United States
Environmental Protection
Agency

EPA 510-R-13-001

Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds

U.S. Environmental Protection Agency
Office of Underground Storage Tanks
Washington, DC 20460

[This page intentionally left blank.]

Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds

Prepared by

Dr. Ian Hers
Golder Associates
500 - 4260 Still Creek Drive
Burnaby, British Columbia
Canada V5C 6C6

and

Robert S. Truesdale
RTI International
3040 East Cornwallis Road
Post Office Box 12194
Research Triangle Park, NC 27709-2194

under contract to
Skeo Solutions
921 Second Street SE
Charlottesville, VA 22902
Contract No. GS-10F-0309N

for

U.S. Environmental Protection Agency
Office of Underground Storage Tanks
Washington, DC 20460

January 2013

[This page intentionally left blank.]

Disclaimer

Acknowledgements

James B. Cowart, David J. Folkes, and Dr. Jeffrey P. Kurtz (EnviroGroup Limited); Todd A. McAlary (Geosyntec Consultants) and Dr. Mark A. Widdowson (Virginia Polytechnic Institute and State University) provided reviews.

Robin Davis (Utah Department of Environmental Quality) provided the May 2011 database, which served as the basis for the database described in this report. Peter Eremita (Maine Department of Environmental Protection) and Jackie Wright (Australia's Department of Sustainability, Environment, Water, Population and Communities) provided significant data contributions that enhanced the Davis database.

Table of Contents

Disclaimer ... v

Acknowledgements ... vi

List of Acronyms ... xiii

Executive Summary ... ES-1
  ES.1 Purpose and Document Focus ... ES-1
  ES.2 Methodology ... ES-2
  ES.3 Findings and Conclusions ... ES-3

1. Introduction ... 1
  1.1 Background ... 1
  1.2 Goal and Objectives ... 2
  1.3 Document Development and EPA Peer Review ... 2
  1.4 Document Organization ... 3

2. Conceptual Site Model and Select Case Studies ... 3
  2.1 Aerobic Biodegradation Processes in the Vadose Zone ... 4
  2.2 Factors Influencing Biodegradation of Petroleum Hydrocarbons ... 5
  2.3 Dissolved versus LNAPL Vapor Sources ... 6
  2.4 Anaerobic Biodegradation and Methane Generation ... 7
  2.5 Conditions for Increased Potential for Petroleum Vapor Intrusion ... 8
  2.6 Case Studies Indicating Confirmed or Likely Complete Transport Pathway for Petroleum Vapor Intrusion ... 9
    2.6.1 Refinery Site, Perth, Australia (Patterson and Davis, 2009) ... 10
    2.6.2 Chatterton Petrochemical Site, Vancouver, B.C., Site (Hers et al., 2000; Hers et al., 2002) ... 10
    2.6.3 Refinery Site, Casper, Wyoming (Luo et al., 2009) ... 11
    2.6.4 Former Refinery Site (confidential location) (Luo et al., 2010) ... 11
    2.6.5 Refinery Site, Hartford, Illinois (Illinois Department of Public Health, 2010) ... 11
    2.6.6 UST Site, Stafford, New Jersey (Sanders and Hers, 2006) ... 11
    2.6.7 UST Site, Ogden, Utah, Mini-Mart Release (McHugh et al., 2010) ... 12
    2.6.8 UST Site, Gunnison, Utah, Top Stop Release (McHugh et al., 2010) ... 12

3. Summary of Modeling Studies ... 12
  3.1 Abreu Three-Dimensional Model Simulations ... 13
    3.1.1 Three-Dimensional Model Simulations—Below-Building Contamination Source and Homogeneous Soil Conditions ... 13
    3.1.2 Three-Dimensional Model Simulations—Lateral Migration Scenario and Homogeneous Soil Conditions ... 16
    3.1.3 Three-Dimensional Model Simulations—Surface Capping Scenario ... 18

3.1.4 Comparison of Modeled to Measured Soil Vapor Concentration Data 21
3.2 DeVaull (2007b) Study (BioVapor Model Development) 21
3.3 DeVaull (2010) Study of BioVapor Application 21
3.4 Summary of Modeling Studies 23
4. Review of Empirical Database Studies of Petroleum Hydrocarbon Vapor Attenuation 23
5. EPA PVI Database Development, Structure, and Content 24
5.1 EPA PVI Database Development and Checking 25
5.1.1 Quality Control and Data Quality Ranking 25
5.2 EPA PVI Database Structure 27
5.3 EPA PVI Database Content 28
6. EPA PVI Database Analysis Approach and Methods 29
6.1 Source Zone Identification (LNAPL versus Dissolved Indicators) 30
6.1.1 Groundwater Concentration Data 31
6.1.2 Soil Concentration Data 31
6.1.3 Proximity to Fuel Storage/Dispensing Facilities 32
6.2 Data Analysis Methods 32
6.2.1 Exploratory Data Analysis 32
6.2.2 Vertical Distance Method 32
6.2.3 Clean Soil Method 33
6.3 Soil Vapor Concentration Thresholds 36
6.3.1 Sub-slab to Indoor Air Attenuation Factors 36
6.3.2 Risk-based Concentration Thresholds 36
7. EPA PVI Database Analysis Results 37
7.1 Exploratory Data Analysis 37
7.1.1 Comparison of Groundwater and Soil Vapor Concentrations 37
7.1.2 TPH Vapor versus Oxygen Concentrations 39
7.1.3 Methane Concentrations 41
7.1.4 Comparison between Benzene and TEX Vapor Concentrations 42
7.2 Vertical Distance Method 43
7.2.1 All Data 43
7.2.2 Influence of Surface Cover 52
7.2.3 Influence of Soil Type 56
7.3 Clean Soil Method 56
8. Discussion 59
8.1 Conceptual Site Model and Mathematical Models 59
8.2 Methods and Characteristics of the Database 60
8.3 Data Analysis Results 61

8.4 Exclusion Distance Assessment Framework ... 61
8.5 Lateral Inclusion Distances ... 62
8.6 Comparison with Other Studies ... 63
9. Findings and Conclusions ... 63
10. References ... 66
Appendix A: Review of Exclusion/Inclusion Distances in Existing Vapor Intrusion Guidance
Appendix B: Data Quality and Database Content
Appendix C: Analysis of Australian PVI Database
Appendix D: PVI Database Data Dictionary
Appendix E: PVI Database Entity Relationship Diagram
Appendix F: Analysis of Lead Scavengers: Ethylene Dibromide and 1,2-Dichloroethane

List of Tables

1. Summary of Case Study Sites with Confirmed or Likely Occurrences of Petroleum Vapor Intrusion....9
2. Select Three-Dimensional Abreu and Johnson (2005) Model Simulation Results from U.S. EPA (2012c)....20
3. Number of Sites by Country and States in the EPA PVI Database (November 2012)....28
4. Potential LNAPL Hydrocarbon Indicators....30
5. Risk-based Indoor Air Concentration for Primary Chemicals of Potential Concern....37
6. Summary of Results for Vertical Distance Method....48
7. Summary of Results for Clean Soil Method....57

List of Figures

1. Typical vertical concentration profile in the unsaturated zone for PHCs, carbon dioxide, and oxygen (modified from U.S. EPA, 2012a)....5
2. Conceptual model illustrating the potential for vapor intrusion for a) free-phase LNAPL sources, b) residual-phase LNAPL sources, and c) dissolved-phase sources. (Source: Lahvis et al., In prep.; used with permission)....7
3. Vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model for a range of source total hydrocarbon (benzene) vapor concentrations and separation distances for a residential house scenario (adapted from Abreu et al., 2009)....14
4. Effect of source depth on soil gas distribution and vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model for a source total hydrocarbon (benzene) vapor concentration of 100 mg/L, biodegradation rate of 0.79 h^{-1}, and three source depths: 3 m (top), 7 m (middle), and 9 m (bottom) bgs. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, and the building is a residential house (from Abreu et al., 2009)....15
5. Vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model as a function of separation distance below foundation and first-order biodegradation rate for a residential house scenario and 10 mg/L vapor source concentration (from Abreu et al., 2009)....16
6. Relationship between source-building lateral separation distance and normalized indoor air concentration (α) for a NAPL source, two source depths, and three biodegradation rates (λ). The source-building lateral separation is measured from the edge of the source zone to the center of the building with a basement; negative values and values of less than 5 m indicate that the source is to some extent beneath the building. The source vapor concentration is 200 mg/L. (Source: 33 in U.S. EPA [2012c])....17
7. Effects of various layered soil scenarios (rows A–D) on hydrocarbon and oxygen distribution in soil gas and normalized indoor air concentration (α) for an

underpressurized basement (-5 Pa, left panels) and an overpressured basement (+5 Pa, right panels). Hydrocarbon and oxygen concentration contour lines are normalized by source and atmospheric concentrations, respectively. The source vapor concentration is 200 mg/L located 8 m bgs. Biodegradation rate (λ) = 0.18 h^{-1}. (Source: 37 in U.S. EPA [2012c]) 19
8. Effect of source vapor concentration on hydrocarbon and oxygen distribution in soil gas and normalized indoor air concentration (α) for scenarios with low permeability soils at the ground surface (e.g., soil layer scenario on row D of 7). Hydrocarbon and oxygen concentration contour lines are normalized by source and atmospheric concentrations, respectively. Source located at 8 m bgs (basement scenario). Biodegradation rate (λ) = 0.18 h^{-1}. (Source: 38 in U.S. EPA [2012c]) 20
9. Estimates of indoor air benzene concentrations using Biovapor model for varied effective airflow through the basement foundation. Foundation effective airflow statistics: 5th percentile = 0.3 L/min, 50th percentile = 3 L/min, 95th percentile = 30 L/min. Key model parameters: Vapor mixing height = 2.44 m; indoor air exchange rate = 0.25 h^{-1}; building footprint area = 100 m^2 (1,076 ft^2) (from DeVaull, 2010) 22
10. Example calculation of clean soil method distances 35
11. Groundwater concentrations measured near soil vapor sampling locations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites). 38
12. Groundwater concentrations measured near soil vapor sampling locations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites). Only detectable benzene vapor concentrations shown. 39
13. TPH vapor versus oxygen concentrations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites). Data points shown are where both TPH vapor and oxygen concentrations were above detection limits. Shaded areas and ellipse encompass data that generally support the aerobic mineralization paradigm. 41
14. Methane concentrations versus distance and benzene vapor concentrations (all refers to UST, fuel terminal, refinery, and petrochemical sites) 42
15. Relationship between benzene and ethylbenzene (left) and benzene and xylenes (right) vapor concentrations. (All refers to UST, fuel terminal, refinery, and petrochemical sites.) Data points are shown where both compounds were above detection limits. 42
16. Vertical distance method: benzene (a), oxygen (c), and xylenes (d) data for dissolved-source sites (KM = Kaplan-Meier). Panel b shows the benzene probability data. 44
17. Vertical distance method: PHC fraction (a–c) and hexane (d) data for dissolved-source sites. 45
18. Vertical distance method: benzene (a, b), oxygen (c), and xylenes (d) data for LNAPL sources at UST sites (KM = Kaplan-Meier). 46
19. Vertical distance method: PHC fraction (a–c) and hexane (d) data for LNAPL sources at UST sites. 47

20. Vertical distance method: 2,2,4-trimethylpentane (TMP), MtBE, 1,2,4-trimethylbenzene (TMB), and naphthalene data for LNAPL sources at UST sites..........48
21. Vertical distance method–benzene, xylenes, and oxygen data for LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites. Red plots over blue. 51
22. Vertical distance method–2,2,4-trimethylpentane (TMP), naphthalene, and 1,2,4-trimethylbenzene (TMB) data for LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites. 52
23. Comparison of probability for benzene soil vapor concentrations to be less than threshold and oxygen concentrations for different surface covers for LNAPL sources at UST sites. Below detection limit concentrations replaced with half the detection limit for analysis. 53
24. Comparison of probability for benzene soil vapor concentrations to be less than threshold and oxygen concentrations for different surface covers for LNAPL sources at all sites (UST, fuel terminal, refinery, and petrochemical). Below detection limit concentrations replaced with half the detection limit for analysis. 55
25. Comparison of probability for benzene soil vapor concentrations to be less than the threshold for different soil types (coarse and fine grained). Below detection limit concentrations replaced with half the detection limit for analysis. 56
26. Results of clean soil method for dissolved-source sites. 47 sites, N = 170. 58
27. Results of clean soil method for LNAPL sources at UST Sites. 53 sites,N = 172. 58
28. Results of clean soil method for LNAPL sources at fuel terminal, refinery and petrochemical (non-UST) sites. 60 sites, N = 216. 59

List of Acronyms

ATSDR	Agency for Toxic Substances and Disease Registry
CO_2	Carbon Dioxide
CSM	Conceptual Site Model
1,2-DCA	1,2-Dichloroethane
DQ	Data Quality
DRO	Diesel Range Organics
EPA	U.S. Environmental Protection Agency
EDB	Ethylene Dibromide
GRO	Gasoline Range Organics
H_2O	Water
IARC	International Agency for Research on Cancer
ILCR	Incremental Lifetime Cancer Risk
IRIS	Integrated Risk Information System
IUR	Inhalation Unit Risk
LIF	Laser Induced Fluorescence
LNAPL	Light Nonaqueous Phase Liquid
MassDEP	Massachusetts Department of Environmental Protection
MCL	Maximum Contaminant Level
MCLG	Maximum Contaminant Level Goal
MMR	Massachusetts Military Reservation
MRL	Minimal Risk Level
MtBE	Methyl Tert-Butyl Ether
NaCl	Sodium Chloride
OUST	EPA’s Office of Underground Storage Tanks
PAH	Polycyclic Aromatic Hydrocarbon
PHC	Petroleum Hydrocarbon
PID	Photoionization Detector
PVI	Petroleum Vapor Intrusion
QA/QC	Quality Assurance/Quality Control
RBC_v	Risk-Based Soil Vapor Concentration
SFO	Oral Cancer Slope Factor

TEX	Toluene, Ethylbenzene, and Xylenes
1,2,4-TMB	1,2,4-Trimethylbenzene
2,2,4-TMP	2,2,4-Trimethylpentane
TPH	Total Petroleum Hydrocarbons
UST	Underground Storage Tank
UV	Ultraviolet
UVIF	Ultraviolet Induced Fluorescence
VI	Vapor Intrusion
VOC	Volatile Organic Compound

Executive Summary

This report presents an evaluation of empirical data and select modeling studies of the behavior of petroleum hydrocarbon (PHC) vapors in subsurface soils at petroleum release sites and how these vapors can affect subsurface-to–indoor air vapor intrusion. Specifically, the report develops an inclusion distance approach for screening petroleum release sites for vapor intrusion that should improve the efficiency of petroleum release site investigations and help focus resources on the sites of most concern for petroleum vapor intrusion (PVI).

ES.1 Purpose and Document Focus

The purpose of this report is to support the development of a new soil vapor screening approach for PHC compounds. Consequently, the report focuses primarily on characterizing the vapor intrusion pathway at Solid Waste Disposal Act Subtitle I underground storage tank (UST) sites with petroleum fuel releases. However, the report also presents and discusses PVI data from other types of sites with PHC contamination (i.e., fuel terminals, petroleum refineries, and petrochemical plants).

In support of its general guidance development effort for the PVI exposure pathway, the U.S. Environmental Protection Agency (EPA) compiled an empirical database of measurements of subsurface media (soil gas, soil, and groundwater) and supporting data from PHC sites. The rationale for this focus on subsurface media measurements is that in the presence of oxygen, PHC vapors can rapidly biodegrade. Compared with chlorinated hydrocarbons, PHC vapors bioattenuate to much lower concentrations in soil gas (EPA, 2012a). Therefore, screening for PVI using the same methodology used for chlorinated hydrocarbons is overly conservative; a different approach is needed for PVI.

