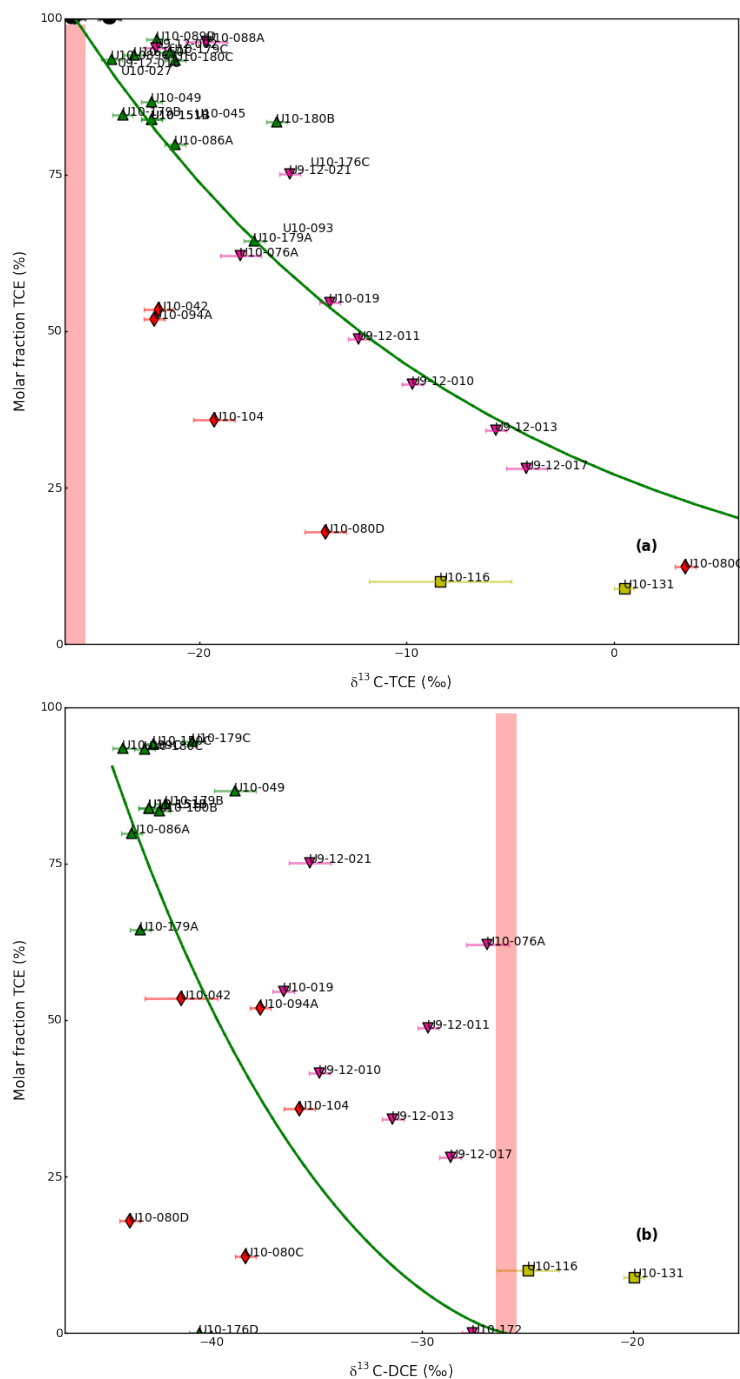


Figure 6.5AB. Scenario 1 (Table 6.1): Model for TCE Reductive Dechlorination only, cis-DCE Stall.

A) C Isotope Ratios of TCE vs. Molar Fraction of TCE; B) C Isotope Ratios of cis-DCE vs. Molar Fraction of TCE. The shaded rectangle represents the carbon TCE source signature's uncertainty range. Symbols depict individual monitoring wells: Shallow Plume (pink); western part of the Deep Plume (green); wells with depleted C-IMB, E/NE area of the Deep Plume (red); wells with enriched C-IMB, E/NE area of the Deep Plume (yellow).

