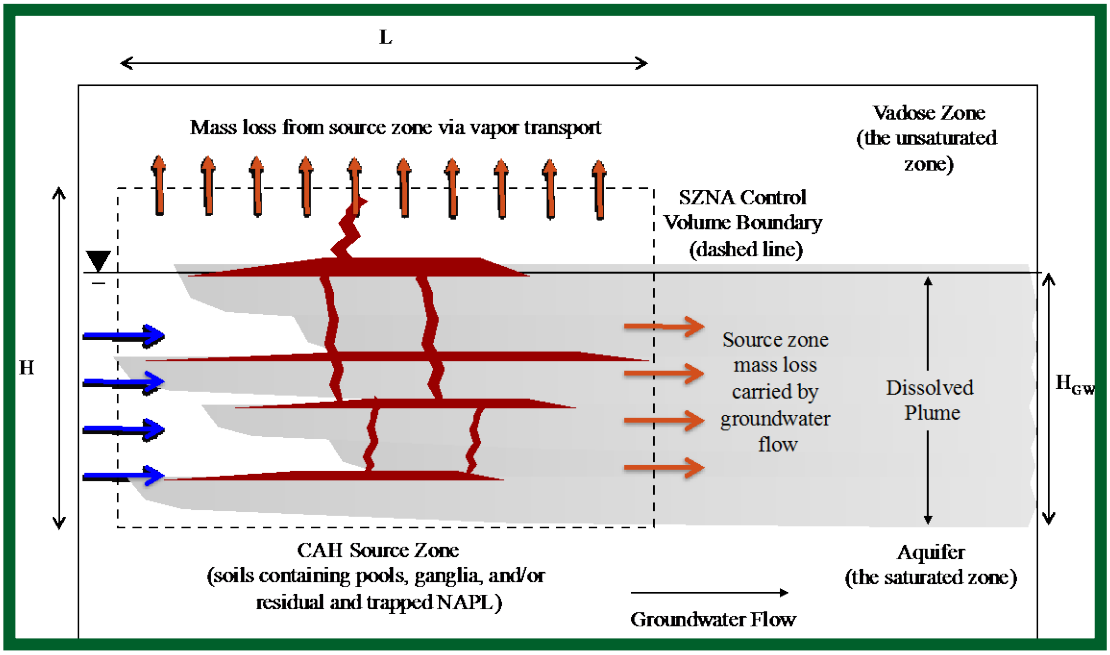
ESTCP
Cost and Performance Report

(ER-200705)



Assessment of the Natural Attenuation of NAPL Source Zones and Post-Treatment NAPL Source Zone Residuals

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ESTCP

ENVIRONMENTAL SECURITY
TECHNOLOGY CERTIFICATION PROGRAM

U.S. Department of Defense

COST & PERFORMANCE REPORT
Project: ER-200705

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ACRONYMS AND ABBREVIATIONS

AFB	Air Force Base
bgs	below ground surface
CAH	chlorinated aliphatic hydrocarbon
cm/s	centimeters per second
D_{eff}	effective vapor diffusion coefficient
DCE	dichloroethylene
DNAPL	dense non-aqueous phase liquid
DPT	direct push technology
ESTCP	Environmental Security Technology Certification Program
ft	feet/foot
ISCO	in situ chemical oxidation
ITRC	Interstate Technology Research Council
K	hydraulic conductivity
kg	kilogram
km	kilometer
LMTA	Little Mountain Test Annex
LNAPL	light non-aqueous phase liquid
m	meter
MCRD	Marine Corp Recruit Depot
NA	not applicable
NAS	Naval Air Station
NAVFAC	Naval Facilities Engineering Command
NRC	National Research Council
NS	not sampled
PCE	perchloroethylene
RPM	Remedial Project Managers
SDB	sludge drying bed
SZNA	source zone natural attenuation
TCA	trichloroethane

TCE	trichloroethylene
USEPA	U.S. Environmental Protection Agency
VC	vinyl chloride
VOC	volatile organic compound
y	year

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EXECUTIVE SUMMARY

OBJECTIVE OF THE DEMONSTRATION

The objective of this project was to demonstrate and document the use of a proposed source zone natural attenuation (SZNA) assessment approach at three chlorinated aliphatic hydrocarbon (CAH)-impacted sites over a multi-year assessment period. The data-driven approach leads to confirmation that SZNA is occurring and site-specific quantification of the source zone mass loss rate.

TECHNOLOGY DESCRIPTION

The CAH SZNA assessment paradigm presented here is built on the SZNA conceptualization and calculation approach described by Johnson et al. (2006) and is structured around three groups of data collection and analyses. In brief, Group I measurements provide evidence that SZNA is occurring, Group II measurements and analyses are focused on quantifying current SZNA mass loss rates, and Group III measurements and analyses are focused on answering longer-term questions concerning the longevity of source zone impacts. This project focused mainly on Group II measurements and analyses, as often the immediate question of greatest interest is "*what is the SZNA rate?*"

As a data-driven, macroscopic, multiple-lines-of-evidence approach, the paradigm is consistent with the Nation Research Council (NRC) (2000) philosophy. Furthermore, it is complementary to theexisting dissolved plume natural attenuation protocols and makes use of dissolved mass flux techniques (e.g., Guilbeault et al. 2005) and the source zone evolution with time modeling work discussed above. Lundegard and Johnson (2006) demonstrated the SZNA assessment approach at a multiple-source hydrocarbon spill site. Their paradigm was adopted by the Interstate Technology Research Council (ITRC) and reframed as "source zone natural depletion" in their guidance document (ITRC, 2009).

DEMONSTRATION RESULTS

The approach was demonstrated over four assessment events at three CAH-impacted sites. The SZNA loss rates estimated were: 2.9, 8.4, 4.9, 2.8 kilograms per year (kg/y) as perchloroethylene (PCE) at Site 1,1.6, 2.2, 1.7, 1.1 kg/y as PCE at Site 2, and 570, 590, 250, 240 kg/y as trichloroethylene (TCE) at Site 3. There were no clear temporal trends in the results and the differences in results for Site 3 are attributable to a change in groundwater sampling procedures. It was concluded that it is likely that different practitioners will sample sites in somewhat different ways, especially regarding sampling density on a groundwater transect. The effects on discharge estimates from varied sampling densities and spacings were examined and sampling guidelines with practical site sampling densities were developed to reduce the variability in discharge estimates and to improve confidence in SZNA rates.