The goal of this report is to provide information on the subsurface vapor attenuation of PHCs that would support establishing a better approach for evaluating PVI potential, with the intent of determining when PVI may result in indoor air PHC concentrations that exceed safe levels for human health (i.e., when the PVI exposure pathway is complete).

Because bioattenuation processes for PHCs are well documented and widespread (EPA, 2012a), the analysis of subsurface soil gas data from actual petroleum release sites provides an opportunity to develop improved and more realistic approaches for evaluating the potential for PVI when PHCs are released into the subsurface. Data from real-world sites can be used to identify an inclusion distance, defined in this report as the vertical separation distance from the contamination source beyond which the potential for PVI is insignificant. Applying the inclusion distance approach is potentially more efficient than current approaches for investigating PHC release sites and can quickly focus resources on the sites where distances less than the inclusion criteria or exceptional conditions indicate a greater potential for PVI.

This report describes the activities EPA conducted to develop and support an inclusion distance approach:

- Assemble an empirical database from petroleum release sites where the PVI pathway has been evaluated primarily via soil gas and groundwater measurements;

- Consolidate and independently evaluate the quality of both existing and new data;
- Analyze the data and available case studies to determine when and under what conditions there is the potential for a complete PVI pathway at petroleum release sites;
- Summarize published modeling studies on PHC vapor transport and intrusion as supporting evidence of aerobic biodegradation and PHC vapor concentration attenuation; and
- Identify an approach and criteria that can be used determine when to exclude petroleum release sites from further PVI investigation and concern. Detailed protocols, such as site investigation methods, to implement this approach are beyond the scope of this report.

ES.2 Methodology

Given the importance of the contamination source type on soil vapor concentrations, the analyses described in this report were conducted separately for light nonaqueous phase liquid (LNAPL) and dissolved PHC sources. Therefore, the first step of the data analysis used LNAPL indicators to determine source type (LNAPL or dissolved-phase). Once source type was identified, the data analysis consisted of three main parts:

- Exploratory data plots to identify trends and relationships;
- Estimation of vapor concentration attenuation distance using the vertical distance method, (Lahvis et al., In prep.); and
- Estimation of non-contaminated vertical soil thickness needed for concentration attenuation using the clean soil method (Davis, 2009).

The vertical distance method plots soil vapor concentration versus distance above a contamination source and estimates the probability for the soil vapor concentrations to be less than a risk-based concentration threshold. The probabilities were calculated for two benzene concentration thresholds, 50 and 100 $\mu g/m^3$.

The clean soil method (Davis, 2009; 2010) is an analysis of the thickness of unimpacted clean soil (i.e., soil without NAPL) required for soil vapor benzene concentrations to attenuate to below a defined threshold, which for this study is 100 $\mu g/m^3$. A clean soil thickness was not calculated when the vertical distance between soil gas probes was greater than 10 ft (3.0 m) because there is then insufficient resolution (i.e., spacing between probes) for meaningful estimation.

The analysis method either replaced benzene vapor concentrations that were below the reporting limits with half the reporting limit, a common first approximation, or used the Kaplan-Meier method (Kaplan and Meier, 1958) to estimate the concentration distribution of the entire dataset, including non-detects.[1] The analysis used risk-based soil gas vapor concentration thresholds for a

---

[1] The Kaplan-Meier method is a robust, non-parametric method for considering data below reporting limits, particularly when there are multiple reporting limits (Helsel, 2005; 2006).

residential receptor scenario, continuous lifetime exposure to vapors, and a shallow soil vapor-to-indoor air attenuation factor of 1 x 10^{-2}.

ES.3 Findings and Conclusions

Critical factors affecting PVI include facility type (e.g., UST versus non-UST: fuel terminal, refinery, petrochemical plant), which influences the size of the release; PHC source type (dissolved versus LNAPL); and the vertical separation distance between the source and receptor (or building foundation). These factors are important metrics for site screening.

Findings from analysis of dissolved sources in the PVI database include:

- For the vertical distance method, approximately 97 percent of the benzene soil vapor concentrations are less than 100 µg/m^3 and 94 percent of the concentrations are less than 50 µg/m^3 for contamination source–building separation distances as small as 0 ft. For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations for distances greater than 3 ft (0.9 m).
- For the clean soil method, the 95th percentile vertical clean soil thickness for benzene vapor attenuation to below 100 µg/m^3 is approximately 5.4 ft (1.6 m).
- The analysis indicates there is a low probability of exceeding risk-based concentrations even for small separation distances.

Findings from analysis of LNAPL sources at UST sites in the PVI database include:

- Approximately 95 percent of the benzene soil vapor concentrations are less than 100 µg/m^3, and 93 percent of the concentrations are less than 50 µg/m^3 at a contamination source–building separation of approximately 15 ft (4.6 m). For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations beyond 11 ft (3.4 m).
- For the clean soil method, the 95th percentile vertical clean soil thickness for benzene vapor attenuation is approximately 13.5 ft (4.1 m).

Findings from analysis of LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites in the PVI database include:

- For the vertical distance method, approximately 90 percent of the benzene soil vapor concentrations are less than the thresholds for a contamination source–building separation of approximately 18 ft (5.5 m). The probability does not increase above 90 percent beyond this distance because data are limited for larger separation distances. For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations beyond 12 ft (3.6 m).
- For the clean soil method, there are insufficient data to estimate percentiles, but the maximum vertical clean soil thickness for benzene vapor attenuation is approximately 20 ft (6.1m).

Other conclusions from this work include the following.

- The available data indicate benzene is the risk driver for the sites evaluated, with exceedances of the risk-based vapor concentrations for benzene occurring at larger contamination source–building separation distances than observed for the other PHCs with EPA toxicity values.
- There was significantly less attenuation in vapor concentrations for the aliphatic hydrocarbon 2,2,4-TMP compared with benzene, although data were relatively limited. However 2,2,4-TMP does not have a toxicity benchmark and so cannot be evaluated in the vertical distance or clean soil method.
- The data analysis indicates a poor correlation between benzene concentrations in groundwater and deep soil vapor taken above a groundwater source. The implication is that a screening approach for vapor intrusion based on groundwater concentrations is not appropriate for PVI sites. However, groundwater concentrations can be used as an approximation to identify LNAPL sources.
- The analysis of surface cover indicated:
    - For LNAPL sources at UST sites, there were lower oxygen concentrations and less benzene vapor attenuation below paved surfaces, but not below buildings, compared to bare ground cover, and
    - For fuel terminal and refinery sites, there were lower oxygen concentrations below buildings but not below paved surfaces. The lower oxygen levels beneath buildings may result from larger petroleum releases and consequent increased oxygen demand at such sites, compared with typical LNAPL releases at UST sites.

  The results are variable and not conclusive as to the effect of surface cover, but they suggest that there can be reduced oxygen availability below hard surfaces (pavement or building foundations), for the sites evaluated.
- Because the vertical distance method evaluation includes soil vapor concentration data from below buildings at 39 sites, the results are considered reasonably robust with respect to the potential influence of surface cover (although further evaluation of this factor is recommended).

The mathematical modeling studies reviewed strongly support the empirical analysis and inclusion distances for dissolved sources. For LNAPL sources, although the modeling generally supports the empirical analysis, further evaluation of factors potentially influencing oxygen supply and demand is warranted. Such factors include source vapor concentration, source size, building size, surface cover and soil layer properties, and natural soil oxygen demand.

Inclusionary criteria or conditions not analyzed in this report include non-UST facilities, organic-rich soils (e.g., peat), large building foundations (e.g., apartment complexes, commercial or industrial buildings), and significant subsurface preferential pathways (e.g., utilities, karst, fractured rock). Where these conditions are present at a site, a more detailed PVI assessment may be warranted, especially when LNAPL is present.

Releases of certain ethanol blends of gasoline may also warrant additional consideration for inclusion and PVI assessments, although further research is required to determine the significance of ethanol content with respect to inclusion distances. Biodegradation of ethanol may generate methane at a greater rate than gasoline alone, consuming oxygen that would otherwise be available for biodegradation of PHCs and thus increasing the potential for PVI.In addition, inclusion criteria may not apply at sites where there is significant methane generation because of the potential for safety hazards, advective soil gas transport, and reduced biodegradation of other PHCs (due to oxygen demand represented by methane). High methane generation potential has been documented at large diesel and gasoline spills at non-UST sites.

[This page intentionally left blank.]

1. Introduction

This report describes an evaluation of empirical data and select modeling studies of the behavior of petroleum hydrocarbon (PHC) vapors in subsurface soils at petroleum release sites and how these vapors can affect subsurface-to–indoor air petroleum vapor intrusion (PVI). The purpose of this report is to support the development of a soil vapor screening methodology for PHC compounds that can be used for characterizing PVI at Solid Waste Disposal Act Subtitle I[2] UST sites with petroleum fuel releases. However, PVI data from other types of petroleum release sites (fuel terminals, petroleum refineries) are also presented and discussed.

1.1 Background

In support of its general guidance development effort for the PVI exposure pathway, EPA compiled an empirical database of measurements of subsurface media (soil gas, soil and groundwater) and supporting data at PHC sites. The rationale for this focus on subsurface media measurements is that in the presence of oxygen, PHC vapors can rapidly biodegrade. Compared to chlorinated hydrocarbons, PHC vapors attenuate to much lower concentrations in soil gas (U.S. EPA, 2012a). Therefore, screening for PHCs using the same methodology as chlorinated hydrocarbons is overly conservative.

Because bioattenuation processes are well documented and widespread (U.S. EPA, 2012a), the analysis of subsurface soil gas data from sites provides an opportunity for developing improved and more realistic screening evaluation methods for PHC compounds based on the observed attenuation. These data can be used to identify an inclusion distance[3], defined in this report as the contamination source–separation distance beyond which the potential for PVI may be insignificant. An inclusion distance approach is potentially more efficient than current approaches for investigating PVI sites. It also focuses resources on sites within the inclusion zone that may have significant potential for PVI issues.

Davis (2011a) compiled a large quantity of the data in the EPA PVI database. The May 2011 version of the Davis database was used as the starting point for the EPA PVI database. A significant quantity of data from other sources was added to the EPA PVI database for this effort, including data from Maine (Eremita, 2011), Canada, and Australia (Wright 2011, 2012). However, for purposes of evaluation of inclusion distances, the North American data (primarily sites from the U.S.) and Australian data were analyzed separately, given the differences in site conditions in these two countries.

Several similar complementary efforts using somewhat different datasets are in progress in the U.S. (Lahvis et al., In prep.; Peargin and Kolhatkar, 2011). Section 8 (below) compares these complementary studies and their results with those in this report.

---

[2] Subtitle I of the Solid Waste Disposal Act

[3] An exclusion distance concept and compilation of a PVI database to support estimation of exclusion distances was first developed by Davis (2009, 2010, 2011a, and 2011b). The exclusion and inclusion distance concepts are similar, although each has a slightly different focus. The inclusion concept establishes criteria for identifying sites that are screened in for further assessment, whereas the exclusion concept establishes criteria that, when met, indicate low potential for PVI and thus a basis for screening sites out the PVI assessment process.

Several states, including New Jersey, California, and Wisconsin, are in the process of developing or have recently developed guidance for PHCs based on a pathway inclusion or exclusion distance approach. Appendix A provides a review of existing state vapor intrusion guidance focusing on approaches for PHCs.

1.2 Goal and Objectives

The goal of this report is to provide information on the behavior of PHCs with respect to subsurface vapor attenuation that would support establishing an assessment framework for evaluating potential petroleum vapor migration from subsurface to indoor air. The main intent of the evaluation is to determine if the vapor migration pathway is complete (or incomplete) to indoor air, which in this context is the potential to exceed human health-based concentration criteria in indoor air due to PVI.

This report provides data and analyses in support of a key part of this framework: the evaluation of PHC vapor attenuation and identification and justification of inclusion distances between contamination and receptors that can be used to quickly assess whether the PVI pathway is likely to be complete. However, the scope of this report does not include development of the detailed protocols that will be needed to apply these inclusion distances, which are described in separate guidance on PVI being prepared by EPA (Wilson et al., In press).

To develop and support the inclusion distances, the objectives of work described in this report were to:

- Assemble an empirical database from petroleum release sites where the PVI pathway has been evaluated via primarily soil gas and groundwater measurements;
- Consolidate and independently evaluate the quality of selected existing databases and newly available data;
- Analyze the database and available case studies to determine when and under what conditions there is the potential for a complete PVI pathway at petroleum release sites;
- Summarize published modeling studies on PHC vapor transport and intrusion as supporting evidence of aerobic biodegradation and vapor concentration attenuation; and
- Identify an approach and criteria that can be used to screen out certain petroleum release sites from further PVI investigation and concern so that resources may be focused on sites within the inclusion zone where the PVI pathway may potentially be complete.

1.3 Document Development and EPA Peer Review

The draft document was subjected to EPA’s external peer review process from May to June 2012. The peer review contractor independently selected five experts not affiliated with EPA. The experts were James B. Cowart, David J. Folkes, and Dr. Jeffrey P. Kurtz of EnviroGroup Ltd.; Todd McAlary of Geosyntec Consultants; and Dr. Mark A. Widdowson of Virginia Polytechnic Institute and State University. The expertise of the peer review panel includes:

- Practical and theoretical understanding of the petroleum vapor intrusion pathway, including how volatile organic contaminants move and distribute in the subsurface (soil gas), indoor air, and outdoor air from dissolved and nonaqueous phase liquid sources;
- Experience in planning and conducting site-specific vapor intrusion studies, including developing and refining conceptual site models of the migration and distribution of volatile contaminants; and
- Expertise in collecting and statistically analyzing vapor intrusion pathway data, applying and calibrating models using site-specific data, and interpreting results to make decisions at vapor intrusion sites.

The peer reviewers were tasked to review the draft report and provide opinion and perspective regarding:

- The scientific appropriateness of the database for EPA's purposes;
- Whether the reported analyses are based on sound scientific principles, methods, and practices; and
- Whether the reported conclusions are adequately supported by the data and analyses.

1.4 Document Organization

This report is organized as follows:

- Section 2 describes the conceptual site model (CSM) for aerobic biodegradation of PHC vapors and select case studies where PVI has been documented.
- Section 3 provides a summary of select modeling studies of the biodegradation of PHCs in the subsurface.
- Section 4 provides a review of empirical database studies of PHC vapor attenuation.
- Section 5 describes the EPA PVI database development, structure, and content.
- Section 6 describes the EPA PVI database analysis approach and methods.
- Section 7 describes the EPA PVI database analysis results.
- Section 8 provides a discussion of the results and comparisons with other studies.
- Section 9 provides findings and conclusions of this report.

The key sections of this report supporting the inclusion distance approach are the empirical database methods and analysis in Sections 6 and 7. The CSM discussion and summary of model studies are intended as supporting evidence for the PVI inclusion criteria.

2. Conceptual Site Model and Select Case Studies

The CSM for PVI described in this section builds on the general vapor intrusion CSM described in U.S. EPA (2012a), with additional emphasis on the difference in PHC vapor concentrations for light nonaqueous phase liquid (LNAPL) and dissolved groundwater contamination sources.

The scope of this CSM discussion is on specific aspects relating to PHC fate and transport and does not address general aspects of the general vapor intrusion CSM, which are covered in other documents (e.g., U.S. EPA, 2012a,b,c). In addition, select case studies indicating a confirmed or likely complete transport pathway for PVI are described.