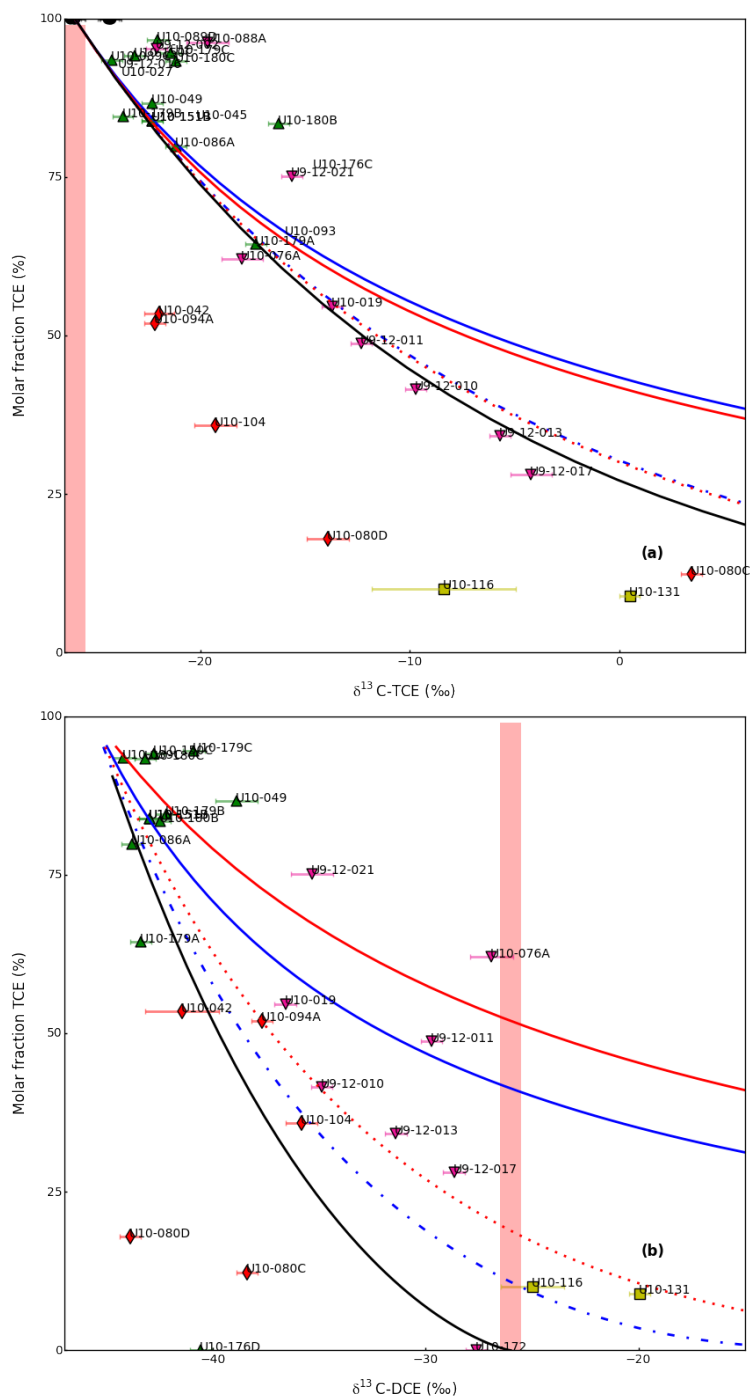


Figure 6.6AB. Scenario 2 (Table 6.1): DCE Oxidation Model (blue dashed, $k_{DCE} = 0.2 \times k_{TCE}$; blue solid, $k_{DCE} = 1 \times k_{TCE}$) versus DCE Reductive Dechlorination Followed by Quick VC Oxidation Model (red dashed, $k_{DCE} = 0.2 \times k_{TCE}$; red solid, $k_{DCE} = 1 \times k_{TCE}$).

A) C isotope ratios of TCE vs. molar fraction of TCE; B) C isotope ratios of cis-DCE vs. molar fraction of TCE. Black line represents the model with TCE reductive dechlorination only (Scenario 1). Symbols: identical as in Fig. 6.5.