IMPLEMENTATION ISSUES

The approach used in this project for the assessment of SZNA at CAH sites uses fairly standard and readily available sampling and analytical tools. No barriers to the collection of the necessary

data are anticipated other than those presented by unique site conditions. Many of the data needs/lines-of-evidence are similar to those appearing in dissolved plume natural attenuation guidance, with the exception of the assessment of effective vadose zone diffusion coefficients in Group II (to characterize gas transport processes) and the use of “bench-scale weathering tests” to provide Group III data. No special permits are required for implementation of the approach.

1.0 INTRODUCTION

This ESTCP project demonstrated a generalized data-driven paradigm for the assessment of source zone natural attenuation (SZNA) at chlorinated aliphatic hydrocarbons (CAH) cleanup sites. Application of the method was demonstrated at three field sites, with multiple events per site spread out over about three years.

1.1 BACKGROUND

The selection of corrective action options at most dense non-aqueous phase (DNAPL) and light non-aqueous phase (LNAPL)-impacted sites is a non-trivial exercise, involving decision-making based on uncertain projections of technology performance and cost. In these analyses, one end-member of the spectrum of remediation options is SZNA, which is sometimes also referred to as source zone natural depletion (Interstate Technology Research Council [ITRC], 2009). SZNA relies on unassisted natural loss processes such as dissolution, biodegradation, advection and/or volatilization to achieve source zone remediation goals. SZNA is often used as a basis for assessing the performance and relative benefits of engineered remediation, and sometimes also to define remediation end-points. SZNA is also an implicit component of engineered remediation schemes, as it is relied upon to provide the reduction of post-treatment residuals.

1.2 OBJECTIVE OF THE DEMONSTRATION

The objective of this project was to demonstrate and document the use of a proposed SZNA assessment approach at three CAH-impacted sites and over a multi-year sampling period. The data-driven approach is innovative because it builds on recommendations in National Research Council (NRC) reports (1994, 2000) and the fundamental understanding of source zone natural attenuation mechanisms, and translates those into practicable site-specific guidance. Johnson et al. (2006) proposed guidance for petroleum LNAPL-impacted sites and its application was illustrated in Lundegard et al. (2006), Lenski (2004) and Liu (2004). That work was extended in this project for applicability to CAH-impacted sites.

1.3 REGULATORY DRIVERS

Based on the authors' experience, decision-makers (e.g., regulators, project managers, members of the public) are often interested in answers to the following critical questions:

a) Is SZNA occurring, and if so, what natural processes are contributing to SZNA?

b) What is the current rate of source zone mass reduction associated with SZNA, and how might this change in the future?

c) What are the longer-term implications of SZNA for future groundwater and vapor migration impacts (compounds present, their concentrations and mass discharges) at the site?

d) Are the SZNA processes and rates sustainable?

e) What is the projected longevity of the source zone or post-treatment residual?

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2.0 TECHNOLOGY

SZNA is the final component of most remediation projects because engineered processes typically do not result in complete cleanup; SZNA is then relied upon as a polishing step for the post-engineered treatment residuals (Kavanaugh and MacDonald, 1994; NRC, 1994; ITRC, 2002; U.S. Environmental Protection Agency [USEPA], 2003; Stroo et al., 2012; NRC, 2013). As a result, being able to validate that SZNA is occurring, quantify mass loss rates attributable to SZNA, and project longevity and source zone changes with time are of interest. The SZNA mass loss rate is an important benchmark when assessing the benefits of, and selecting, engineered source zone remediation schemes, and when deciding to terminate remediation (Brooks et al., 2008; Brusseau et al., 2011).

2.1 TECHNOLOGY DESCRIPTION

The CAH SZNA assessment paradigm presented here is built on the SZNA conceptualization and calculation approach described by Johnson et al. (2006) and is structured around three groups of data collection and analyses. In brief, Group I measurements provide evidence that SZNA is occurring; Group II measurements and analyses are focused on quantifying current SZNA mass loss rates; and Group III measurements and analyses are focused on answering longer-term questions concerning the longevity of source zone impacts. Table 1 summarizes specific data requirements for Group II, as often the immediate question of greatest interest is "*what is the SZNA rate?*" Tables for Group I and III data requirements are provided in the ESTCP Final Report (Ekre et al., 2014).

Table 1. Group II Data - Information needed in addition to the Group I measurements to estimate SZNA rates.

Data Need	Explanation
Collocated effective vapor diffusion coefficients and multi-level soil gas concentrations distributed above the source zone footprint	Used to estimate source zone mass removal due to vapor diffusion of CAH parent and daughter compounds
Collocated hydraulic conductivities and dissolved parent and daughter compound concentrations along transects oriented perpendicular to groundwater flow and located immediately up- and down-gradient of the source zone	Used to estimate CAH source zone mass removal carried by groundwater flow

In this work, CAH "source zones" are DNAPL-containing soil zones in direct contact with, or in close proximity to, groundwater as shown in Figure 1. DNAPL-impacted source zone soils are continuously subjected to a combination of processes, including dissolution, volatilization, and biodegradation. This leads to a depletion, or "natural attenuation," of the hydrocarbons from these soils with time.