2.1 Aerobic Biodegradation Processes in the Vadose Zone

Petroleum liquids (e.g., gasoline, diesel) are moderately soluble in water and often form separate phase liquids commonly referred to as LNAPLs when released into the environment. When an LNAPL reaches the water table, it tends to accumulate and spread laterally and vertically (as the water table rises and falls), to form a smear zone where residual LNAPL partially occupies soil pore spaces across the water table. A dissolved hydrocarbon groundwater plume that extends beyond the LNAPL source zone is formed as PHC compounds dissolve from the LNAPL into groundwater or as water percolates through residual LNAPL in the unsaturated soil (vadose) zone.

Volatilization of PHCs occur from both LNAPL and dissolved (groundwater) hydrocarbon sources. In addition to PHCs, fuel oxygenates, such as ethanol and methyl tert-butyl ether (MtBE), and fuel additives, such as ethylene dibromide (EDB) and 1,2-dichloroethane (DCA), can also be present in the vapor phase in the unsaturated zone proximate to LNAPL source zones. The biodegradation of PHC vapors is relatively rapid when oxygen is present; therefore, aerobic biodegradation can typically limit the concentration and subsurface migration of PHC vapors in unsaturated soils and in groundwater. Modeling studies (Abreu and Johnson, 2006; DeVaull, 2007a; Abreu et al., 2009) and field studies (Ririe et al., 2002; Hers et al., 2000; Roggemans et al., 2001; Fitzpatrick and Fitzgerald, 2002) indicate that the potential for PVI is greatly reduced (orders-of-magnitude concentration attenuation) when aerobic biodegradation processes occur in soils between the hydrocarbon source and receptor (building foundation). A typical vertical concentration profile in the unsaturated zone for PHCs, carbon dioxide, and oxygen is shown in **Figure 1**.

The aerobic biodegradation processes between the hydrocarbon source and receptor may be conceptualized with respect to fluxes where the oxygen availability must exceed microbial metabolically driven oxygen demand associated with the hydrocarbon source (Lahvis et al., In prep.). The PHC and oxygen fluxes are primarily due to diffusion, which is influenced by soil moisture and porosity. PHC biodegradation rates are rapid (e.g., half-lives on the order of hours to days; DeVaull, 2007b, 2011; Davis et al., 2009) and much faster than the rate of hydrocarbon transport by diffusion within the unsaturated zone. For this reason, there are typically sharp reaction fronts where the PHC vapor concentrations attenuate by orders of magnitude over short distances (e.g., 1 to 5 ft [0.3 to 1.5 m]) and where there is a corresponding decrease in the oxygen concentrations, as observed in several field studies (Lahvis and Baehr, 1999; Hers et al., 2000; Sanders and Hers, 2006; Davis et al., 2009; Luo et al., 2009). DeVaull et al. (2007b) report that the lower threshold oxygen concentrations required to support aerobic biodegradation of PHC vapors range from 1 to 4 percent.

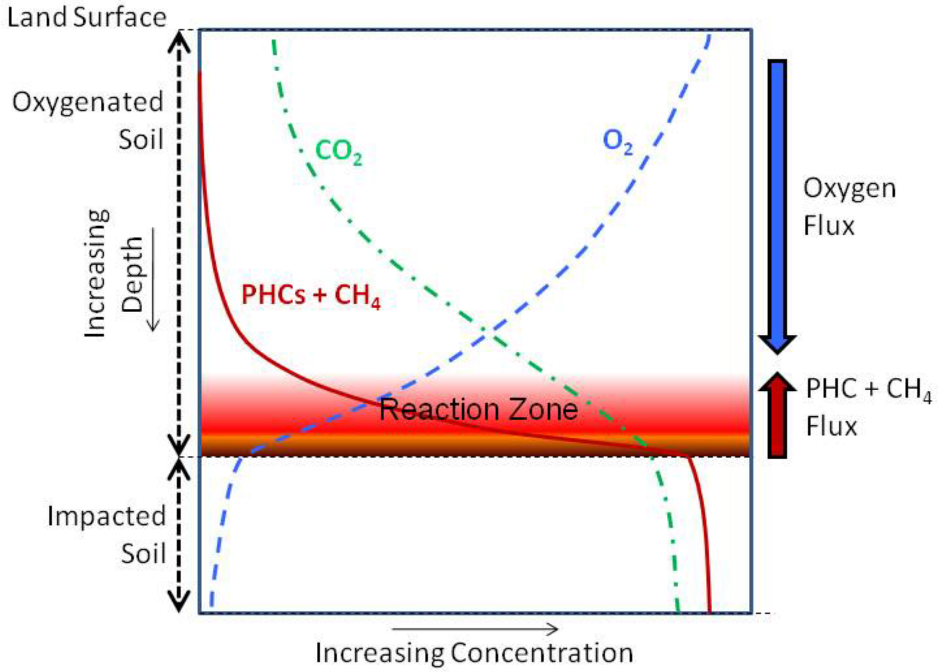


Figure 1. **Typical vertical concentration profile in the unsaturated zone for PHCs, carbon dioxide, and oxygen (modified from U.S. EPA, 2012a).**

2.2 Factors Influencing Biodegradation of Petroleum Hydrocarbons

Biodegradation of PHCs has been documented in publications for more than 70 years (Zobell, 1946; Atlas, 1981; Leahy and Colwell, 1990). These papers describe biodegradation of many types of PHC: liquids and gases; straight, branched, and ring-structure compounds; and compounds with single and multiple carbon bonds. Many microbial species, including more than 30 genera of bacteria, more than 25 genera of fungi, and several algae degrade PHCs, although not every microbial species degrades every chemical. PHC biodegradation has been documented in marine, freshwater, sediment, and soil environments and by direct metabolism and co-metabolism (co-oxidation). Microbial degradation of petroleum produces biomass, intermediate products (e.g., alcohols, aldehydes, organic acids), and the ultimate mineralization products carbon dioxide (CO_2) and water (H_2O).

In general, relatively fast acclimation times are observed, absent other limits, by population enrichment (fast biomass growth) and/or plasmid transfer. Acclimation times tend to be shorter with prior chemical exposure. Environmental conditions under which petroleum biodegradation has been observed range from 0° to 70°C, salinity up to 25 parts per thousand sodium chloride (NaCl), and pH from 6 to 10, although optimal conditions can be narrower. Aerobic biodegradation is the primary mechanism in the unsaturated zone, but anaerobic biodegradation near source zones may also occur in the presence of other strict or facilitative electron acceptors (e.g., nitrate, sulfate) or under fermentative or methanogenic conditions (DeVaull et al., 1997; Madigan et al., 2010). There have been extensive compilations of rates of aerobic degradation specific to vadose zone aerobic soils (e.g., Leeson and Hinchee, 1996; DeVaull et al., 1997; Hers et al., 2000; Ririe et al., 2002; Davis et al., 2009; DeVaull, 2011).

The U.S. Air Force Bioventing Initiative study of 125 sites indicated that environmental factors, such as soil moisture, nutrients, and pH, did not significantly influence biodegradation activity and respiration rates, except for one site located in the Mohave Desert (California, USA) with very dry soils (moisture content of 2 percent), although some biological activity did still occur there (Leeson and Hinchee, 1996). Biological activity is limited when the moisture content is at or below the permanent wilting point (Zwick et al., 1995; Holden et al., 1997), a condition expected to be rare in most geological and climatic environments. A literature search for soil moisture effects did not indicate other studies specifically addressing vadose zone attenuation of PHC vapors under dry conditions. However, the empirical database assembled for this study includes sites in relatively dry climates (e.g., Utah, Australia) that can be considered fairly direct indicators for the influence of soil moisture.

Aerobic biodegradation of PHCs is a robust process that has been demonstrated under a wide range of environmental conditions. Important factors influencing aerobic biodegradation of PHC vapors include:

- Vapor source hydrocarbon concentration, flux, and composition (including methane);
- Minimal oxygen concentration required to support aerobic biodegradation;
- Oxygen demand (i.e., the oxygen required to biodegrade the available hydrocarbons) and supply (i.e., flux balance);
- Distance between the vapor source and the building;
- Soil type and properties (e.g., soil porosity and moisture); and
- Size and characteristics of the building and adjacent land surface.

2.3 Dissolved versus LNAPL Vapor Sources

The PHC vapor source concentration is highly dependent on whether partitioning occurs from compounds present as a dissolved phase in groundwater or directly from LNAPLs present above the capillary fringe[4] (either as mobile LNAPL or trapped as residual LNAPL in the smear zone in soils above the water table). The vapor mass flux from LNAPLs present in the unsaturated zone soils will be higher than for a dissolved groundwater source. In the case of a dissolved source, chemicals must diffuse through water in the capillary fringe before reaching continuous gas-filled soil pores, and hydrocarbons may also be attenuated through biodegradation and sorption within the capillary fringe. The vapor mass flux for LNAPL source zones will also tend to be sustained for longer periods of time because of the larger contaminant mass compared with dissolved sources. In addition, the vapor composition will differ depending on whether the vapor source is LNAPL or the dissolved phase. For LNAPL sources, there will tend to be a higher proportion of relatively insoluble PHC compounds, including aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs), such as naphthalene. For dissolved sources, there will tend to be higher concentrations of the more soluble chemicals, including single-ring aromatic hydrocarbons, such as benzene, toluene, ethylbenzene, and xylenes (Lahvis et al., In prep.).

---

[4] The capillary fringe is the tension-saturated zone in soils just above the water table. It will vary in height depending on soil permeability with greater heights with lower permeability soils.

The distribution of LNAPL sources and presence of residual LNAPL within the unsaturated soil zone (i.e., in release zones) compared with LNAPL at the water table can influence the volatilization potential. For LNAPL sources at the water table, the position of the water table relative to the smear zone can be important, and seasonally higher volatilization rates can occur when the water table is low and below a portion of the smear zone. The differences in the PHC vapor concentrations and fluxes for LNAPL and dissolved vapor sources are an important distinction for defining exclusion distances (**Figure 2**). A free-phase and residual-phase LNAPL source will tend to act the same with respect to a vapor source. A residual-phase LNAPL source will not yield separate-phase LNAPL to the monitoring well and therefore may look the same as a monitoring well that intercepts a dissolved source with limited concentration attenuation. Conceptually, the source type (dissolved or LNAPL) will affect the position of the aerobic reaction front in the unsaturated zone relative to the oxygen source. For dissolved sources, the reaction front will be located close to the hydrocarbon source (Roggemans et al., 2001; Golder Associates, 2006; Abreu et al., 2009), while for LNAPL sources, the reaction front position is more variable but typically is located at greater distances from the source compared with dissolved sources because of the greater PHC flux (Roggemans et al., 2001; Golder Associates, 2006; Abreu et al., 2009). For dissolved vapor sources, case studies and database evaluations reported in the literature indicate no confirmed cases of PVI for a wide range of site conditions (Davis, 2009; McHugh et al., 2010).

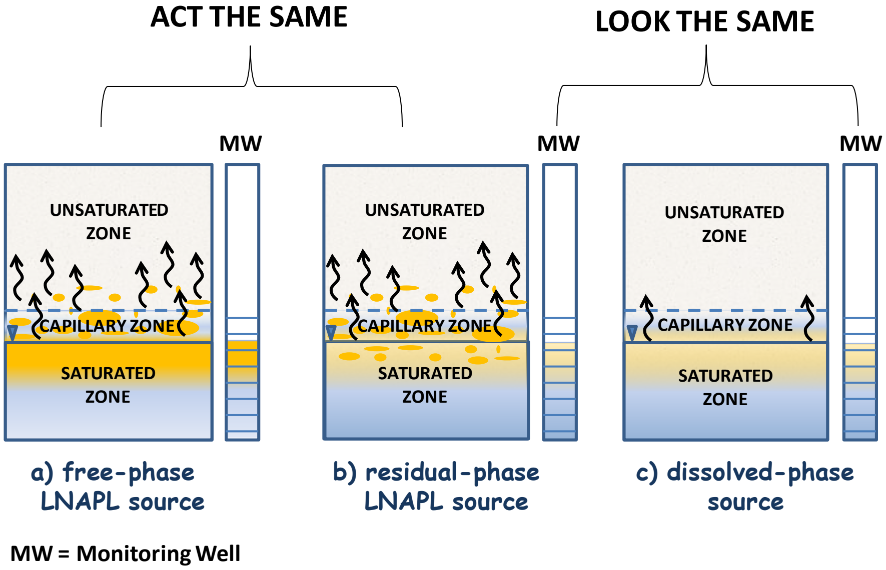


Figure 2. Conceptual model illustrating the potential for vapor intrusion for a) free-phase LNAPL sources, b) residual-phase LNAPL sources, and c) dissolved-phase sources. (Source: Lahvis et al., In prep.; used with permission)

2.4 Anaerobic Biodegradation and Methane Generation

Where anaerobic conditions exist, methane may be produced through the breakdown of PHC compounds and ethanol, if present, by microbes through the process of methanogenesis. The terminal electron acceptor in methanogenesis is carbon, and either carbon dioxide or acetic acid can act as terminal electron acceptors (Ririe and Sweeney, 1995; Wiedemeier et al., 1996). The formation of the biogases methane and carbon dioxide is of potential concern with respect to explosion hazard and asphyxiation. Concentrations of methane above the lower explosive limit can present a flammability and explosion risk. Methane generation also poses potential issues for PVI, as discussed in Section 2.5.

2.5 Conditions for Increased Potential for Petroleum Vapor Intrusion

As described in U.S. EPA (2012a), site conditions that may result in increased potential for PVI include:

- **Direct contact between contamination (either dissolved or LNAPL) and a building foundation.** Most documented cases of PVI are for this condition (McHugh et al., 2010).
- **Insufficient separation distance.** For biodegradation to limit the potential for PVI, there needs to be a sufficiently thick layer of clean, oxygenated soil between the building foundation and the contamination. (Clean soil is defined as unimpacted by residual LNAPL.) The required thickness will depend on hydrocarbon source concentration and oxygen supply and demand.
- **Preferential transport pathways.** If a preferential pathway, such as coarse-grained utility backfill, fractured rock, or karst, connects a contamination source to a building, the chemical transport can be faster and extend farther than transport through the surrounding soils.
- **Surface capping effect.** Building foundations, paved surfaces, and surficial soils with low effective diffusivity and soil-air permeability (e.g., moist clay layers) can act as a surface cap to reduce oxygen transfer to the subsurface. The importance of this effect is not well understood, although significant diffusive oxygen transport through intact concrete can occur, as indicated by measured rates (typically between 1×10^{-6} and 5×10^{-4} cm^2/s) reported in the literature (Branco and de Brito, 2004; Kobayashi and Shuttoh, 1991; Tittarelli, 2009). Advective transport of atmospheric air to the subsurface also can occur through openings (e.g., cracks, drains, sumps) in the building foundation during periods when the building is positively pressurized. These mechanisms can limit the potential for low oxygen conditions beneath a building.
- **Production of methane.** Methane may be produced through microbial breakdown of PHC compounds in anaerobic source zones. The presence of ethanol in a source zone may increase the methane generation rate compared with a gasoline LNAPL-only source zone (Nelson et al., 2010; Spalding et al., 2011; Jourabchi et al., 2012). Note that some sites with releases of fuel containing 10 percent ethanol (E10) are probably present in the EPA PVI database (see Section 5.3) and in other data compilations (e.g., Lahvis et al., In prep.). Evaluation of methane generation from ethanol fuel blends is an area of active research (Jewell and Wilson, 2011). Methane production can result in soil gas pressures and flow toward receptors and may deplete oxygen that otherwise could be used for biodegradation of the PHC vapors (Jourabchi et al., 2012). Elevated methane therefore could increase the potential for PVI at a PHC release site. However, no published cases were identified where pressure build-up at a UST site caused soil gas advection to be an issue.