6.3 CSIA-RTM TO IMPROVE CSM OF THE STUDY SITE

6.3.1 The Value of CSIA/RTM to Resolve Complex Attenuation Pathways

As discussed above, we obtained evidence of several processes contributing to CEs attenuation at the site. The initial lines of evidence were the dual-element CSIA (cf. Figures 6.7 and 6.8), used to identify the patterns of two-element (C, Cl) isotope fractionation consistent with known degradation/attenuation mechanisms and calculation of C-IMB for the sum of CEs for each sample, to identify potential losses of RD dechlorination products. The next level of mechanism identification was the scenario modeling, performed to resolve ambiguities in the initial evidence. The results are summarized below:

1. **Reductive dechlorination of TCE in Shallow and Deep Plumes.** Dual-element CSIA provided strong evidence of RD occurring in both plumes. Direct validation of that interpretation by the model was unnecessary, but model scenarios combining RD with oxidation of RD products and/or TCE permitted to assess the relative significance of RD in the overall degradation budget.
2. **Degradation of cis-DCE in Shallow and Deep Plumes.** In the Shallow Plume, the evidence from the enriched C-IMBs was consistent with model results. Together, CSIA and the model evidence permitted a robust confirmation of DCE degradation. In the Deep Plume, the evidence was more ambiguous. Due to significant element of diffusion/back-diffusion, C-IMB data varied significantly, in particular in the E/NE section of the plume where anomalous, ^{13}C -depleted readings of C-IMB were obtained. Scenario simulations involving DCE degradation appeared to fit only certain individual wells, but the overall fit to the data set was poor.
3. **Oxidation of TCE in Shallow Plume.** Only well U9-12-021 produced dual-element signatures consistent with significant contribution of TCE oxidation. This was also confirmed by the model. However, modeling excludes significant role of oxidation mechanisms that are known to produce relatively strong isotope fractionation (e.g., cometabolic degradation by toluene oxygenases). As discussed in the previous section, we cannot exclude TCE oxidation if the associated isotope fractionation is minimal.
4. **TCE mass attenuation by diffusion out of the mobile porosity in Shallow Plume.** Strong evidence of TCE mass removal by diffusion is provided by dual-element CSIA (Figure 6.7). The 0-D model used in this study does not address that process.
5. **Diffusion/back-diffusion of CEs in Deep Plume.** Anomalous C-IMB values of several wells in the Deep Plume and problems with fitting the simulations suggest that the isotope ratios and concentrations of TCE and DCEs are affected by non-degradative processes that are not included in the model. In the Deep Plume the difficulties are likely caused by diffusion/back-diffusion.

Conclusions

1. Consistent conclusion from “classic” CSIA and the modeling provide the most robust mechanism identification.
2. Degradation and non-degradative pathways can be identified.

3. Existing model is not adequate for accurate simulation of certain data sets. In the Deep Plume, significant element diffusion/back-diffusion appears to be too significant to apply the 0-D modeling approach.

6.3.2 Degradation Constants

In 0-D modeling, the field degradation rates are not obtained directly from the simulation but can be estimated indirectly, using the extent of overall CEs degradation and the time elapsed since the onset of degradation at given monitoring, using Eq. 6, where A is the groundwater age at the sampling location (years), and f_{CE} , the fraction of the remaining contaminant (TCE, DCE, or the total CEs). In principle, this is the approach of CSIA-based calculation of the rates of degradation that was already described by various authors, including in Sections 4.3 and 4.4 of the CSIA Guidance Document published by USEPA (USEPA, 2008).

$$k_{CE} = -\frac{\ln(f_{CE})}{A} \quad (\text{Eq. 6})$$

Using Eq. 6 is straightforward for evaluation of the primary contaminant (TCE at this site), because f_{CE} is calculated directly by the Rayleigh equation (Eq. 3). To calculate f_{DCE} (DCE degradation product), $\delta^{13}C_{DCE,0}$ must be obtained first, using Eq. 7. (Hunkeler et al., 2005).

$$\delta^{13}C_{DCE,0} = \delta^{13}C_{TCE,0} + \frac{\varepsilon_{TCE \rightarrow DCE} \cdot f_{TCE} \cdot \ln(f_{TCE})}{1 - f_{TCE}} \quad (\text{Eq. 7})$$

The values of enrichment factors for Eq. 3 and Eq. 7 can be taken from the modeling, given that the model fitted the field data (this is the approach producing most accurate rate estimates, Figure 6.7). If that is not possible, conservative values of enrichment factors should be taken from the literature, to avoid over-prediction of the extent of degradation (USEPA, 2008). Note that rate constants using groundwater ages might over- or underestimate the localized degradation rate constants. At OU10, large degradation rate constants close to the source, in the vicinity of the aquitard, are likely overestimated by back-diffusion of highly degraded and thus enriched TCE and DCE from clay into water with relatively recent age. However, generally, it can be assumed that degradation occurs in local zones and thus the obtained integral rate constants underestimate the true rates at these local hotspots. A more conservative approach, similar to the standard CSIA data evaluation protocol, would be to use the age of the spill as the maximum age of the contaminant (see Sections 4.3 and 4.4 of the CSIA Guidance Document published by USEPA; USEPA, 2008).