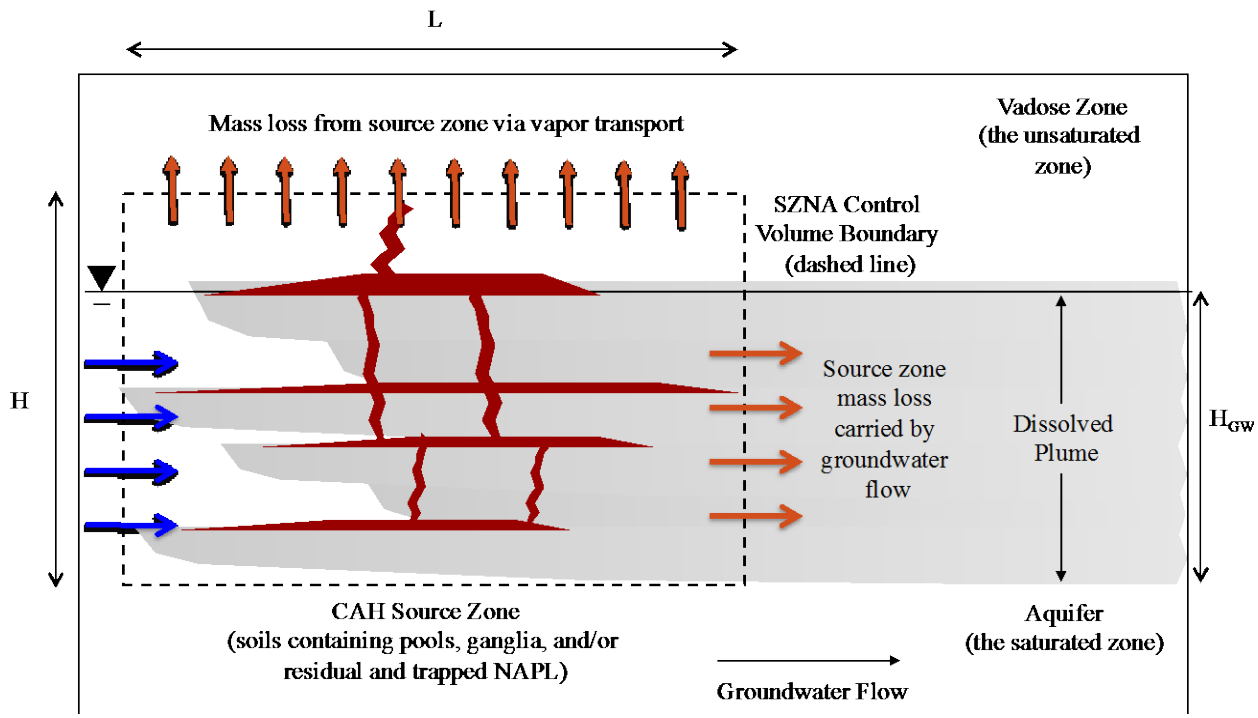

Figure 1. CAH source zone conceptualization showing SZNA mass loss rate control volume in cross section view.

2.1.1 Group II Data Collection and Interpretation: What is the SZNA mass loss rate?

A macroscopic mass balance analysis approach defines the Group II data requirements listed in Table 1. Following the Johnson and Lundegard (2006) approach, the SZNA rate is determined by quantifying mass transport across the faces of a control volume encompassing the source zone as shown in Figure 1. For each mass loss mechanism, equations are written to quantify the loss in terms of the control volume.

The SZNA control volume is chosen in such a way that: a) it encompasses the source zone and b) the CAH mass transport across the lateral, up-gradient, and lower planes is negligible. The attractive features of this approach are:

- It is not necessary to identify or quantify individual loss mechanisms to assess the overall mass loss rate.
- It is not necessary to have detailed delineation of the source zone architecture or mass; this is known to be impracticable at most sites.
- The data needed are obtainable with conventional, and commonly used field tools (e.g., dissolved and vapor concentrations), and the analyses are not overly complex.

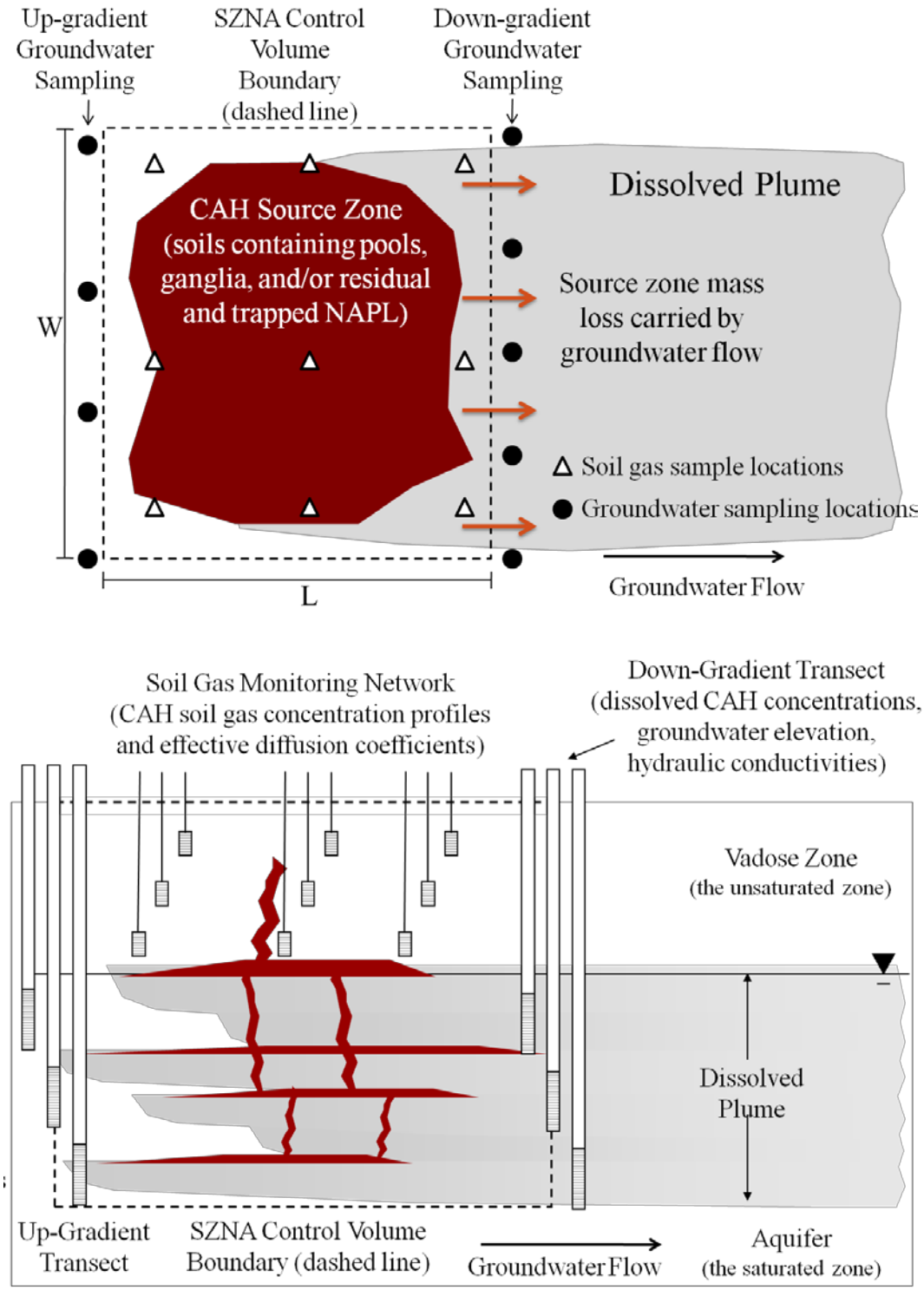

Figure 2. CAH source zone conceptual model showing SZNA mass loss rate control volume and sampling locations in plan and cross-sectional view.