- **High organic matter content.** Oxygen that would otherwise be used to degrade PHC vapors may be consumed in settings with high soil organic matter content (e.g., peat bogs).
- **Atmospheric pressure changes.** Atmospheric pressure changes could result in transient advective soil gas flow at sites with deep water tables and coarse-grained soils. However, such processes are not expected to result in longer-term conditions where there would be significant differences in the aerobic biodegradation profile, compared with a diffusion-only transport paradigm.

2.6 Case Studies Indicating Confirmed or Likely Complete Transport Pathway for Petroleum Vapor Intrusion

Confirmed occurrences of subsurface PVI to indoor air or elevated sub-slab hydrocarbon vapor concentrations at petroleum sites are rare in the literature[5] but important for defining the inclusion criteria—that is, sites that warrant PVI evaluation because PVI is likely to be found.

Eight case study sites were identified in the literature where PVI was confirmed or likely (**Table 1**). Five sites were refinery or petrochemical sites, and three were UST sites. Common site conditions involved the following: large fuel releases, extensive LNAPL contamination at the water table, and shallow depth to LNAPL contamination, although at two sites the separation distances between the building and LNAPL source were approximately 25 to 30 ft (7.6 to 9.1 m). Factors that appeared to contribute to PVI at the two sites with deeper contamination were a possible geological capping effect at a former refinery site (unknown location) and heavy rain and a sharp water table rise at a site with a very large petroleum fuel release (Hartford, Illinois).

Table 1. Summary of Case Study Sites with Confirmed or Likely Occurrences of Petroleum Vapor Intrusion

Site	Distance LNAPL to Building	Building Size	Source Vapor Concentrations	Facility	Comments
Perth, Australia (Patterson and Davis, 2009)	10 ft (3.0 m)	2,700 ft^2	TPH = 20 mg/L	Refinery	30-ft (9.1-m) building apron on 3 sides of building
Chatterton, Vancouver, B.C. (Hers et al., 2000)	5 ft (1.5 m)	610 ft^2	TPH = 40 mg/L	Petro-chemical	PVI only when building depressurization was ~ 10 Pa
Casper, Wyoming (Luo et al., 2009)	1–5 ft (0.3–1.5 m)	2,300 ft^2	TPH = 100 mg/L	Refinery	Shallow LNAPL source
Unknown (Luo et al., 2010)	25–30 ft (7.6–9.1 m)	2,100 ft^2	TPH ~ 60-160 mg/L	Refinery	Capping effect from geology observed
Hartford, Illinois (Illinois DPH, 2010)	Depth to groundwater ~ 23–33 ft (~7–10 m)	N/A	N/A (gasoline source)	Refinery	Very large spill, episodic PVI events when heavy rain or sharp rise in water table

(continued)

---

[5] There are also anecdotal accounts of PVI occurrances at buildings typically with shallow fuel sources and preferential pathways (e.g., sewer lines, drains) connecting the fuel source to the building.

Table 1. Summary of Case Study Sites with Confirmed or Likely Occurrences of Petroleum Vapor Intrusion (continued)

Site	Distance LNAPL to Building	Building Size	Source Vapor Concentrations	Facility	Comments
Stafford, New Jersey (Sanders and Hers, 2006)	5.25 ft (1.6 m)	700 ft^2	Benzene = 0.66 mg/L; 2,2,4-TMP = 2.1 mg/L; MtBE = 5.9 mg/L	UST	PVI observed for MtBE, 2,2,4-TMP and cyclohexane but not for BTEX
Ogden, Utah, Mini-Mart (McHugh et al., 2010)	3.3 ft (1.0 m)	N/A	N/A (gasoline source)	UST	Large release, odors detected in building
Gunnison, Utah, Top-Stop (McHugh et al., 2010)	Depth to groundwater ~ 13–16 ft (~4–5 m)	N/A	N/A (gasoline source	UST	Sudden 20,000-gallon (75,708 L) release, odors detected in buildings up to 500 ft (152 m) downgradient of source

TPH = total petroleum hydrocarbons; N/A = not available

2,2,4-TMP = 2,2,4-trimethyl pentane; MtBE = methyl tert-butyl ether; BTEX = benzene, toluene, ethylbenzene, and xylenes

2.6.1 Refinery Site, Perth, Australia (Patterson and Davis, 2009)

Monitoring at a former refinery site near Perth, Australia, with a kerosene LNAPL source indicated elevated (up to 20 mg/L) PHC vapor concentrations and depleted oxygen (<1 percent) below the interior of a building but much lower hydrocarbon and near-atmospheric oxygen concentrations near the edge and beside the building. The slab-on-grade building footprint area was 2,700 ft^2 (251 m^2) with a 30-ft (9.1-m)-wide concrete apron on three sides of the building and uncovered open ground on the other side. The building is underlain by sand with a LNAPL zone across the water table at approximately 10 ft (3.0 m) below ground surface (bgs). The effective diffusion coefficient for chemical transport through concrete measured at the site was relatively low compared with published data, indicating the concrete slab is not overly porous. The relatively low diffusivity of the concrete may have reduced oxygen transport to the subsurface under the building. In addition, because of the wide concrete aprons, the effective area of the building with respect to oxygen transport restrictions may be larger than its footprint.

2.6.2 Chatterton Petrochemical Site, Vancouver, B.C., Site (Hers et al., 2000; Hers et al., 2002)

At the former Chatterton petrochemical site near Vancouver, B.C., a greenhouse was constructed above a residual LNAPL source comprising benzene, toluene, and xylene. Monitoring indicated depletion of oxygen (<1 percent) and a complete PVI pathway when the building was continually depressurized (to approximately 10 Pa), but only partial oxygen depletion and no complete pathway under natural (near-neutral) pressure conditions. The slab-on-grade building footprint was 610 ft^2 (57 m^2), the building was underlain by sand, and the depth to the LNAPL smear zone was 5 ft (1.5 m) below the building foundation slab.

2.6.3 Refinery Site, Casper, Wyoming (Luo et al., 2009)

Monitoring at a site in Casper, Wyoming, indicated a complete PVI pathway at a refinery site with a light distillate (gasoline-range) LNAPL source. LNAPL contamination was present in the unsaturated zone at depths between about 1 and 5 ft (0.3 and 1.5 m) below a small warehouse-type building with a slab-on-grade foundation. Monitoring of sub-slab soil gas indicated oxygen was depleted (<1 percent) below the interior regions of the building (except near the saw-cut expansion joints during times of positive building pressures) but not below the edges of the building.

2.6.4 Former Refinery Site (confidential location) (Luo et al., 2010)

Monitoring at a former refinery site with a building overlying a light distillate (gasoline-range) LNAPL source indicated relatively uniform and elevated (60 to 160 mg/L) PHC vapor concentrations and depleted oxygen beneath and around the building foundation. The building footprint area is 2,100 ft^2 (195 m^2) with a basement depth of 5 ft (1.5 m) bgs. The ground surface is predominantly grass covered, except on one side of the building where there is an asphalt/concrete parking lot. Soils with LNAPLs were first encountered at about 30 to 35 ft (9.1 to 10.7 m) bgs; therefore, the separation distance between the building foundation and contamination (LNAPL) is approximately 25 to 30 ft (7.6 to 9.1 m). Detailed soil respiration and soil-air permeability test results suggest two possible reasons for the observed behavior and elevated shallow PHC concentrations: 1) significant background oxygen uptake in surface soils or 2) physically limited oxygen transport from the atmosphere. Soil oxygen uptake rates in shallow soil ranged from 2 to 25 mg-oxygen/kg-soil/day. There were silt and clay layers between 2 to 5 ft (0.7 to 1.5 m) and 7 to 8 ft (2.1 to 2.4 m) bgs, both with soil-air permeabilities of less than 1×10^{-14} m^2. The results from Luo et al. (2010) suggest both of these reasons are plausible for the observed soil vapor behavior.

2.6.5 Refinery Site, Hartford, Illinois (Illinois Department of Public Health, 2010)

Soil gas monitoring at a Hartford, Illinois refinery site with a very large petroleum fuel spill (several million gallons) indicated episodic PVI into buildings when there were heavy rains and a sharp rise in the water table. (Note that there are sites where the opposite effect is observed: soil vapor concentrations rise when the water table falls below LNAPL source zones.) The vadose zone soils consisted of coarse sand overlain by fine sediments, and the depth to groundwater ranged from 23 to 33 ft (7 to 10 m) bgs.

2.6.6 UST Site, Stafford, New Jersey (Sanders and Hers, 2006)

Monitoring of a house with a basement above a residual gasoline LNAPL source at a site with sandy soils indicated PVI of methyl tert-butyl ether (MtBE), 2,2,4-trimethylpentane (2,2,4-TMP), and cyclohexane but not benzene, toluene, and xylene compounds. The depth to the LNAPL source was 10.75 ft (3.27 m), which was 5.25 ft (1.60 m) below the basement foundation. The source soil vapor concentrations of benzene, 2,2,4-TMP, and MtBE were 0.66 mg/L, 2.1 mg/L, and 5.9 mg/L, respectively. It was inferred that, compared with benzene, MtBE attenuated to a lesser degree because of its lower degradation rate. Also, 2,2,4-TMP attenuated to a lesser degree than benzene because of its lower solubility (biodegradation occurs in the water phase). No PVI was detected at a nearby slab-at-grade building above residual LNAPL or other buildings above a dissolved groundwater source.

2.6.7 UST Site, Ogden, Utah, Mini-Mart Release (McHugh et al., 2010)

A large release at a UST site in Ogden, Utah resulted in free product gasoline floating on shallow groundwater less than 3.3 ft (1 m) below the bottom of the slab. Petroleum odors reported in a building were mitigated by installing a positive pressure HVAC system.

2.6.8 UST Site, Gunnison, Utah, Top Stop Release (McHugh et al., 2010)

A large, sudden gasoline release (20,000 gallons [75,700 L]) occurred at a UST site in Gunnison, Utah. The vadose zone soils consisted of silty sand and gravel overlain by sandy silt, and the depth to groundwater was 13 to 16 ft (4 to 5 m) bgs. The soil headspace photoionization detector (PID) readings in the LNAPL source zone were in the range of 100's to 1,000's ppmv (parts per million by volume). In the first several months after the release occurred, people complained of gasoline odors, and elevated PID readings were reported in several buildings up to 1,640 ft (500 m) from the release site in the direction of groundwater flow.

3. Summary of Modeling Studies

Numerous modeling studies of aerobic biodegradation have been conducted to evaluate biodegradation processes, identify factors influencing biodegradation, compare modeled to measured hydrocarbon vapor attenuation, and estimate first-order biodegradation rates (e.g., Jury et al., 1983; Lahvis and Baehr, 1999; Hers et al., 2000; Ririe et al., 2002; Grathwohl and Maier, 2002; Robinson and Tursczynowisz, 2005; Abreu and Johnson, 2005; Abreu and Johnson, 2006; DeVaull, 2007b; Abreu et al., 2009; Davis et al., 2009; DeVaull, 2011; Hers et al., In prep.; U.S. EPA, 2012c). Modeling studies using representative first-order biodegradation rates indicate that aerobic biodegradation is a rapid and, in some cases, essentially instantaneous process and that attenuation of petroleum hydrocarbon vapor concentrations occurs over relatively short distances (a few feet), consistent with the observed field data (e.g., Hers et al., 2000; Davis et al., 2009). An important input to modeling studies is the first-order biodegradation rate; a comprehensive compilation of such rates is provided in DeVaull (2011).

The biodegradation of aliphatic hydrocarbon compounds is less well studied, but available data suggest bioattenuation distances may be greater for aliphatic hydrocarbons than for aromatic hydrocarbon compounds. For example, greater concentration attenuation between deep and shallow soil vapor was observed for benzene (and aromatics in general) than for 2,2,4-TMP (and aliphatics in general). Examples from two sites illustrate this behavior:

- At the Stafford site (discussed previously in Section 2.6.6), the ratio between deep and shallow soil vapor concentrations was 220 times lower for benzene than for 2,2,4-TMP (Sanders and Hers, 2006); and
- At a site in North Battleford, Saskatchewan, this ratio was 40 times lower for benzene than for 2,2,4-TMP (Hers et al., In prep.).

The modeling studies reviewed below were selected to provide insight on the vertical and lateral attenuation of PHC vapors and, where possible, the influence of factors such as source vapor concentrations and layered soil deposits on PHC vapor migration and attenuation. By examining model results that predict distances over which PHC vapor concentration attenuation occurs for varying site conditions, this review offers evidence that can help inform the development of inclusion distances for sites where PVI is being assessed.

3.1 Abreu Three-Dimensional Model Simulations

Abreu and Johnson (2005) present the theoretical basis for a three-dimensional model for predicting soil vapor-to-indoor air attenuation factors incorporating subsurface processes of diffusion, gas-phase advection through building depressurization, oxygen-limited first-order biodecay, and uniform mixing of vapors entering a building. Three-dimensional modeling scenarios of interest are summarized below.

3.1.1 Three-Dimensional Model Simulations—Below-Building Contamination Source and Homogeneous Soil Conditions

Abreu et al. (2009) presents model simulation results for oxygen-limited aerobic biodegradation for a scenario where the building parameters assumed were representative of a residential house above a homogeneous sand unsaturated zone. The hydrocarbon modeled was assumed to have the same fate and transport properties as benzene. Oxygen-limited decay was simulated in the aerobic portion of the unsaturated zone (i.e., when oxygen concentrations exceeded 1 percent). A first-order biodegradation rate of 0.79 h^{-1} was assumed for the hydrocarbon, which is consistent with published rates for benzene (e.g., DeVaull, 2011).

Potentially conservative attributes of the Abreu et al. (2009) model simulations include the following:

- oxygen transport occurs only through cracks in the foundation and not through intact concrete;
- the building is continuously depressurized; thus, for cases where pressure cycling is a relevant condition, no atmospheric air moves downward into the soil at times when the building is pressurized; and
- there is no oxygen recharge through pressure effects caused by wind and/or atmospheric pressure changes.

Spatially variable soil properties (e.g., moisture, porosity, permeability) were not considered, a potentially non-conservative modeling assumption. Conceptually, there are scenarios where layered systems consisting of a fine-grained, wet surface soil layer underlain by a coarser-grained, drier soil layer could increase the potential for oxygen limitations below buildings.

The Abreu et al. (2009) model results are summarized in **Figure 3**. For context, the EPA PVI database indicates representative total hydrocarbon vapor concentrations (excluding methane) between 100 and 200 mg/L above gasoline LNAPL distributed above the capillary fringe, and the approximate lower end of this range likely indicates weathered gasoline sources. The total hydrocarbon vapor concentration range simulated by Abreu et al. (2009) is representative of a gasoline source but, because of the additional oxygen demand represented by the oxidation of methane, less representative of a source that also includes elevated methane concentrations. The empirical analysis indicates methane concentrations at most sites with methane data were low (Section 7.1.3). For a dissolved vapor source, the database indicates that the maximum total petroleum hydrocarbon (TPH) vapor concentration measured in vapor was 10 mg/L, with more than 99 percent of the data indicating TPH vapor concentrations less than 1 mg/L.