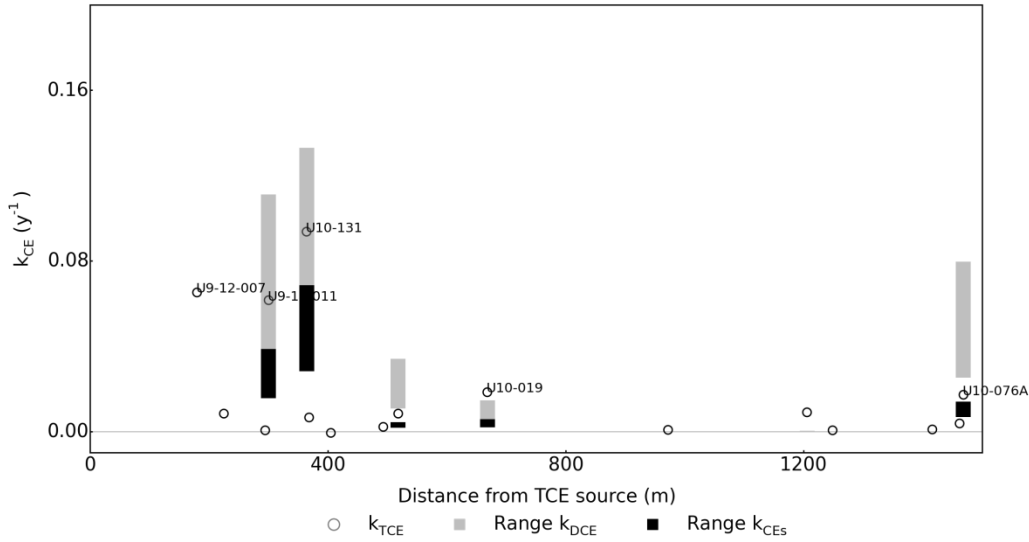


Figure 6.7. First-Order Integral Degradation Rate Constants for TCE (circles), DCE (grey bars), and CEs Mineralization (black bars).

The rate constant represent average values along the flow paths leading to the specific monitoring wells.

Bars indicate the range obtained with different model parameters for low-fractionating oxidative degradation of DCE (upper end) and for high-fractionating reductive degradation of DCE (lower end). Both shallow and deep wells are presented. Age of groundwater was obtained by tritium-helium dating (cf. Figure 6.4).

Finally, cumulative mineralization of CEs (inclusive of the parent CE and the RD products) can also be obtained, using Eq. 8 (f_{CEs} is the cumulative fraction of all CEs remaining after degradation). For TCE and DCE, Eq. 8 is written as:

$$f_{CEs} = 1 - (1 - f_{TCE})(1 - f_{DCE}) \quad (\text{Eq. 8})$$

Figure 6.8 shows an example of model-assisted estimation of the fraction of mineralized (oxidized) CEs. The modeled reference lines are based on Scenario 2 (RD of TCE combined with oxidation of RD products; Table 6.1). It should be noted that Fig. 6.8 is not absolutely quantitative even if the reference model displayed good fit to the field data. Calculation of the remaining fraction of the contaminant (f in Eq. 3) is sensitive to the chosen value of the enrichment factor. In the present case, no analysis was performed on the goodness of model fit for a wider range of enrichment factors.

Conclusions

- The main benefit of the 0-D model is a decrease of uncertainty of the applicable range of enrichment factors.
- The modeling permitted a quantitative assessment of the fate of the RD intermediates (cf. Figure 6.14). “Classic” CSIA assessment of the fate of the intermediates is qualitative.