2.2 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The method of SZNA assessment demonstrated in this study is applicable to a wide variety of field settings. As a data-driven approach, few assumptions are required, in contrast to modeling-only based approaches. If representative data are obtained, results of the assessment can be expected to reasonably represent actual SZNA mass loss rates in the field. It is not necessary to identify or quantify individual loss mechanisms to assess the overall mass loss rate. It is also not necessary to have detailed delineation of the source zone architecture or mass. The data needed are obtainable with conventional, and commonly used field tools (e.g., dissolved and vapor concentrations), and the analyses are not overly complex.

A disadvantage of the proposed method of SZNA assessment is that the source zone mass loss rate is specific to the point in time when the data are collected. It is not clear yet how to extrapolate the point-in-time results to future site conditions.

3.0 PERFORMANCE OBJECTIVES

Performance objectives for this study are conceptually different than those that would be established for the evaluation of an engineered remediation technology. There are no *a priori* target end-point criteria. The objective of this project was to demonstrate and document the use of a proposed SZNA assessment approach at three CAH-impacted sites. Thus, the performance objectives focus on preparation and application of the SZNA assessment guidance as discussed below in Table 2.

Table 2. Performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives			
Revision of the SZNA approach for chlorinated solvent impacted sites	None	Revised guidance is prepared and published in peer-reviewed literature and the guidance is practicable for RPMs	Journal manuscript was submitted to and accepted in *Ground Water Monitoring and Remediation*
The application of the SZNA assessment approach is illustrated at three sites	Group I and II data as specified in the SZNA protocol	Group I and II data are collected, reduced, and used to answer the Group I and II questions	Site 1: success Site 2: success Site 3: success
Qualitative Performance Objectives			
Answer Group I Question at Field Site(s): Is SZNA occurring?	Group I Data as defined in Table 2.1	Data are sufficient to establish if SZNA is occurring	Site 1: success Site 2: success Site 3: success
Answer Group II Question at Field Site(s): What is the current rate of SZNA?	Group II data as defined in Table 2.2	Data are sufficient to calculate SZNA rate	Site 1: success Site 2: success Site 3: success

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4.0 SITE DESCRIPTION

The CAH SZNA paradigm was applied to three field sites: Naval Air Station (NAS) Jacksonville PSC48; Parris Island Marine Corp Recruit Depot (MCRD) Site 45; and Hill Air Force Base (AFB) Little Mountain Test Annex (LMTA), herein referred to as Site 1, Site 2, and Site 3. Basic information for each is given in Table 3.

Table 3. Overview of demonstration sites.

	Site 1	Site 2	Site 3
Location	NAS Jacksonville PSC48 Building 106	Parris Island MCRD Site 45	Hill AFB LMTA
Depth to Groundwater	~1.8 m bgs (~6 ft bgs)	~0.9 m bgs (~3 ft bgs)	24 - 45 m bgs (80 - 150 ft bgs) (large elevation changes with time)
Geologic Setting	Interbedded sands, silts, and clays	Interbedded sands, silts, and clays	Fractured Rock
Source of Contamination	Former dry cleaner facility	Former dry cleaner facility	Industrial water treatment sludge drying beds
Chemicals Present	PCE, TCE, DCE, VC	PCE, TCE, DCE, VC, weathered LNAPL	PCE, TCE, TCA, DCE, VC
Approximate Source Zone Width	105 m (350 ft)	46 m (150 ft)	400 m (1300 ft)
Depth of Contamination	0 – 18 m bgs (0 – 60 ft bgs)	0 – 5.5 m bgs (0 – 18 ft bgs)	0 – 91 m bgs (0 – 300 ft bgs)
SZNA Assessment Period	1.8 y	3 y	2.75 y
Sampling Events	4	4	4

bgs – below ground surface
DCE - dichloroethene
ft – feet/foot
m – meter
PCE - perchloroethene
TCA - trichloroethane
TCE - trichloroethene
VC – vinyl chloride
y -- year

4.1 SITE LOCATION AND HISTORY

The three field sites are described in sequence below. Detailed reports on the data collection and analysis at each site are included in Appendices B, C, and D of the ESTCP Final Report (Ekre et al., 2014).

4.2 SITE HYDROGEOLOGY AND CONTAMINANT DISTRIBUTION

4.2.1 Site 1 NAS Jacksonville

Site 1 geology, as shown in Figure 3, consists primarily of fine sands and silty sands to a depth of approximately 5.5-6 m bgs (18-20 ft bgs), followed by a clay unit approximately 1.8-2.4 m (6-8 ft) thick. While clay units often act as a barrier to downward chemical migration, contaminants are present in the unconsolidated deposits beneath. These include sand, clayey sand, sandy clay, and clay with traces of shell fragments to a depth of approximately 18 m bgs (60 ft bgs), where a limestone confining unit is encountered.