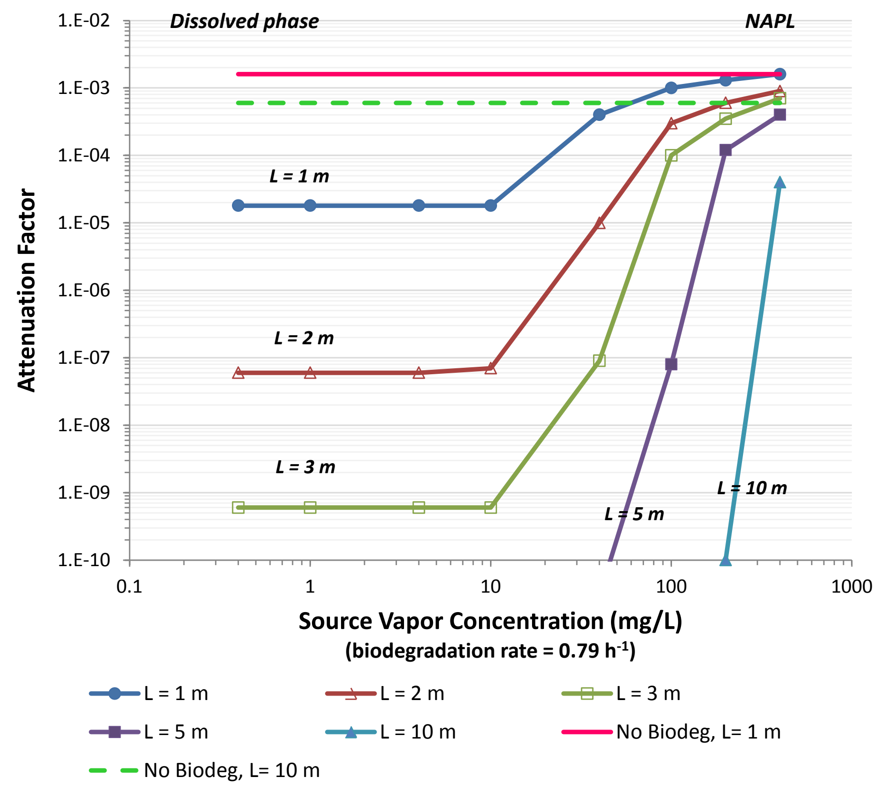


Figure 3. Vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model for a range of source total hydrocarbon (benzene) vapor concentrations and separation distances for a residential house scenario (adapted from Abreu et al., 2009).

The model-predicted vapor attenuation factors presented in **Figure 3** are highly sensitive to source hydrocarbon concentrations above 10 mg/L. Below 10 mg/L, the attenuation factors are relatively constant for a given separation distance. For a source vapor hydrocarbon concentration representative of weathered gasoline (100 mg/L), the model predictions in **Figure 4** for source-building distances of 3.3 ft (1 m) and 16.4 ft (5 m) predict oxygen concentrations less than 1 percent below the building. It is not until the source-building distance is increased to 23 ft (7 m), shown in the lower panel of **Figure 4,** that an aerobic reaction front and corresponding orders-of-magnitude reduction in hydrocarbon vapor concentrations below the building is observed. As previously discussed, a potentially conservative aspect of the model predictions in **Figure 4** is that they assume no oxygen transport through the building foundation.

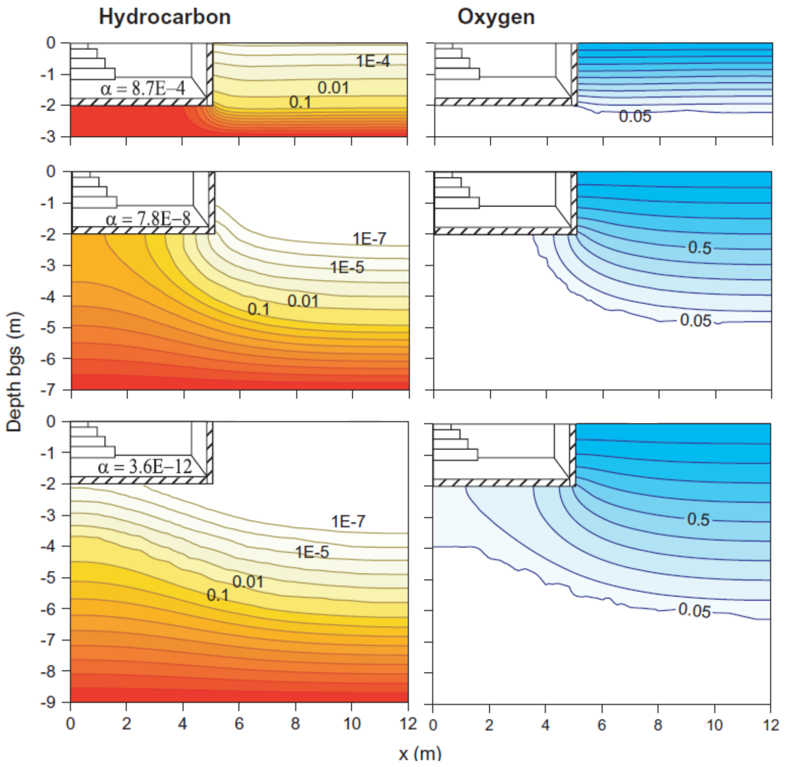


Figure 4. **Effect of source depth on soil gas distribution and vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model for a source total hydrocarbon (benzene) vapor concentration of 100 mg/L, biodegradation rate of 0.79 h^{-1}, and three source depths: 3 m (top), 7 m (middle), and 9 m (bottom) bgs. Hydrocarbon and oxygen concentrations are normalized by source and atmospheric concentrations, and the building is a residential house (from Abreu et al., 2009).**

Abreu et al. (2009) also present a chart that provides representative attenuation factors (α) that apply to all source hydrocarbon vapor concentrations below 10 mg/L and for a range of biodegradation rates and source depths beneath the foundation (**Figure 5**). The attenuation factors are much lower when the aerobic biodegradation process is included compared to the non-biodegradation case. For example, there is an approximate three order-of-magnitude reduction in the attenuation factor for a source-foundation separation distance of 5 ft (1.5 m) and first-order biodegradation rate of 0.79 h^{-1}.

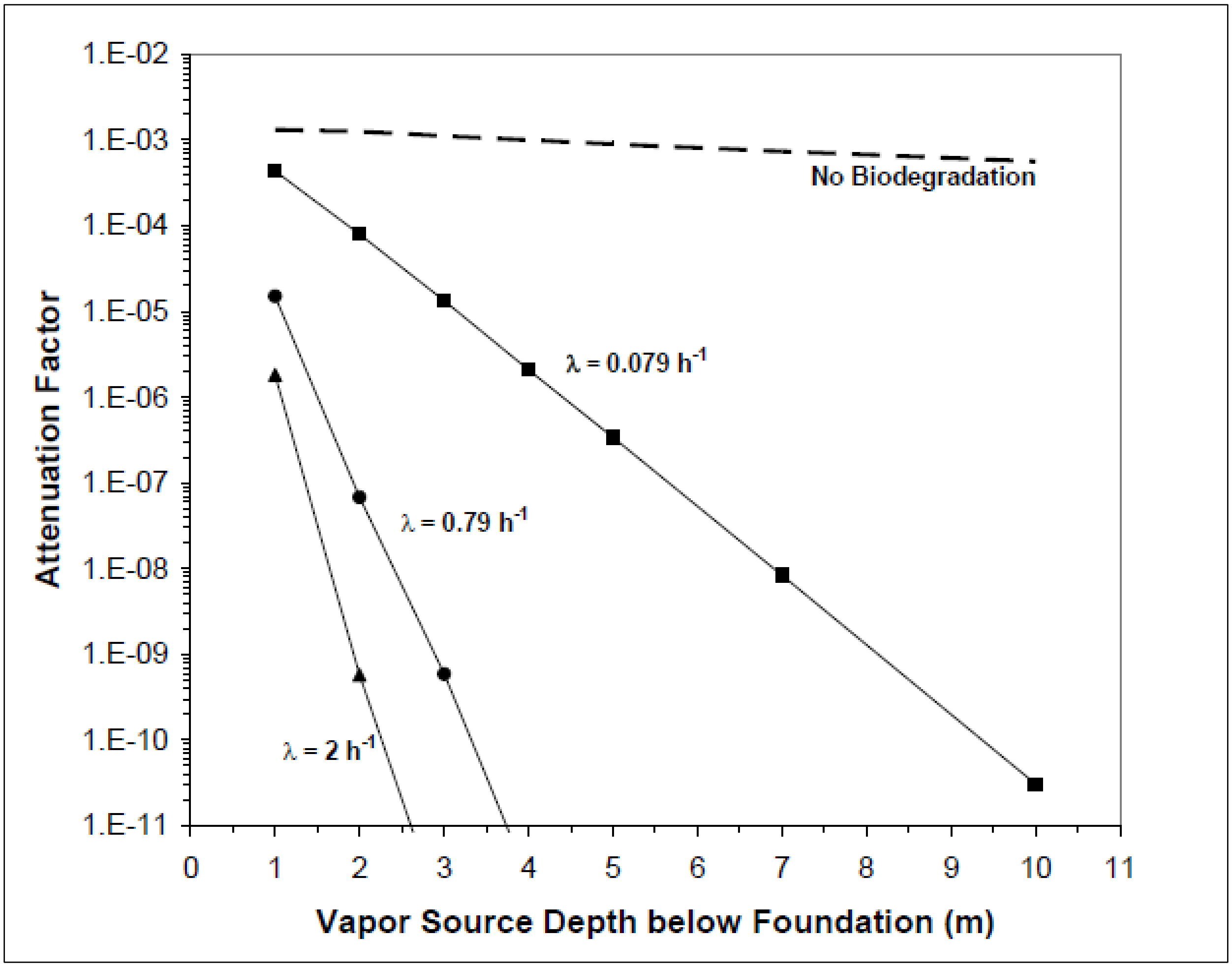


Figure 5. **Vapor intrusion attenuation factors predicted by Abreu and Johnson (2005) three-dimensional model as a function of separation distance below foundation and first-order biodegradation rate for a residential house scenario and 10 mg/L vapor source concentration (from Abreu et al., 2009).**

3.1.2 Three-Dimensional Model Simulations—Lateral Migration Scenario and Homogeneous Soil Conditions

U.S. EPA (2012c) presents a modeling study of conceptual model scenarios for the vapor intrusion pathway where the Abreu and Johnson (2005) model was used for a range of simulation scenarios, including oxygen-limited aerobic biodegradation of PHC compound vapors (using benzene as a surrogate for TPH). The building assumptions in U.S. EPA (2012c) are similar to those described in Abreu et al. (2009). One of the scenarios evaluated was the influence of PHC source and building lateral separation distance on the predicted vapor attenuation factor (**Figure 6**). The simulations were conducted for a TPH vapor concentration of 200 mg/L, a 2-m (6.6 ft) deep basement, two contamination source depths (3 m and 8 m [9.8 ft and 26 ft] bgs), and a range of first-order biodegradation rates (0.018, 0.18, and 1.8 h^{-1}). The different biodegradation rates compared to the earlier Abreu study reflect the progression in studies of rates over time. The different rates do not materially change the findings described herein. The predicted vapor attenuation factors decrease rapidly as the lateral distance increases.

For example, the vapor attenuation factor for a shallow LNAPL source that is offset approximately 15 ft (4.6 m) from the edge of the building is 1 × 10^{-6} for a biodegradation rate of 0.018 h^{-1} and less than 1 × 10^{-10} for a biodegradation rate of 0.18 h^{-1}. The vapor attenuation factor for a shallow below-building LNAPL source and the same biodegradation rate is approximately 1 × 10^{-3}. A key point is that there is greater attenuation and hence, lower vapor attenuation factors, for lateral building–contamination source separation scenarios compared with vertical ones.

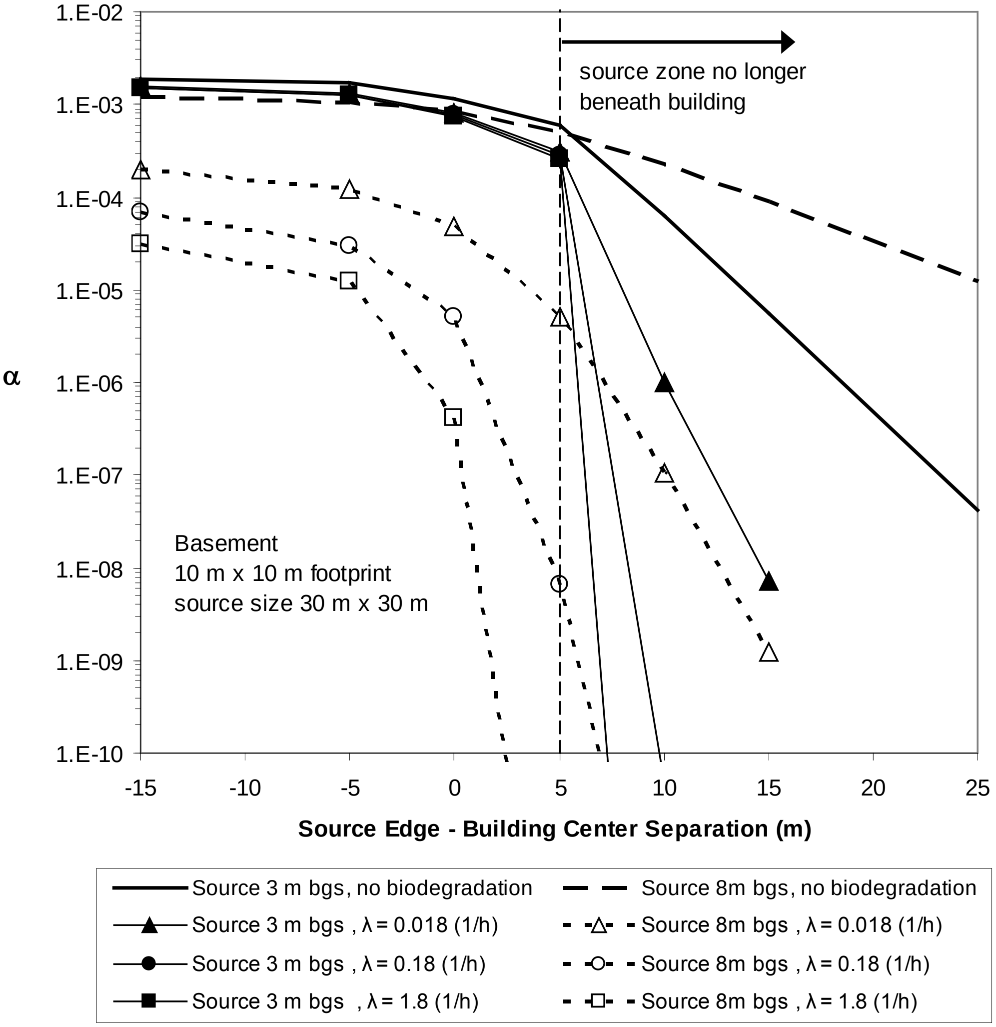


Figure 6. Relationship between source-building lateral separation distance and normalized indoor air concentration (α) for a NAPL source, two source depths, and three biodegradation rates (λ). The source-building lateral separation is measured from the edge of the source zone to the center of the building with a basement; negative values and values of less than 5 m indicate that the source is to some extent beneath the building. The source vapor concentration is 200 mg/L. (Source: Figure 33 in U.S. EPA [2012c])