- The accuracy of the calculated rate constant improves for well-defined reaction mechanisms, with well-defined enrichment factors.
- The groundwater age is not directly representative of the time of degradation and introduces some uncertainty in the calculate degradation rate constants.

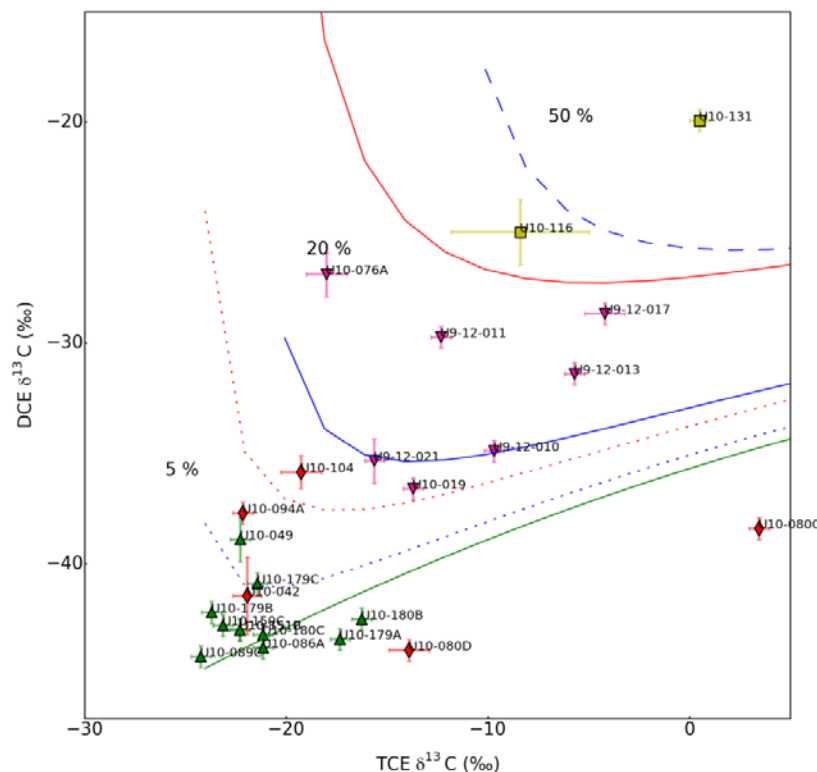


Figure 6.8. Estimation of Cumulative CEs Mineralization, Comparing Observed Values (markers) with the Modeled Contour Lines of the Percentage of Total CEs Mineralization.

The modelled lines are based on model Scenario 2, where RD of TCE was followed by DCE reductive dechlorination followed by quick VC oxidation (red), or DCE reductive dechlorination was followed directly by DCE oxidation (blue). The percentage of mineralization: short dashes, 5 %; solid lines, 20 %; long dashes, 50 %. As a reference, a contour line of the model without further DCE transformation is shown in green (this model represents 0 % of mineralization). Symbols depict individual monitoring wells: Shallow Plume (pink); western part of the Deep Plume (green); wells with depleted C-IMB, E/NE area of the Deep Plume (red); wells with enriched C-IMB, E/NE area of the Deep Plume (yellow). Note that based on the model fit quality the most reliable data are those from the Shallow Plume and from the western part of the Deep Plume.

6.3.3 Summary of the Refined CSM for Demonstration Site

The conclusions from the CSIA/RTM characterization of CEs attenuation in the Shallow and Deep Plumes are summarized, following Sections 6.2.1 and 6.3.2. The type of information obtained is relatively similar to that provided by the “classic” CSIA, with the most significant added benefit of more accurate quantitative conclusions regarding the degradation rates and the extent of contaminant mass attenuation.

Key benefits of the model

1. In the Shallow Plume, the 0-D model was a good approximation of the transformations of the contaminants of concern. For that Plume, validation of the conclusions from “classic” lines of CSIA evidence (e.g., mechanism identification using the dual-element CSIA plot) and then by validation of the proposed degradation scenarios by means of modeling was informative and strengthened the final conclusion.
2. Modeling (scenario testing) can be applied as a negative evidence (to confirm the absence or insignificance of an attenuation scenario). For example, it was possible to assess the potential for TCE oxidation (specifically, cometabolic oxidation by toluene oxygenase that is known to result with significant carbon isotope fractionation). That mechanism appears to be negligible. This conclusion could not be reached using the “classic” approach (compare Figures 6.7A vs. 6.7B).
3. Possibly the most valuable contribution of the modeling is in improving the precision of quantitative assessment of biodegradation, for the RD intermediates (Figure 6.8), and in general through providing more precisely constrained values of enrichment factors. Typically, estimates of degradation rates obtained from CSIA (Eq. 3) are highly conservative. Modeling helped to improve the precision of the calculated extent of biodegradation.