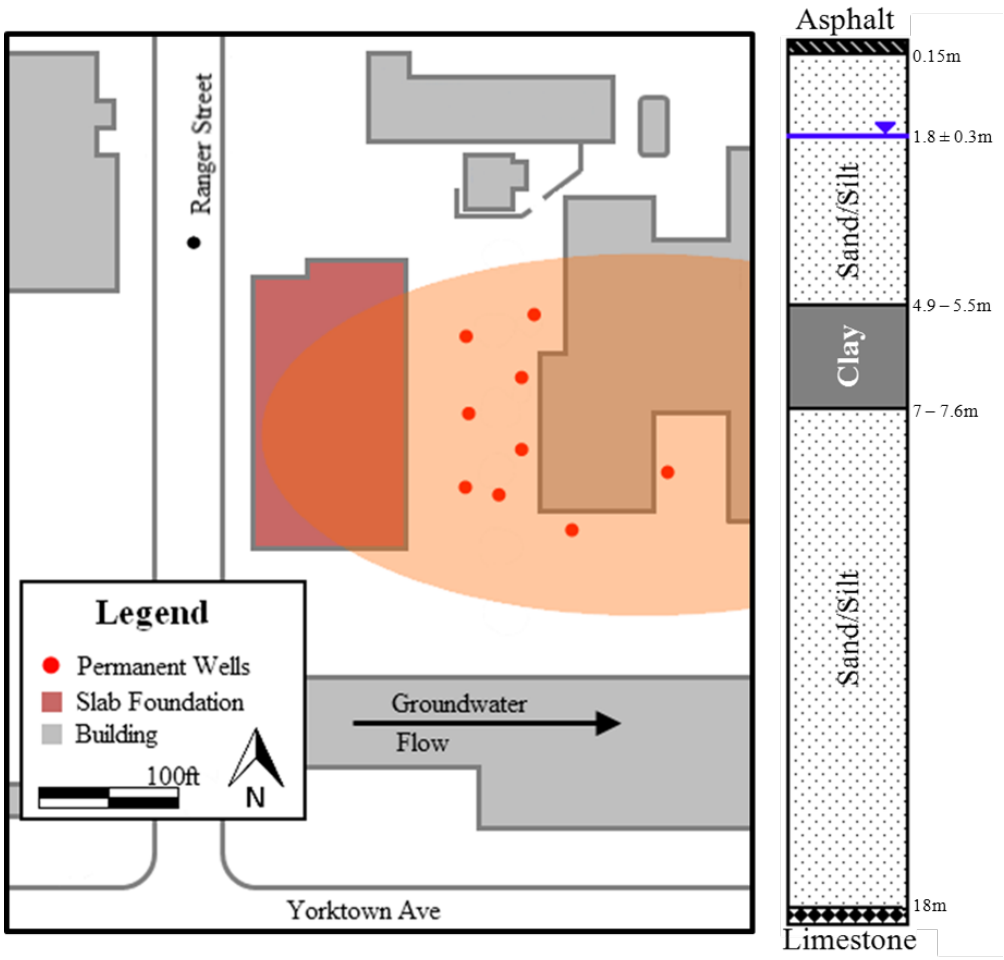

Figure 3. Site 1 plan view and simplified geologic cross-section.

Depth to groundwater onsite is approximately 1.8 m (6 ft), with seasonal variations that are generally about 0.3 m (1.0 ft) or less. Groundwater flow onsite is to the east, with an approximate gradient of 0.005 m/m.

CAHs are present in the groundwater above and below the clay unit to a depth of approximately 18 m bgs (60 ft bgs). A plan view conceptual model built from pre-SZNA assessment information is found in Figure 4.

4.2.2 Site 2 Parris Island MCRD

The surficial aquifer extends down to approximately 5.2-5.5 m bgs (17-18 ft bgs) and consists primarily of fine sands and silty sands with a few discontinuous lenses of finer-grained silty clay and clayey sand. A thin peat unit (0.3-1 m thick) below the surficial aquifer is followed by a clay layer (1-2 m thick) at depths from approximately 5.5 to 8.2 m bgs (17-27 ft bgs). A simplified geological profile is provided in Figure 4.

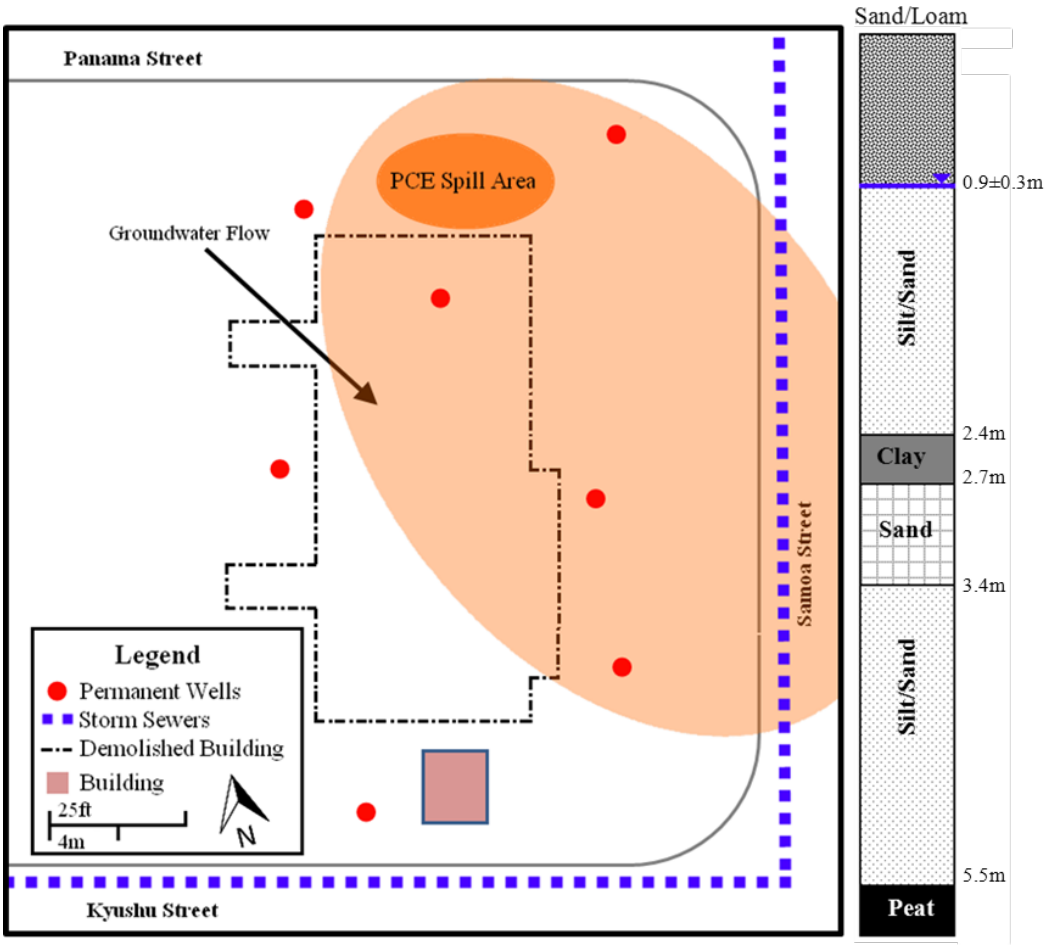

Figure 4. Site 2 plan view and simplified geologic cross-section.

The interval from approximately 2.4 to 3.4 m bgs (8-11 ft bgs) is the dominant groundwater flow zone. Two distinct hydraulic gradients are present above and below this layer (0.005 and 0.006 m/m respectively). Flow is generally towards the southeast; however, groundwater movement is locally impacted by storm sewers present on the eastern and southern boundaries of the site (Vroblesky et al., 2009).

CAH contaminants are present in the surficial aquifer to approximately 5.5 m bgs (18 ft bgs). Available data suggest that the peat and clay, with a hydraulic conductivity of less than 10-6 cm/s, appear to act as a barrier to downward migration. Several wells penetrate the peat and clay layer beneath the surficial aquifer, and no evidence of CAH contamination has been found beneath the clay/peat layer in these wells to date.

From the point of release, the primary dissolved contaminant plume extends southeast approximately 61 m (200 ft), where it is partially captured by the storm sewer system (Figure 4.3). The core of the plume is located within the 2.4 to 3.4 m bgs (8-11 ft bgs) interval.