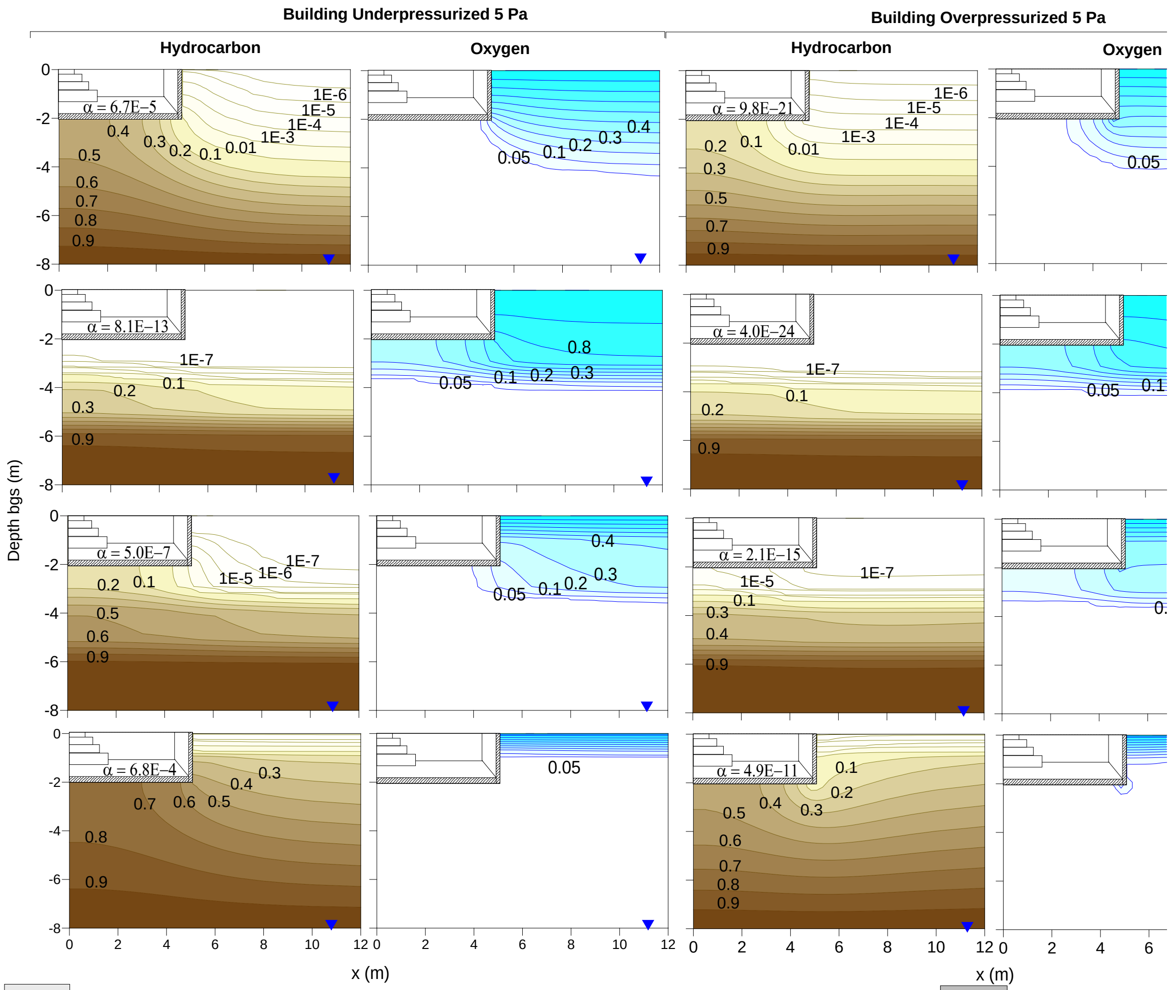
3.1.3 Three-Dimensional Model Simulations—Surface Capping Scenario

U.S. EPA (2012c) also provided aerobic biodegradation modeling simulations showing the influence of variable soil moisture and layered soil deposits on subsurface hydrocarbon concentrations and vapor intrusion. The simulations included various multilayer configurations involving up to three 1-m (3.3-ft)-thick soil layers with higher moisture content (60 percent saturation) and lower permeability within a general soil profile with a lower moisture content (20 percent saturation) and higher permeability (**Figures 7** and **8**). The hydrocarbon source for these simulations was located at 8 m (26 ft) below ground surface, beneath a house with a 2-m (6.6-ft)-deep basement and both positive (5 Pa) and negative (−5 Pa) building pressurizations.

For a relatively high source hydrocarbon vapor concentration (200 mg/L), low permeability (high moisture) layers beneath the building tend to limit the diffusion of hydrocarbon vapors from the source, while a low permeability layer at the surface (i.e., a surface cap) limits oxygen diffusion and biodegradation in the subsurface. The individual and combined effects of low permeability surface and subsurface layers on source-to-building attenuation factors can be seen in **Figure 7**, which shows the effects of four configurations of such layers (rows A-D) on an under pressurized (left panels) and over pressurized (right panels) residence. **Figure 8** shows that the attenuation factor predicted for a surface capping scenario with a 200 mg/L source was an order of magnitude greater than the homogeneous (one-layer) soil scenario (**Table 2**).

For the lower source vapor concentration (2 mg/L) shown in **Figure 8** and **Table 2**, the vapor attenuation factor for the two-layer scenario was 7.1×10^{-15}. Although a single-layer simulation was not performed for the lower source strength, this two-layer scenario attenuation factor is very low and indicates essentially complete biodegradation, with the cap having little or no effect on oxygen levels or hydrocarbon vapor bioattenuation below the building.

It is acknowledged that available modeling addresses a limited number of capping scenarios, and additional work in this area would be valuable. The capping scenario inputs are considered reasonably representative. For clay soils, saturations could be greater than 60 percent over short time periods (i.e., weeks), but the fine-grained layer modeled is relatively thick (1 m).



▭ High permeability: percent saturation (S) = 20%; soil gas permeability (Kg) = 1E-11 m^2 ▩ Low permeability: S = 60%, Kg = 1E-13 m^2.

Figure 7. **Effects of various layered soil scenarios (rows A–D) on hydrocarbon and oxygen distribution in soil gas and normalized indoor air concentration (α) for an under pressurized basement (-5 Pa, left panels) and an overpressure basement (+5 Pa, right panels). Hydrocarbon and oxygen concentration contour lines are normalized by source and atmospheric concentrations, respectively. The source vapor concentration is 200 mg/L located 8 m bgs. Biodegradation rate (λ) = 0.18 h^{-1}. (Source: Figure 37 in U.S. EPA [2012c])**

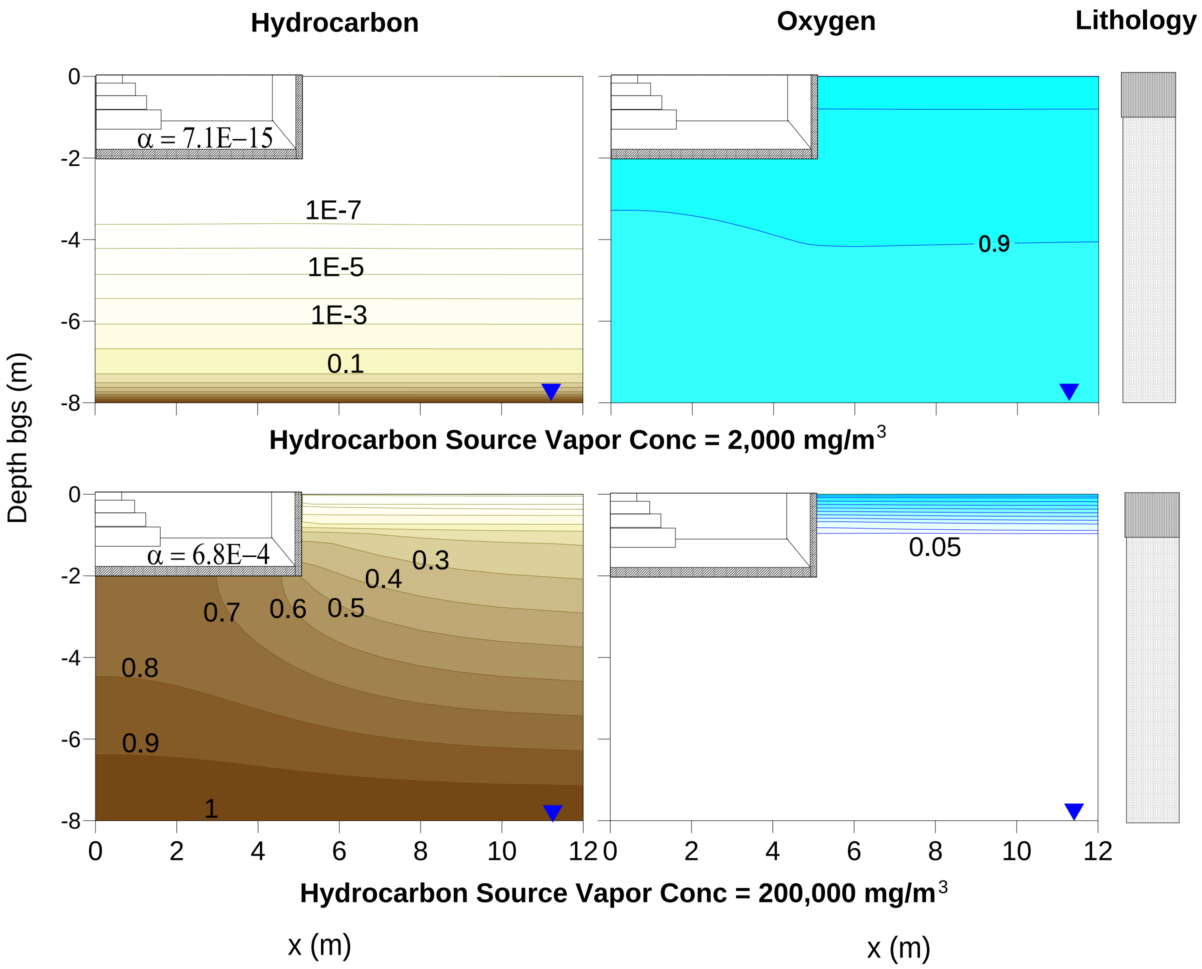


Figure 8. Effect of source vapor concentration on hydrocarbon and oxygen distribution in soil gas and normalized indoor air concentration (α) for scenarios with low permeability soils at the ground surface (e.g., soil layer scenario on row D of Figure 7). Hydrocarbon and oxygen concentration contour lines are normalized by source and atmospheric concentrations, respectively. Source located at 8 m bgs (basement scenario). Biodegradation rate (λ) = 0.18 h^{-1}. (Source: Figure 38 in U.S. EPA [2012c])

Table 2. Select Three-Dimensional Abreu and Johnson (2005) Model Simulation Results from U.S. EPA (2012c)

Source Hydrocarbon Vapor Concentration (mg/L)	Building pressurization (Pa)	Vapor Intrusion Attenuation Factor			
		Single Soil Layer (no surface cap)	Two Soil Layers (surface cap)	Five Soil Layers (no surface cap)	Six Soil Layers (surface cap)
200	5	9.8 × 10^{-21}	4.9 × 10^{-11}	4.0 × 10^{-24}	2.1 × 10^{-15}
200	−5	6.7 × 10^{-5}	6.8 × 10^{-4}	8.1 × 10^{-13}	5.0 × 10^{-7}
2	−5	N/A	7.1 × 10^{-15}	N/A	N/A

Notes: Residential house with 2-m (6.6-ft)-deep basement, depth to hydrocarbon vapor source = 8 m (25.3 ft), first-order biodegradation constant equal to 0.18 h^{-1}. Lower attenuation factors indicate higher attenuation. N/A = not available

3.1.4 Comparison of Modeled to Measured Soil Vapor Concentration Data

The three-dimensional model predictions of vertical profiles of hydrocarbon vapor and oxygen concentrations showed good agreement between measured and modeled data for three sites evaluated by Abreu and Johnson (2006). The estimated first-order biodegradation rate for these studies ranged between 0.18 and 0.4 h^{-1}. The three-dimensional model was also applied to compare measured and modeled hydrocarbon vapor concentrations for the former refinery site (confidential location), described in Section 2 of this report (Luo et al., 2010). A good comparison was obtained when the model incorporated site-specific conditions (a surface soil layer of low diffusivity and low soil-air permeability), but when generic (homogeneous) soil conditions were assumed, the model was not conservative and underpredicted the measured concentrations by a factor of approximately 100. The first-order rate incorporated in the Luo et al. (2010) model simulations was 0.18 h^{-1}.

3.2 DeVaull (2007b) Study (BioVapor Model Development)

DeVaull (2007b) presents the theory and one-dimensional model simulation results for a subsurface soil vapor-to-indoor air chemical PVI model that includes oxygen-limited biodegradation. (The model described is the basis for the BioVapor model [American Petroleum Institute (API), 2012].) The processes simulated by the algebraic model are one-dimensional upward diffusion and aerobic biodegradation of chemicals in a homogeneous subsurface soil layer and mixing of vapors within a building enclosure. The soil is divided into a shallow aerobic layer where first-order decay is assumed to occur and a deeper anaerobic layer in which biodegradation does not occur because of oxygen limitations. The boundary between the aerobic and anaerobic zones is determined iteratively to match oxygen demand to supply.

The model results indicate that vapor intrusion of PHCs can be orders of magnitude less than indicated by estimates that neglect biodegradation. A model sensitivity analysis using specified ranges of scenario parameters showed a high degree of sensitivity to oxygen availability, soil properties, and biodegradation rates. The attenuation factor varied by more than nine orders of magnitude about a specified attenuation factor of 1×10^{-8}; however, the corresponding variation in contamination source-to-foundation separation distance was within only a factor of approximately three (the attenuation factors for the non-biodegradation scenario ranged from approximately $1 \text{ x } 10^{-3}$ to $1 \text{ x } 10^{-5}$). DeVaull (2007b) concludes that identifying a distance where PVI is unlikely to occur is a more robust screening tool than an attenuation factor for PHC compounds.

Favorable comparison of the one-dimensional model to the three-dimensional results of Abreu and Johnson (2005) is shown in DeVaull (2007b). With matched model parameters, the models show similar estimates of indoor air–to–subsurface source vapor concentrations and similar sensitivities of both attenuation factor and exclusion distance to changes in model parameters.

3.3 DeVaull (2010) Study of BioVapor Application

DeVaull (2010) presents BioVapor model simulations in which the sensitivity of the model predictions was evaluated for a scenario characterized by a building with a basement separated by a distance of 5 ft (1.5 m) from a dissolved hydrocarbon vapor source (**Figure 9**). The model simulations were designed, in part, to provide insight on the applicability of the dissolved-source exclusion distance of 5 ft (1.5 m) proposed by Davis et al. (2009). The source groundwater concentrations were 1 mg/L benzene and 3 mg/L for each of toluene, ethylbenzene, and xylenes, for a total benzene, toluene, ethylbenzene, and xylenes (BTEX) source concentration of 10 mg/L. The source vapor concentrations were estimated from the Henry's Law constant and a groundwater to deep soil vapor attenuation factor of 0.1, resulting in source benzene and BTEX vapor concentrations of 12 mg/m^3 and 120 mg/m^3, respectively.