Page Intentionally Left Blank

7.0 COST ASSESSMENT

7.1 COST MODEL

The scale of the present demonstration was significantly larger than the anticipated scale of routine applications. In routine application, fewer samples will be collected and analyzed and two-element or three-element CSIA data will be required only at case-specific basis. The cost estimates assume that the CSIA is performed on commercial basis by a lab charging fixed price per sample (cost of method development is not included). The cost estimates assume that data interpretation (CSIA and modeling) is performed by trained consultants and that the model will be implemented similarly to the present study, using the 0/1-D option. Cost of software training and software is not included in the model.

Table 7.1. Cost Model for a CSIA/Model Application

Cost Element	Data Tracked
Project Planning	Unit Cost: \$ per labor hour - Labor hours for preliminary site assessment (on-site) - Labor hours for preliminary site assessment (consultant)
Groundwater Sampling	Unit Cost: \$ per monitoring well Mobilization and sampling, including personnel labor, sampling supplies, and shipping of the samples to the laboratory
Laboratory Analysis	Unit Cost: \$ per analysis - Number of routine concentration analyses - Number of CSIA analyses - Number of groundwater geochemistry parameter analyses
Data Interpretation	Unit Cost: \$ per labor hour - Labor hours for preliminary ('classic') CSIA interpretation (consultant) - Labor hours for modeling (consultant) - Labor hours for reporting (consultant)

7.2 COST DRIVERS

Cost of CSIA per sample. Unlike conventional VOCs concentration analysis, the CSIA cost per sample varies significantly, depending on the number of target analytes and on the isotope ratios to be determined.

Number of samples collected. The USEPA guide for CSIA (USEPA, 2008) recommends collecting of 12-20 samples from separate monitoring wells for "classic" CSIA projects. If the modeling is potentially to be used, the number of samples should probably fall close the maximum of the recommended range. Model fitting works best if the simulation is matched vs. a group of field data, to identify common mechanisms affecting the target contaminants. Results from modeling of smaller data sets may be also useful, if the tested scenarios are relatively simple and the hydrogeology conditions suggest low heterogeneity.

Table 7.2. Cost Analysis: CSIA/RTM vs. MNA

Cost Element	Cost Unit	No. Units	Subtotal Classic CSIA	Subtotal CSIA+model	Subtotal MNA (3 yrs, semiannual)
Project Planning	\$150/hour	4	\$600	\$600	\$ -
Groundwater Sampling	\$100/well (MNA)	10	\$ -	\$ -	\$ 6,000
	\$125/well (CSIA)	10	\$1,250	\$1,250	\$ -
Laboratory Analysis	\$100/sample; VOCs concentrations and geochemistry	10	\$1,000	\$1,000	\$6,000
	\$900/sample; CSIA (see Table 7.2 for further cost details)	10	\$9,000	\$9,000	\$ -
Data Interpretation	\$150/hour ("classic" CSIA)	15	\$2,250	\$2,250	\$ -
	\$150/hour (modeling)	15	\$ -	\$2,250	\$ -
TOTAL			\$14,100	\$16,3550	\$12,000
TOTAL (sampling cost excluded) ¹			\$12,100	\$14,350	

¹ Assumes the sample collection and VOCs data are shared with the routine site assessment. Monitoring well mobilization cost and standard VOCs and geochemistry analyses are removed from the total.

7.3 COST ANALYSIS

Cost analysis is shown for a hypothetical Case Study utilizing methodology similar to that applied at the Demonstration Site (C, or C+Cl CSIA, 0-D modeling). The cost is compared to the cost of conventional MNA sampling and analysis. The Case Study example concerns a simple data set collected to answer the question whether RD stalls at cis-DCE or whether cis-DCE is also mineralized. 10 samples are collected. C and Cl CSIA are conducted for TCE and for cis-DCE (Table 7.2). The cost of CSIA/modeling is compared to the cost of three years of MNA sampling. The cost analysis demonstrates CSIA and CSIA/modeling (totals include sample collection, analysis and interpretation) compare favorably with standard. Additional cost saving is possible if sample collection and routine analytical work is integrated into scheduled site monitoring activities. The added cost of modeling conducted by a consultant who is already set for this type of work is relatively minor in comparison to the total cost of implementation.