4.2.3 Site 3 Hill Air Force Base LMTA

Site 3 is located on a bedrock outcropping approximately 0.4 kilometers (km) from the edge of salt flats of the Great Salt Lake. The site conceptual model consists of a thin surficial veneer of colluvium followed by a bedrock stratigraphic sequence: tillite (up-gradient), greenstone, calcareous phyllite, and slate (Figure 5). Site investigations identified the phyllite as the dominant hydrogeologic unit with respect to CAH fate and transport. The unit is slightly metamorphosed, highly fractured, and displays a significant number of voids and folds. Hydraulic testing of each unit has been performed and the resulting range of conductivities clearly demonstrate the dominance of the phyllite.

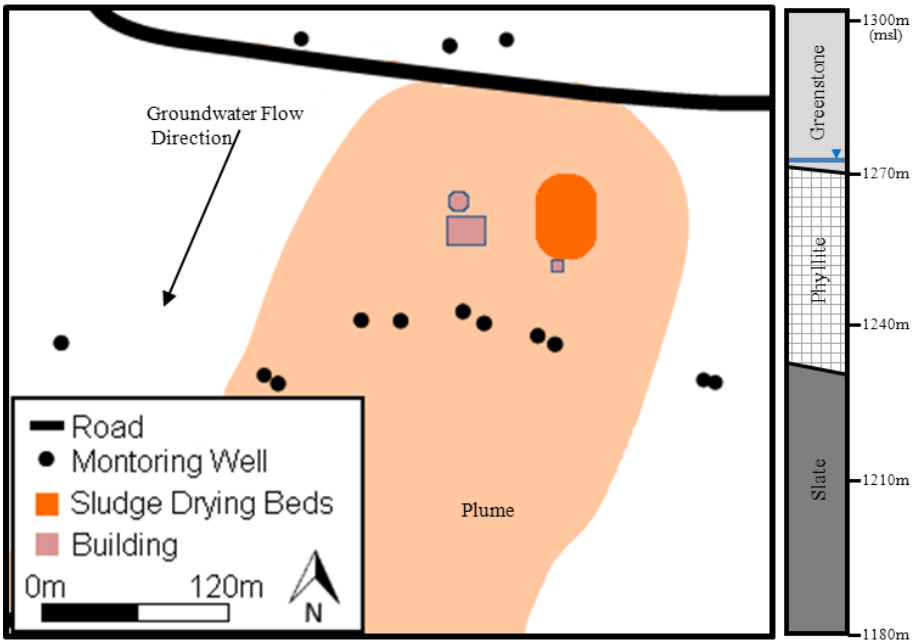

Figure 5. Site 3 plan view and simplified geologic cross-section.

The bedrock units have a 20 to 25 degree dip towards the west and there are steep changes in elevation down towards the salt flats. Atop the bedrock ridge near the sludge drying beds (SDB), groundwater is approximately 46 m bgs (150 ft bgs), whereas at the base of the mountain near the salt flats groundwater is encountered at approximately 3 m bgs (10 ft bgs).

CAHs have infiltrated through the thin veneer of unconsolidated sediments and have migrated throughout the fractured bedrock to groundwater 46 m (150 ft) bgs. Contamination is primarily found within the phyllite layer, likely due to both the depth to water below the SDBs and the favorable hydraulic properties of that unit; however CAHs have been shown to extend to depths greater than 61 m (200 ft) below the water table and into the slate unit. The contaminant plume is transported from the site in a generally southwest direction (Figure 5).

5.0 TEST DESIGN

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

The experimental design is reflected in Figure 2, which shows the sampling of a groundwater transect perpendicular to groundwater flow and down-gradient of the source zone, and vertical soil vapor profile sampling above the source zone footprint. The initial design for a given site is based on the current site conceptual site model developed from standard site assessment data. In-the-field confirmation of the location, length, width and depth of the source zone is critical. A multi-depth groundwater sampling transect oriented perpendicular to groundwater flow and placed just down-gradient of the suspected source zone location is the approach recommended here for determining the width and depth of the source zone. Experiences from Guilbeault et al. (2005), Triplett-Kingston et al. (2012), and this work suggest that this approach can provide a faster, more reliable assessment of the source zone width and depth and provide valuable insight to the spatial variability (Stroo et al., 2012). Once the footprint of the source zone is established, the spatial density of the groundwater and soil gas sampling is selected to meet the required confidence in the SZNA mass loss rate results.

5.2 BASELINE CHARACTERIZATION

No baseline characterization was required for this project.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

No treatability studies were required for the assessment of source zone natural attenuation.

5.4 FIELD TESTING

For each of the three sites, four sampling events were conducted over a two- to three-year time period. During each event a vertical groundwater transect and a horizontal vapor phase areal footprint were sampled. Visual inspection notes and the complete summary of all site events, data, and analyses are available in the appendices of the Final Report (Ekre et al., 2014).

5.5 SAMPLING METHODS

Numbers of groundwater and soil gas samples collected during each sampling event are summarized in Table 4. Sampling methods, analyses, and holding times employed during implementation of the CAH SZNA assessment paradigm are summarized in Table 5.

Table 4. Numbers of samples.

Site/Event	Number of Groundwater Samples	Number of Vapor Samples
Site 1		
Event 1	39	17
Event 2	82	29
Event 3	61	30
Event 4	94	30
Site 2		
Event 1	92	5
Event 2	81	9
Event 3	130	9
Event 4	79	9
Site 3		
Event 1	34	4
Event 2	35	8
Event 3	16	8
Event 4	16	0

Table 5. Sampling methods and analyses.

Analyte	Collection Method		Analysis Method	Maximum Holding Time
Groundwater VOC	DPT	Low purge volume	EPA 8260B (USEPA, 2012)	14 days (most analyzed onsite during sampling)
	Permanent well	Conventionally purged		
	Permanent well	No purge		
Hydraulic gradient	Water level indicator		Devlin et al. (2003)	NA
Hydraulic conductivity	Pump tests		Cho et al. (2000)	NA
Soil gas	Purged lung sampler		8260B modified (USEPA, 2012)	24 hours
Effective diffusion coefficients	Tracer test		Johnson et al. (1998)	NA

DPT – direct push technology
VOC – volatile organic compound
NA – not applicable

5.6 SAMPLING RESULTS

Full data reports containing the sampling results from all events at each site are contained in appendices B, C and D of the project Final Report (Ekre et al., 2014). Their use and significance to the assessment of source zone natural attenuation rates is discussed in Section 6.0 (Performance Assessment) of this report.