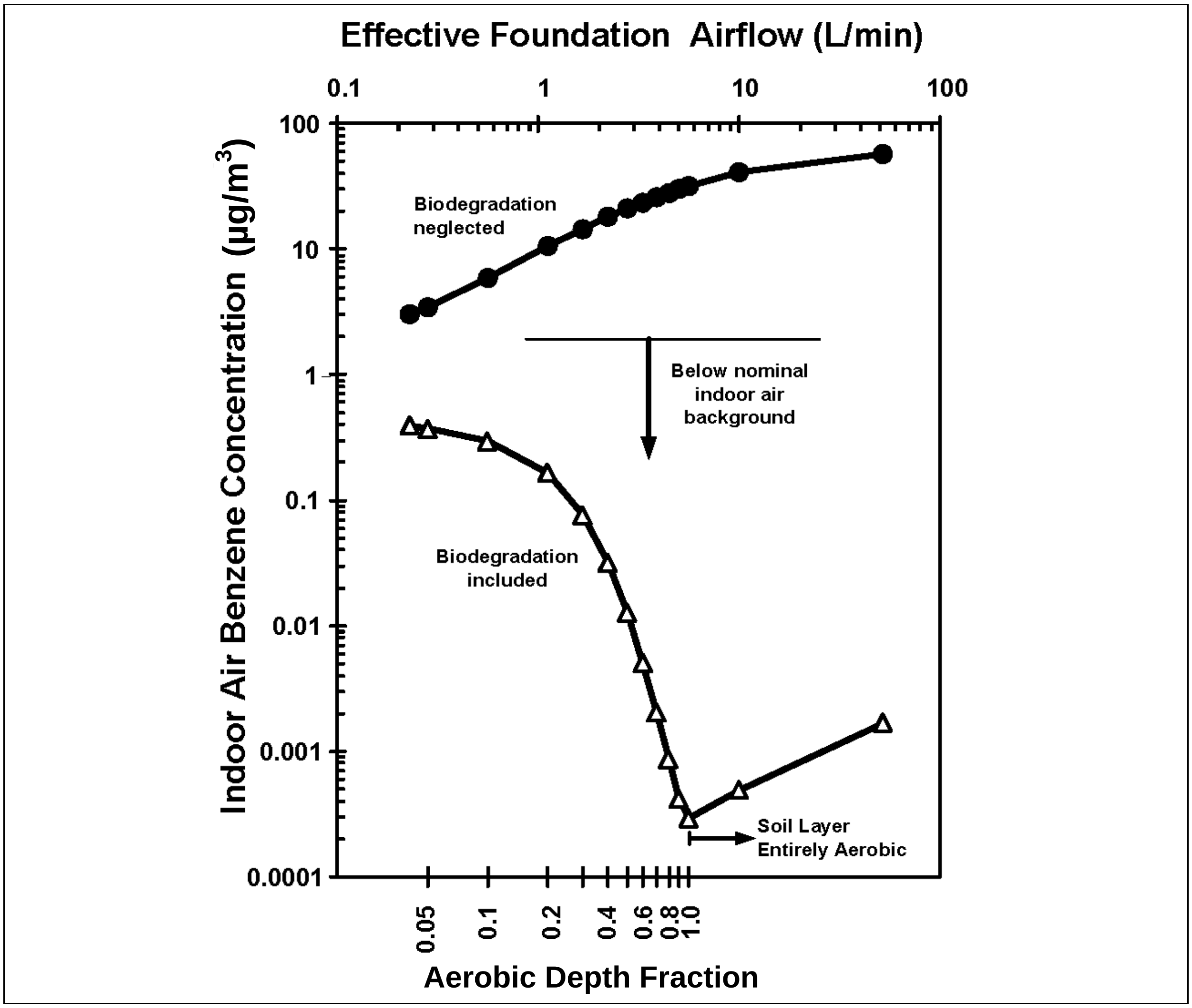


Figure 9. **Estimates of indoor air benzene concentrations using Biovapor model for varied effective airflow through the basement foundation. Foundation effective airflow statistics: 5th percentile = 0.3 L/min, 50th percentile = 3 L/min, 95th percentile = 30 L/min. Key model parameters: Vapor mixing height = 2.44 m; indoor air exchange rate = 0.25 h^{-1}; building footprint area = 100 m^2 (1,076 ft^2) (from DeVaull, 2010).**

A key input parameter for the BioVapor model simulations was the oxygen mass transfer from the atmosphere through the soil beneath the building (DeVaull, 2010). A range of oxygen mass transfer rates were estimated from 13 studies where the soil gas advection rate and/or diffusive oxygen mass transfer rate were measured for small buildings. For the purposes of **Figure 9**, the oxygen mass transfer rate was converted to an effective foundation airflow rate by considering the density and oxygen content of air. The effective foundation airflow rate is conceptually easier to understand than the oxygen mass transfer rate because of the common usage of the soil gas advection rate (Q_{soil}) parameter in modeling studies. The model predicts low indoor air benzene concentrations (less than 1 µg/m^3) for the range of effective foundation airflow rates considered. It is also instructive to note that the model results for recalcitrant non-degrading chemicals show an opposite trend: the indoor air VOC concentration increases as the effective foundation airflow rate increases.

3.4 Summary of Modeling Studies

Modeling study results, particularly for LNAPL sources, cannot be easily and precisely correlated to distances (or inclusion distances) beyond which PVI is unlikely to occur. This is, in part, because of the sensitivity of the model predictions to key site-specific variables such as source vapor concentration, separation distance, biodegradation rates, and oxygen diffusion through building foundations.

For LNAPL vapor sources, the Abreu et al. (2009) three-dimensional model simulations for a residential house scenario and homogeneous soil conditions predict that a vertical separation distance of 23 ft (7.0 m) or more is required for aerobic reaction front development within the unsaturated zone. The modeling results for smaller separation distances and an LNAPL source indicate the attenuation factor calculated by the model is sensitive to a surface capping effect.

For dissolved vapor sources, the model simulations indicate very low attenuation factors and negligible potential for a complete PVI pathway, including a modeling scenario where a surface capping effect was simulated. The model simulations strongly support the inclusion distances for dissolved sites subsequently described in this report.

The modeling results indicate further evaluation of factors potentially influencing oxygen supply and demand is warranted for the LNAPL source scenario. These factors include source vapor concentration strength, building size, surface foundation and soil layer properties, and natural soil oxygen demand.

4. Review of Empirical Database Studies of Petroleum Hydrocarbon Vapor Attenuation

Three published studies that analyze empirical data on PHC vapor attenuation are summarized below.

Davis (2009) obtained soil gas data from 53 geographical locations in the United States and Canada and from an analysis of 259 benzene and 210 TPH samples. For dissolved-phase sources, the analysis indicates 5 ft (1.5 m) is sufficient to significantly attenuate benzene and TPH vapors. Dissolved-phase sites were defined as sites where benzene concentrations in groundwater were less than 1,000 µg/L. Analysis of a dataset that includes LNAPL sources of all types (e.g., USTs, refineries, fuel terminals), indicates that a separation distance of 30 ft (9.1 m) is required for benzene vapor attenuation. The data obtained by Davis (2009) are incorporated into the database and further analysis of these data is described in this report.

Peargin and Kolhatkar (2011) evaluated 218 pairs of benzene soil vapor and groundwater concentration data from 25 sites. A rigorous quality assurance/quality control (QA/QC) program was followed for data collection, including installation of properly sealed permanent probes and leak tracer tests. Data were categorized in bins based on 10^{-2} to 10^{-6} excess cancer risk and assuming a soil vapor–to–indoor air attenuation factor of 0.01 (U.S. EPA, 2002). No benzene soil vapor concentrations exceeding 300 µg/m^3 (air concentration for 10^{-5} cancer risk multiplied by 0.01) were observed at vertical separation distances greater than 15 ft (4.6 m). Benzene soil vapor concentrations exceeding 300 µg/m^3 were only observed above groundwater sources where benzene concentrations exceeded 1,000 µg/L. The authors concluded that the data support a CSM where benzene vapor transport at concentrations exceeding target screening values can only occur where groundwater source benzene concentrations are high, defined for the current study as greater than 1,000 µg/L. Some of the data analyzed by Peargin and Kolhatkar (2011) that were provided to Davis (2009) are incorporated in the current EPA PVI database. The remaining Peargin and Kolhatkar (2011) data were not readily accessible during the data analysis performed for this report.

Wright (2011) presents data from 124 sites in Australia. There are 1,080 pairs of benzene soil vapor and groundwater concentration data; 41 percent of the data were obtained at sites with fractured rock aquifer systems and 12 percent represent data obtained below building foundations (i.e., sub-slab). After removing the data from fractured rock sites and from sites or sets of probes that did not have clean soil between the source and the soil gas sampling port, the analysis resulted in vertical exclusion distances of 5 to 10 ft (1.5 to 3.0 m) for relatively low-strength dissolved-phase sources (benzene < 1 mg/L and TPH < 10 mg/L) and ~30 ft (~10 m) for LNAPL and poorly characterized dissolved-phase sources (including sites with large building slabs). The lower threshold benzene and TPH soil vapor concentration for estimating the exclusion distances was based on 5 percent of the lowest Australian health screening levels (Friebel and Nadebaum, 2011).[6]

The Australian data analyzed by Wright (2011) were incorporated into the EPA PVI database but in this report were analyzed separately from the North American sites; Lahvis et al. (In prep.) has analyzed the two datasets together. The analysis of the Australian database presented in Appendix C suggests that the conclusions of the empirical analysis would not change if the Australian data were included, although site conditions differ between the United States and Australia.

5. EPA PVI Database Development, Structure, and Content

The database compiled by Davis (2009, 2011a) was the starting point for the EPA PVI database. The Davis database contained data on PHC vapor behavior from over 50 sites and included information on groundwater and soil vapor chemistry, soil properties, and other site data. The May 2011 version of the Davis database was imported and used in this analysis.

---

[6] The soil vapor concentrations corresponding to 5 percent of the Australian Health screening levels are as follows: benzene = 50 µg/m^3, toluene = 65,000 µg/m^3, ethylbenzene = 16,500 µg/m^3, xylenes = 11,000 µg/m^3, and TPH(6–16) = 15,500 µg/m^3.

5.1 EPA PVI Database Development and Checking

The Davis database was imported into Microsoft Access and then exported into a working Microsoft Excel spreadsheet to enable data checking, addition, and analysis. The original Davis database was expanded by adding new data fields to describe the data types needed to meet the objectives of this report. The data in the spreadsheet were checked against the original data when reports, journal articles, and other references were available, and all available references are included as electronic files linked to the EPA PVI database. As additional sets of data were imported into the database, each was examined and corrected for internal consistency.

Once the checks and additions were complete, the Excel spreadsheets were re-imported into the Access database and checked for consistency and accuracy of import using queries and manual checks. The EPA PVI database is available in Microsoft Access format as a companion to this report, along with Microsoft Excel spreadsheet outputs of the basic data used in the data analysis. Abridged summaries of these data are provided in **Appendix B**.

5.1.1 Quality Control and Data Quality Ranking

For the two-part data verification process, data were screened to establish minimal acceptable data quality for inclusion in the database and use in the analysis, and data quality indicators were developed to ensure the included data are of known, acceptable, and documented quality. Data that were determined to be of unacceptable quality were either not added to the final dataset or flagged to facilitate their separation during data analysis. This effort focused on identifying data of questionable quality for use in the subsequent analysis. Data that were considered questionable included:

- Analytical data obtained by unacceptable methods, or data with no reported methodology or evidence of QA/QC processes;
- Soil gas data from fractured rock systems (because of the potential for preferential soil gas flow);
- Data where the benzene concentrations in groundwater were below the detection level (i.e., no contamination source exists); and
- Data where lateral spacing between a groundwater monitoring well and a soil gas probe (for paired data) was greater than about 30 ft (9 m). (Note that this information was not available for all data).

Hydrocarbon analytical methods considered acceptable for individual air-phase compounds included EPA Method TO-15, EPA Method TO-3, and Modified EPA 8260; for TPH, the Massachusetts Air Phase Hydrocarbons method or the equivalent was preferred. For fixed gases (oxygen, carbon dioxide, methane), the following analytical methods were considered acceptable: ASTM D1946 and EPA Method 3C. Note that data quality checks were not repeated for all the data imported from the Davis database because they had been previously checked (e.g., Davis 2009), but some spot checks were made as the EPA PVI database was assembled.

For the Australian data, analytical methods were generally consistent and equivalent for benzene, but the methods used for TPH and fixed gases (field or laboratory) were not specified or available in time for inclusion in this report. As a result, the Australian fixed gas and TPH data were not evaluated or used in the conclusions of this report (but they are included in the EPA PVI database). Also, the Australian data for fractured settings were included in the database but were flagged and not used in the analysis. The U.S. and Canadian data do not include fractured rock settings.

As part of initial data screening, consideration was given to whether to screen out data for which there were no probe leak tracer test results. Given that a significant proportion of the data were from older studies where leak tracer tests were either not conducted or not reported, the decision was made not to adopt this criterion for data screening. However, it is noted that much of the recent data include leak tracer tests or tests for consistent fixed gas data.

For the second part of the data verification process, each site's data quality was considered to decide whether to use the data in the analysis. Sites were ranked according to several criteria:

- Availability of information to evaluate key data quality indicators such as leak checks, probe purging, analytical method, or sampling probe installation;
- Adequacy of CSM development for locating and sampling soil gas probes;
- Use of appropriate soil gas sampling protocols (i.e., leak checks, purging, permanent probes);
- Appropriateness of analytical methods;
- Consistency of fixed gas and volatile organic compound (VOC) soil gas results;
- Publication in a journal, EPA report, or other peer-reviewed source, and
- Oversight by a federal, state, or local UST regulatory program.

Each site was scored considering these factors on CSM robustness using a three-point ranking (3 highest, 1 lowest) and data quality using a five-point ranking (5 highest, 1 lowest). CSM robustness rankings were defined as follows:

- **CSM-3**: Well-developed CSM, appropriately located soil gas probes, vertical soil gas profiles, well-characterized contamination source (LNAPL and dissolved), and available ancillary data (e.g., soil properties);
- **CSM-2**: Less well-developed CSM with well-located probes but more limited soil gas locations (e.g., single location) and a reasonably well-characterized contamination source; and
- **CSM-1**: Limited data to develop CSM and evaluate appropriateness of soil gas probe locations and results, generally a single soil gas location, limited or no CSM-related information, and/or inadequate data to perform clean soil thickness analyses.

Data quality (DQ) rankings were defined as follows:

- **DQ-5**: Very high-quality data with fully documented QA/QC, permanent probes, leak tracer and/or pneumatic testing, and fixed gas data consistent with hydrocarbon vapor concentrations. In some cases, a site's data were given a DQ-5 ranking when not all of these aspects were met but there was a well-developed CSM and the research was peer reviewed;

- **DQ-4**: High-quality data, with mostly documented QA/QC, generally permanent probes and leak tracer testing, and fixed gas data that were consistent with hydrocarbon vapor concentrations;
- **DQ-3**: Moderate-quality data, with some QA/QC documentation and fixed gas data that may be limited in quantity or inconsistent with hydrocarbon vapor concentration data;
- **DQ-2**: Low-to-moderate quality data, with limited QA/QC documentation (but typically still collected under state program oversight), limited data documentation, and no fixed gas results (minimum data quality for inclusion in database analysis); and
- **DQ-1**: Low-quality data, unacceptable data-quality indicators or methods (data excluded from all analyses).

Table B-1 in **Appendix B** shows these data quality measures for the U.S. and Canadian sites in the database. A detailed table can also be found in the PVI database that accompanies this report. Note that the Australian data were developed using a similar but not identical CSM and data-quality scoring system; these scores are included in the Australian data analyzed in **Appendix C** and included in the EPA PVI database.

5.2 EPA PVI Database Structure

The tables and fields in the EPA PVI database and a comprehensive data dictionary and entity-relations diagrams are provided in **Appendices D** and **E**, respectively. An Excel spreadsheet was designed to facilitate evaluation, analysis, and presentation of data relations in the EPA PVI database and used to perform the analyses described in this report. Filters were added for most data fields, enabling screening of data based on site conditions and other applicable attributes.

The different data types are summarized as follows:

- **Background data:** Site location, geologic setting, contamination type, and generic soil description;
- **Facility type:** UST, fuel terminal, petroleum refinery, and petrochemical plant;
- **Site conditions:** Soil type, water-filled and total porosity, and surface cover at soil vapor probe (bare ground, asphaltic pavement, building);
- **Sampling data:** For each probe, vertical depth from ground surface to water table, to top of contamination, and to media sampling locations. Lateral distance between soil gas probe and groundwater monitoring well and between soil gas probe and UST facility infrastructure (e.g., tanks, fuel dispensers) and buildings;
- **Analytical data:** Sampling date, analytical method, quality control data, and chemistry data for soil, groundwater, and soil vapor. Analyte fields in the database are fixed gases (oxygen, carbon dioxide, methane); benzene, toluene, and xylene; TPH;

naphthalene; MtBE; 1,3-butadiene; hexane; heptane; 2,2,4-TMP, 1,2,4-trimethylbenzene (TMB); and aromatic and hydrocarbon fractions according to analytical methods prescribed by the State of Massachusetts. Not all analyte data are available for every site; and

- **Building data:** Building use (e.g., residential, commercial, institutional), foundation type, and building size.