8.0 IMPLEMENTATION ISSUES

The interaction with the Demonstration Site is limited to collecting of groundwater samples, and identical implementation issues apply as in routine site monitoring work. Therefore, no implementation issues are expected in regards to field sample collection. Also, from the point of view of the end user, no special equipment or software procurement is involved.

Two potential implementation issues are: (i) availability of consultants with appropriate CSIA and modeling training; and (ii) availability of CSIA laboratory facilities. Currently, few consultants in the USA specialize in CSIA data and probably no consultants specialize in isotope effect modeling. Self-training material (User's Guide and the attendant model templates) is intended to be the reference for consultants with general modeling background. Currently, few laboratories in the USA and Canada offer CSIA on commercial basis. Moreover, sample processing capability for certain types of CSIA is even more restricted. Therefore, the processing of CSIA samples tends to be less timely than in the case of standard VOCs analytical data.

On more general level, it is possible that the implementation results may be inconclusive or the modeling may bring no additional benefit vs. "classic" CSIA. The preliminary stage of a routine application should be an assessment of available site data, to first decide if CSIA should be pursued. The cost increment added by the modeling is relatively small in comparison with the cost of sample collection and CSIA. Moreover, modeling of the data is not time-sensitive. The decision of whether the modeling should be pursued can be made based on the results from the "classic" CSIA data (are there uncertainties remaining that can be potentially resolved by scenario modeling?). Finally, the confidence of data interpretation, both in "classic" CSIA and in CSIA/modeling, requires good mechanistic understanding of isotope effects associated with the degradation pathways to be investigated. Currently, relatively few publications are available on isotope effects of Cl and even more so, on isotope effects of H, in key degradation pathways relevant to CEs studies. Preliminary assessment of the site should consider what can be achieved, based on up-to date status of the subject's literature.

Page Intentionally Left Blank

9.0 REFERENCES

- CH2MHILL (2009). Operable Unit 10 Remedial Investigation Report. Salt Lake City, UT, CH2M Hill for Air Force Center for Engineering and the Environment and Hill Air Force Base, Utah. CH2MHILL (2011). Hill AFB OU10 ERPIMS Database. C. M. f. U. A. Force.
- D'Affonseca, F. M., H. Prommer, M. Finkel, P. Blum and P. Grathwohl (2011). "Modeling the long-term and transient evolution of biogeochemical and isotopic signatures in coal tar-contaminated aquifers." Water Resources Research **47**.
- Eckert, D., S. Qiu, M. Elsner and O. A. Cirpka (2013). "Model Complexity Needed for Quantitative Analysis of High Resolution Isotope and Concentration Data from a Toluene-Pulse Experiment." Environmental Science & Technology **47**(13): 6900-6907.
- ER-201029 (2014) Integrated Stable Isotope – Reactive Transport Model Approach for Assessment of Chlorinated Solvent Degradation. User's Guide. Available online at <https://serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/ER-201029>
- Hunkeler, D., B. M. Van Breukelen and M. Elsner (2009). "Modeling Chlorine Isotope Trends during Sequential Transformation of Chlorinated Ethenes." Environmental Science & Technology **43**(17): 6750-6756.
- Hunkeler, D., Aravena, R., Berry-Spark, K., Cox, E. (2005) "Assessment of degradation pathways in an aquifer with mixed chlorinated hydrocarbon contamination using stable isotope analysis". Environmental Science and Technology 2005, **39**: 5975-5981.
- Jin, B., M. Rolle, T. Li and S. B. Haderlein (2014). "Diffusive Fractionation of BTEX and Chlorinated Ethenes in Aqueous Solution: Quantification of Spatial Isotope Gradients." Environmental Science & Technology **48**(11): 6141-6150.
- Karlsen, R. H., F. J. C. Smits, P. J. Stuyfzand, T. N. Olsthoorn and B. M. Van Breukelen (2012). "A post audit and inverse modeling in reactive transport: 50 years of artificial recharge in the Amsterdam Water Supply Dunes." Journal of Hydrology **454**: 7-25.
- Kuder, T. and P. Philp (2013). "Demonstration of Compound-Specific Isotope Analysis of Hydrogen Isotope Ratios in Chlorinated Ethenes." Environmental Science & Technology **47**(3): 1461-1467.
- Kuder, T., B. M. van Breukelen, M. Vanderford and P. Philp (2013). "3D-CSIA: Carbon, Chlorine, and Hydrogen Isotope Fractionation in Transformation of TCE to Ethene by a Dehalococcoides Culture." Environmental Science & Technology **47**(17): 9668-9677.
- Prommer, H., B. Anneser, M. Rolle, F. Einsiedl and C. Griebler (2009). "Biogeochemical and Isotopic Gradients in a BTEX/PAH Contaminant Plume: Model-Based Interpretation of a High-Resolution Field Data Set." Environmental Science & Technology **43**(21): 8206-8212.