5.7 DISTURBANCE TESTING

The local assessment of DNAPL architectural features was explored using four in-situ disturbance tests through proof-of-concept testing in a two-dimensional laboratory physical model. The disturbance tests were applied to the following conditions: dissolved source only, DNAPL ganglia and associated dissolved plume, and a DNAPL pool and its associated dissolved plume. The four different disturbance tests were water injections, in situ chemical oxidation (ISCO), heating, and air sparging. These disturbances were chosen as two are components of remedial technology pilot-testing field activities at some sites (air sparging and ISCO), one would be relatively simple to implement (clean water injection), and the last could possibly be implemented with modification of direct-push characterization tools (heating).

Of the four disturbances tested, the clean water and ISCO solution injections appear to be the most useful for determining the presence or absence of DNAPL. The utility of the ISCO solution will be dependent on its reaction rate and mass oxidant relative to DNAPL mass in ganglia; a slowly-reacting oxidant would provide results similar to a clean water injection, while a rapidly-reacting high-strength oxidant might produce similar results for ganglia and dissolved sources (as the ganglia could be fully treated by the injection in that case). The air sparging disturbance might also have similar behavior, depending on the duration and flow rate of air injection (as it could volatilize the DNAPL in the test zone), so more test combinations of flow rate and disturbance duration need to be investigated.

The data suggest that tests resulting in DNAPL mass depletion (ISCO, air sparging) might be designed to differentiate regions with ganglia and pools; these could be applied after regions containing DNAPL are identified by a first disturbance test. For example, a clean water injection might be used to determine the presence of DNAPL and that might be followed by an air sparging test to determine if the DNAPL is distributed as ganglia or a pool. Knowledge of subsurface geology will be critical in this determination as DNAPL pools tend to form at permeability contrasts.

Details of the testing are included in Appendix E of the Final Report (Ekre et al., 2014).

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6.0 PERFORMANCE ASSESSMENT

In this section the results of the SZNA assessment for each site is provided. Sample data from the groundwater transects and vapor probes are presented below for the three demonstration sites.

6.1 PERFORMANCE OBJECTIVE: DEMONSTRATE THAT SZNA IS OCCURRING

For each of the three sites there is strong evidence that SZNA is occurring in the form of dissolved and vapor phase mass discharges.

6.2 PERFORMANCE OBJECTIVE: ESTIMATE RATE OF SZNA

For each site and for each sampling event, the data from the groundwater transect and vapor transect were contoured. The contoured data were used to compute mass fluxes. The raw and contoured data, along with discussion of sampling limitations and refinements to the sampling plans are presented in the Final Report (Ekre et al., 2014).

6.2.1 SZNA Mass Loss Rates from the Three Demonstration Sites

SZNA mass loss rates determined from demonstration site data are presented in Table 6. The "Range" reported for dissolved mass discharge spans the minimum and maximum GSI Mass Flux Toolkit® output for three different interpolation combinations (linear, logarithmic, nearest neighbor); the "average" value is the averaged result from all interpolation combinations.

Table 6. SZNA mass loss rate results.

SITE	K[a] (cm/s)	D_{eff}[a] (cm^2/s)	Event	Date of Sampling	Hydraulic Gradient (m/m)		Dissolved Mass Discharge As PCE (Sites 1, 2) As TCE (Site 3) (kg/y)		#[b]	Vapor Discharge As PCE (1,2) As TCE (3) (kg/y)	#[b]	Total SZNA Mass Loss Rate (kg/y)
					Upper	Lower	Range[1]	Avg.				
Site 2	8.8×10^{-6} – 1.8×10^{-2}	1.0×10^{-2} – 3.5×10^{-2}	1	10/16-26/08	0.004	0.005	0.8 – 0.97[1]	0.87	48	0.68	5	1.6
			2	8/15-22/09	0.005	0.006	1.1 – 1.6[1]	1.4	48	0.76	9	2.2
			3	7/5-19/10	0.004	0.005	0.92 – 1.2[1]	1.1	43	0.57	9	1.7
			4	6/14-25/11	0.0034	0.0047	0.70 – 1.2[1]	0.96	55	0.13	9	1.1
Site 1	1.1×10^{-5} – 5.1×10^{-3}	1.5×10^{-3} – 8.9×10^{-3}	1	8/6-15/09	0.006		1.8 – 3.4[1]	2.8	39	0.64	17	2.9
			2	1/9-22/11	0.005		6.2 – 9.9[1]	8.3[e]	61	0.95	29	8.4
			3	6/4-13/11	0.0049		2.9 – 6.5[1]	4.9[e]	61	0.21	30	4.9
			4	10/20-30/11	0.0034		1.8 – 3.4[1]	2.7	73	0.79	30	2.8
Site 3	1×10^{-3} – 5×10^{-2}	9.0×10^{-4} – 6.3×10^{-3}	1	7/08-8/08	8.4×10^{-4}		570-730[c]	670	16	0.028	4	570
			2	4/09-5/09	8.4×10^{-4}		590-760[c]	700	16	0.028	8	590
			3	10/16-17/10	8.4×10^{-4}		250-410[d]	350	16	0.039	8	250
			4	8/23-24/11	8.4×10^{-4}		240-370[d]	320	16	NS		240

a –range of values b – Number of samples c – conventional purge sampling method d – No purge method

e – prior to the second event the building covering the site was demolished and paved with asphalt, during which time the ground surface was open allowing elevated infiltration of water locally at a time when the water table was dropping due to drought. It is believed this flushing of the vadose zone may account for the elevated discharge during events 2 and 3

[1] – range is result of multiple iteration methods for calculating mass discharge in Mass Flux Toolkit (log, linear, nearest neighbor)

D_{eff} – Effective vapor diffusion coefficient measured in-situ

K – Hydraulic conductivity measured in-situ NS – Not sampled cm/s – centimeters per second

In comparing discharge rates from the different interpolation combinations it can be seen that there is approximately a factor of two difference between the high and low values. Given the several order-of-magnitude range of concentrations and hydraulic conductivities, this difference is not large and within the normal uncertainty of data from remediation sites. The difference in mass discharge estimates between events reflects all sources of variability and error, including changes in groundwater elevation and infiltration, sampling density, analytical error, interpolation methods, and pump test error. Given this, it is remarkable that the discharge estimates over approximately 3 years are at most a factor of three different from event to event.

In addition to interpolation variation in the discharge estimates there are changes in the SZNA rates between sampling events. Figure 6 plots the mass discharge rates vs. time to examine if there were temporal trends for each site over the sampling period (~2 - 3 y across all sites). It can be seen in Figure 6 that the rates from event to event are relatively similar (≤3X difference). Given the possible opportunities for discrepancy between rate estimates, and in particular the nature of DPT sampling (never the same exact position but generally within ~0.3 m), this range of values is remarkably consistent. Examining the variation in further detail shows that only a single event displays this level of change (Site 1, Event 1 to Event 2), all others are ≤2X difference. In the context of how the rates are likely to be used, the temporal variability over the study period might be considered insignificant.

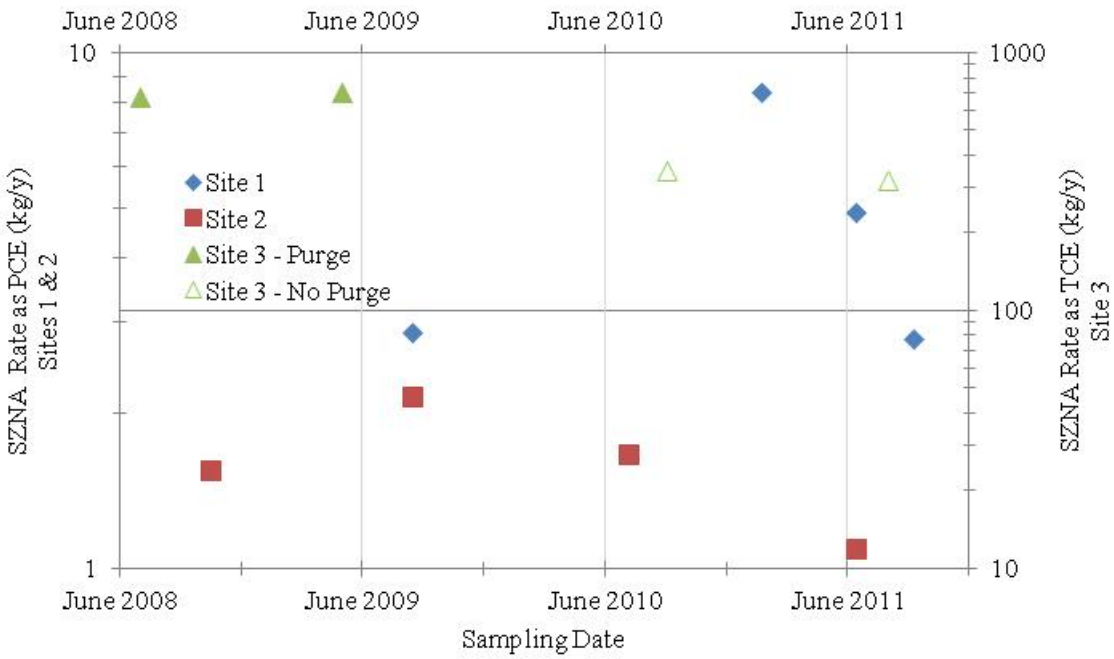

Figure 6. Averaged CAH dissolved contaminant discharge rates versus time for three sites sampled.

Note: Site 1 and 2 and displayed on the left y-axis and Site 3 on the right y-axis.

6.2.2 Spatial Sampling Density

When using point-based groundwater sampling transect approaches, site-specific decisions regarding transect placement and lateral and vertical sampling point spacing must be made. Increasing the number of sample locations is expected by many to correspond to increases in cost and confidence; therefore, there is interest in gaining a better understanding of the trade-offs between sampling density and uncertainty in mass discharge estimates. The issue of heuristic sampling and guidelines is discussed in detail in Appendix G of the Final Report (Ekre et al., 2014).

Based on experience gained from this project, the following sampling guidelines using practical and commonplace sampling tools are suggested for larger CAH source zones:

- Collect a soil core and visually observe to identify distinctive geologic layers.
- Use an initial coarse sampling approach to quickly delineate the boundaries of the plume (~30 m horizontal spacings, ~7.5 m vertical spacings, with a minimum of one sample in each unit); use on-site chemical analysis screening tools to ensure the transect spans the full width of the dissolved contamination.
- Using initial site data for plume boundaries, resample the plume at a higher density.
- Use lateral spacings of no more than the width of contamination divided by 6 across the full width of the plume.
- Collect a minimum of one sample in each distinct hydraulic unit; constrain the largest vertical separation between samples at the same location to the plume thickness divided by 6; consider not exceeding about 7.5 m between points.
- Use highest resolution sampling in the suspected core of the plume (<3m vertical intervals).

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7.0 COST ASSESSMENT

The primary goal of this project was to demonstrate a framework for the assessment of the natural attenuation of CAH source zones, with an emphasis on a data-driven approach to the estimation of rates of source zone attenuation. The main costs associated with this approach are associated with the acquisition of the necessary samples and data.

7.1 COST MODEL

The elements of the cost model considered are:

1. Drilling
2. Sampling
3. Sample analysis, and
4. Data analysis and reporting (including estimation of source zone attenuation rates)

7.2 COST DRIVERS

The primary cost drivers for the assessment of SZNA are the costs associated with the installation of sampling equipment, the collection of samples, and the analysis of samples. The size and complexity of the source zone, depth to ground water, and type of subsurface material (e.g., soft soil versus hard lithified rock) will affect drilling and sampling costs on a site-specific basis.

7.3 COST ANALYSIS

Approximate site costs associated with the sampling efforts of this work, which included about 10 – 14 days onsite per event, are presented in Table 7. While not trivial, the cost per event (~ $68,000) is not prohibitive for many sites. Sampling density decisions are largely driven by balancing the need for confidence in SZNA rate estimates vs. cost. However, sampling density is one of the key options for reducing uncertainty in SZNA rates.

Table 7. Estimated sampling costs.

Activity		Amount	Unit Cost	Total Cost
Drilling	Mobilization	-	$500	$500
	Onsite	6 days	$2000/day	$12,000
Consultant	Prep	80 hours	$150/hour	$12,000
	Onsite	192 hours	$100/hour	$19,200
	Reporting	80 hours	$150/hour	$12,000
Analytical	GW Samples	50	$150/sample	$7,500
	Vapor Samples	20	$150/sample	$3,000
Misc	Waste Disposal	-	-	$1,000
	Consumables	-	-	$1,000
Totals				$68,200

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8.0 IMPLEMENTATION ISSUES

The approach used in this project for the assessment of SZNA at CAH sites uses fairly standard and readily available sampling and analytical tools. No barriers to the collection of the necessary data are anticipated other than those presented by unique site conditions. Many of the data needs/lines-of-evidence are similar to those appearing in dissolved plume natural attenuation guidance, with the exception of the assessment of effective vadose zone diffusion coefficients in Group II (to characterize gas transport processes) and the use of "bench-scale weathering tests" to provide Group III data. No special permits are required for implementation of the approach.

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APPENDIX A

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