- USEPA (1998). Technical Protocol for Evaluating Natural Attenuation of Chlorinated Solvents in Ground Water. Washington DC, US Environmental Protection Agency.
- USEPA (2008). A Guide for Assessing Biodegradation and Source Identification of Organic Ground Water Contaminants using Compound Specific Isotope Analysis (CSIA). USEPA. Washington, DC, US Environmental Protection Agency Office of Research and Development National Risk Management Laboratory: 82.
- Van Breukelen, B. M. and H. Prommer (2008). "Beyond the Rayleigh equation: Reactive transport modeling of isotope fractionation effects to improve quantification of biodegradation." Environmental Science & Technology **42**(7): 2457-2463.
- Van Breukelen, B. M. and M. Rolle (2012). "Transverse Hydrodynamic Dispersion Effects on Isotope Signals in Groundwater Chlorinated Solvents' Plumes." Environmental Science & Technology **46**(14): 7700-7708.
- Van Breukelen, B. M., D. Hunkeler and F. Volkerling (2005). "Quantification of Sequential Chlorinated Ethene Degradation by Use of a Reactive Transport Model Incorporating Isotope Fractionation." Environmental Science and Technology **39**(11): 4189 - 4197.
- Van Breukelen, B. M., Stack, P.E., Thouement, H.A.A., Vanderford, M., Philp and Kuder, T. (2016) Modeling 3D-CSIA Data: Carbon, Chlorine, and Hydrogen Isotope Fractionation during Reductive Dechlorination of TCE to Ethene. Submitted to Environmental Science & Technology
- Wanner, P. and D. Hunkeler (2015) Carbon and chlorine isotopologue fractionation of chlorinated hydrocarbons during diffusion in water and low permeability sediments. Geochimica et Cosmochimica Acta, **157**:198-212.

APPENDIX A POINTS OF CONTACT

Point of Contact Name	Organization Name Address	Phone Fax Email	Role in Project
Paul Philp	Univ. of Oklahoma, 100 E. Boyd St., Norman Oklahoma 73019	405-325-4469 (phone) 405-325-3140 (fax) pphilp@ou.edu	PI Supervising the project
Tomasz Kuder	Univ. of Oklahoma, 100 E. Boyd St., Norman Oklahoma 73019	405-325-3253 (phone) 405-325-3140 (fax) tkuder@ou.edu	Co-PI Supervising the Analytical Lab
Boris van Breukelen	Delft University of Technology, Stevinweg 1, 2628 CN Delft, The Netherlands (former affiliation VU University Amsterdam)	+31-15-278-5227 (phone) b.m.vanbreukelen@tudelft.nl	Performer Developing the Models
Héloïse Thouement	VU University Amsterdam, De Boelelaan 1085, 1081 HV Amsterdam, The Netherlands	+31-20-5983851 (phone) h.a.a.thouement@vu.nl	Performer Developing the model, conducting data modeling
Mindy Vanderford	HydroGeoLogic, Inc., 4407 Jane St., Bellaire, Texas 77401 (former affiliation: GSI Environmental, Houston TX)	713-838-7778 (phone) mvanderford@hgl.com	Performer Supervising Field Program and Logistics



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