As described in Section 5.1.1, the data verification process included data quality indicators that were developed and reviewed to ensure that data of known and acceptable quality were used in the analysis.

5.3 EPA PVI Database Content

The number of sites in the EPA PVI database and their locations are listed in **Table 3**. The contents of the database for key fields are summarized in **Tables B-2** and **B-3** in Appendix B. The majority of the sites were UST release sites, although the database also includes data from fuel terminals, petroleum refineries, and petrochemical sites. Most sites were affected by gasoline releases, although a small number had other types of PHC contamination (e.g., diesel, kerosene). The gasoline composition was unknown and assumed to be variable with respect to fuel oxygenate composition, given the relatively broad time span for data collection (1995 to 2011). Gasoline containing ethanol (10 percent vol/vol) was generally introduced into the United States in 2000, with a large increase in use in 2006 (U.S. EPA, 2009), so some sites in the EPA PVI database where recent releases occurred probably had gasoline containing ethanol. (From the available information, it is not possible to quantify the number of sites with ethanol.)

Table 3. Number of Sites by Country and States in the EPA PVI Database (November 2012)

Location	Sites	Location	Sites
United States			
California	7	Ohio	4
Maine	13	Oklahoma	1
Maryland	1	South Carolina	1
Minnesota	22	Utah	15
New Jersey	3	U.S. unknown	1
North Dakota	1		
Other Countries			
Canada	4	Australia	1
Total Sites = 74			

Sub-slab vapor samples were obtained at the 39 with buildings out of the 74 sites total in the database. Almost all buildings in the EPA PVI database were residential houses or smaller commercial buildings. (**Table B-2** in **Appendix B** includes the building footprint area when available.) Thus, the applicability of the database to large buildings may be limited. At a few sites, soil gas samples were obtained from below and beside a building.

The EPA PVI database is populated to varying degrees depending on the data type. (All statistics with respect to number of sites with data are provided in **Table B-3** in **Appendix B**). The database contains data for most sites and records on facility type, vertical distances, surface cover, soil type, and benzene and TPH vapor concentrations. Groundwater benzene and TPH data are also available for many sites, and the database includes fixed gas data for a majority of the sites. For other analytes (e.g., toluene, ethylbenzene, xylenes, naphthalene, MtBE), the EPA PVI database includes data for fewer sites, although the dataset for aromatic and aliphatic hydrocarbons is substantial due to recent data from 11 sites in Maine. Although indoor air data are included for a few sites, this information was not used in the analysis because of the limited number of indoor air data points and the known effect of background indoor (non-PVI) PHC sources in overestimating soil vapor–to–indoor air attenuation factors for PHCs.

The database includes:

- 893 benzene soil vapor records;
- 655 oxygen soil vapor records; and
- 829 records with paired benzene soil vapor and groundwater data.

Additional information on each site in the EPA PVI database is provided in **Tables B-2** and **B-3** in **Appendix B** and in the database. Many of the original sources of data in the database (e.g., reports, journal articles, figures, data tables) are referenced and linked to a full set of electronic document files organized by site.

Lead Scavengers. Ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA) are synthetic organic chemicals that were historically used as gasoline additives to prevent lead deposits that foul internal combustion engines. For this reason, they are commonly referred to as lead scavengers. The EPA PVI database does not contain any soil gas data for these chemicals, but **Appendix F** provides a comprehensive evaluation of their historical use, toxicity, transport, and fate.

6. EPA PVI Database Analysis Approach and Methods

The data analysis began with an evaluation of whether the soil gas data at the site were obtained in an area of LNAPL or dissolved-phase groundwater contamination. Given the importance of the contamination source type on soil vapor concentrations, the analyses were conducted separately for the LNAPL and dissolved sources. The data analysis consisted of three main parts:

- Exploratory data plots to identify data trends and relationships, discussed in Section 6.2.1;
- Estimation of vapor concentration attenuation distance using the vertical distance method, developed by Lahvis et al. (In-prep.) and discussed in Section 6.2.2; and
- Estimation of non-contaminated vertical soil thickness needed for concentration attenuation using the clean soil method, developed by Davis (2009) and discussed in Section 6.2.3.

6.1 Source Zone Identification (LNAPL versus Dissolved Indicators)

Several indicators were adopted for identifying whether the soil gas probe was located in an area of LNAPL or dissolved-phase contamination (**Table 4**).

The primary indicator was direct evidence of LNAPL, such as a sheen or measurable accumulations of product in a nearby monitoring well, borehole logs indicating a sheen or significant hydrocarbon staining in soil, or a site investigation report indicating the soil gas probe was installed in an LNAPL source zone. The direct indicators in Table 4 were the determining factors for approximately 80 percent of the sites identified as having LNAPL contamination.

Table 4. Potential LNAPL Hydrocarbon Indicators

Type	Indicator	Measures and Screening Values
Adopted for this analysis		
Direct	Current or historic presence of LNAPL in groundwater or soil	Laboratory and/or field observations, sheens, results of paint filter, dye, and shake tests
Indirect	Individual PHC compound and/or TPH concentrations approaching (>0.2 times) effective solubilities or effective soil saturation concentrations (C_{sat} concentration)	Groundwater – benzene > 5 mg/L – TPH > 30 mg/L (gasoline) Soil – benzene > 10 mg/kg – TPH > 250 mg/kg (gasoline)
Indirect	Proximity to source area likely to be impacted with LNAPL	Soil gas probes located near (within 20 ft [6.1 m]) or within former UST fields or fuel dispenser areas
Other potential indicators		
Indirect	Fluorescence response in LNAPL range	UV, LIF, or UVIF fluorescence above background levels (visual observation)
Indirect	Organic vapor analyzer (e.g., photoionization detector)	>500 ppmV
Indirect	PHC vapor, O_2 and CO_2 profiles	PHC vapor and CO_2 concentrations in soil gas that show no decrease (or O_2 concentrations that show no increase) or remain relatively constant with distance from contamination source
Indirect	Elevated aliphatic soil gas concentrations	For example, hexane soil gas concentrations more than approximately 100,000 μg/m^3 suggest LNAPL because dissolved plumes are primarily composed of soluble aromatic hydrocarbons (Lahvis et al., In prep.)

Note: For two sites, #6-046 and #102 Chevron, there were long dissolved plumes (several hundred feet long) with elevated benzene concentrations (up to 12 mg/L) in groundwater that exceeded the above criteria, but there was no evidence for LNAPL at locations where the elevated benzene concentrations were measured. For these sites, the above criteria were overridden (i.e., site was designated as a dissolved source).

Indirect or secondary indicators were:

- **Groundwater Concentration Data.** Benzene and/or TPH groundwater concentration from which the presence of LNAPL near the soil gas probe was inferred. This was the determining indicator for approximately 13 percent of the sites.

- **Soil Concentration Data.** Benzene and/or TPH soil concentration from which the presence of LNAPL near the soil gas probe was inferred. This was the determining indicator for approximately 1 percent of the sites (one site).
- **Proximity to Fuel Storage/Dispensing Facilities.** Determined by soil gas probes installed within 20 ft (6.1 m) of the tank field or dispenser. This was the determining indicator for approximately 5 percent of the sites.

For sites with limited data, the secondary indicators were important to enable appropriate classification with respect to LNAPL versus dissolved sources. However, a sensitivity analysis showed that the exclusion distances were not sensitive to the benzene and TPH groundwater concentration thresholds because direct indicators were the determining factor for 80 percent of the site data (see Section 7.2.1).

6.1.1 Groundwater Concentration Data

Concentrations of chemicals that approach their effective solubility are indirect evidence for LNAPL. For example, Bruce et al. (1991) suggest groundwater concentrations greater than the effective solubility multiplied by 0.2 as possible evidence for LNAPL. For gasoline, when a benzene mole fraction of 0.01 was assumed, the threshold was 3 mg/L, assuming a ratio of 0.2. Given the uncertainty in these estimates, a slightly higher threshold for the benzene groundwater concentration (5 mg/L) was adopted for identification of LNAPL sites. A TPH threshold groundwater concentration of 30 mg/L was adopted based on the calculated approximate average ratio of benzene to TPH groundwater concentrations in the database. An LNAPL source site was identified based on either the benzene or TPH groundwater concentration exceeding the threshold.

6.1.2 Soil Concentration Data

Concentrations of chemicals in soil that approach an estimated LNAPL saturation concentration are indirect evidence for LNAPL. The soil saturation concentration is highly dependent on chemical and soil properties. Concentrations representative of possible LNAPLs suggested in the literature include a gasoline range organics (GRO) concentration greater than the range of 100 to 200 mg/kg and a diesel range organics (DRO) concentration greater than 10 to 50 mg/kg (e.g., ASTM, 2006; Alaska Department of Environmental Conservation, 2011).

The thresholds adopted for identifying LNAPL sites are a benzene soil concentration of 10 mg/kg and a TPH (gasoline) soil concentration of 250 mg/kg. The benzene concentration (10.7 mg/kg rounded down to 10 mg/kg) was estimated from the equation for soil saturation (C_{sat}) and the default input parameters in Exhibit 9 of the EPA Soil Screening Guidance (U.S. EPA, 1996). A TPH soil concentration of 250 mg/kg was adopted to provide a slightly more conservative screening basis (i.e., more sites are included as dissolved sites with higher thresholds) than the ranges reported in the literature cited above. An LNAPL source site was identified based on either the benzene or TPH soil concentration exceeding the threshold.

6.1.3 Proximity to Fuel Storage/Dispensing Facilities

Soil gas probes located near or within former UST tank nests or fuel dispenser areas are considered to have a high probability of being within LNAPL zones. Soil gas probes within 20 ft (6.1 m) lateral distance of the tank nests or dispensers were categorized as being located within a LNAPL source. Fifteen sites included data for soil gas probes that were within 20 ft of tank nests or dispensers, but as indicated above, this criterion was the determining LNAPL indicator for only 5 percent of the sites.

6.2 Data Analysis Methods

The data analysis consisted of an exploratory data analysis followed by the vertical distance and clean soil methods for evaluating vapor attenuation. The analysis using the vertical distance method focuses on benzene, given its importance for risk evaluations; however, the vertical distance method was also performed for select other compounds, including those analyzed at the Maine sites where full-spectrum hydrocarbon analyses (i.e., data on aliphatic and aromatic fractions) were available. Given that the EPA PVI database was set up to allow for filtering, the influence of site type (UST, fuel terminal, petroleum refinery, petrochemical), soil properties, and surface cover (i.e., building, pavement, or ground cover[7]) was evaluated.

6.2.1 Exploratory Data Analysis

The exploratory data analysis evaluated the trends between groundwater and soil vapor concentrations for different vapor constituents. Furthermore, the relationships between oxygen and hydrocarbon concentrations and benzene and methane concentrations were assessed with respect to what would be expected given the conceptual model for aerobic biodegradation (Davis et al., 2009; Sweeney, 2012).

6.2.2 Vertical Distance Method

The vertical distance method involved plotting soil vapor concentration versus distance above a source and estimating the probability for the soil vapor concentration to be less than a given concentration threshold for different distances above the contamination source. The conditional probabilities (P) were estimated as follows:

$$P\ (C_v \leq C_{threshold}/z > d, \text{Contamination}\ (z = 0) = \text{LNAPL or dissolved})$$

where C_v is the soil vapor concentration, $C_{threshold}$ is the soil vapor concentration threshold, z is the vertical direction, d is the vertical distance from the top of the contamination to the soil gas probe, and source contamination either is characterized as an LNAPL or a dissolved source.

First, the data were sorted in a cumulative distribution of specified vertical separation distances from the source (e.g., ≥ 0, ≥ 2, …, ≥ *n* ft). The conditional probabilities were calculated for two benzene vapor concentration thresholds (50 and 100 µg/m^3) using two statistical techniques:

---

[7] e.g., ground that is gravel-surfaced, grassy, or dirt-covered

- Probability $P = N [C_v < C_{threshold}]/N [total]$ where $N [C_v < C_{threshold}]$ is the number of benzene vapor concentrations less than the threshold and N [total] is the total number of concentration measurements. For this analysis, concentrations below the reporting limits were replaced with half the reporting limit, a common first approximation for non-detect measurements, i.e., below specified reporting limits; and
- Probability was estimated from the concentration distribution calculated by the non-parametric Kaplan-Meier method (Kaplan and Meier, 1958).

Approximately 31 percent and 57 percent of the paired data points for benzene vapor concentration and distance associated with LNAPL sources and dissolved-phase sources, respectively, were non-detects. The Kaplan-Meier method is a robust, non-parametric method for considering data below reporting limits, particularly when there are multiple reporting limits (Helsel, 2005; 2006). The Kaplan-Meier method, which has been shown in recent literature to be the preferred method in many cases for estimating statistical parameters (e.g., mean, median, standard deviation), does not rely on underlying assumptions about the data and can be used with multiple reporting limits (Helsel, 2005).

Next, the depth to contamination was estimated. This quantity is important for an accurate estimation of the thickness of clean soil needed for attenuation of soil vapor concentrations. For LNAPL sites, this depth was estimated from boring logs and indications of LNAPL zones (e.g., observations of product, high headspace organic vapor concentrations above 500 to 1,000 parts per million, and soil chemistry data); in the absence of data, the depth to contamination was assumed to be the seasonal high water table where multiple monitoring events were available (on average, there were about two events per site). For dissolved sites, the depth to contamination was the depth to the water table closest to the time the soil gas data were obtained.

6.2.3 Clean Soil Method

The clean soil method (Davis, 2009; 2010) consists of an analysis of the thickness of un-impacted clean soil (i.e., soil without NAPL) required for soil vapor benzene concentrations to attenuate to below a defined threshold, which for this analysis is $100\ \mu g/m^3$. This analysis enabled comparison to published exclusion distances previously reported by Davis (2009; 2010) that were based on this method. A clean soil thickness was calculated except when the vertical distance between soil gas probes was greater than 10 ft (3.0 m), because in those cases there was insufficient resolution (i.e., spacing between probes) for meaningful estimation. Two procedures were used to estimate the clean soil thickness:

- Procedure 1: Distance to first soil gas probe with benzene $C_{vapor} < 100\ \mu g/m^3$ where:
  - Lower depth = D_l = Depth to top of contamination;
  - Upper depth = D_u = Depth to first probe with benzene $C_{vapor} \leq 100\ \mu g/m^3$; and
  - Distance = $D_l - D_u$.
- Procedure 2: Interpolated distance between a soil gas probe with benzene $C_{vapor} > 100\ \mu g/m^3$ and a soil gas probe with $C_{vapor} < 100\ \mu g/m^3$ where:
  - Lower depth = D_l = Depth to top of contamination;

- Upper depth = D_u = Interpolated as halfway between the depths to a probe with benzene $C_{vapor} \leq 40$ µg/m^3 and $C_{vapor} > 100$ µg/m^3; however, if the lower concentration is greater than 40 µg/m^3, then D_u = depth to first probe with benzene $C_{vapor} \leq 100$ µg/m^3; and
- Distance = $D_l - D_u$, subject to minimum thickness of 0.5 ft (0.15 m) because a minimum distance is required for concentration attenuation to occur.

For both procedures 1 and 2, benzene concentrations below reporting limits were replaced in the EPA PVI database with a concentration equal to half the method reporting limit for the sample. (Replacement with half the detection limits is a common assumption.) An example of a clean soil thickness calculation is presented in **Figure 10**. For the soil gas profile data shown, the procedure 1 (left side of figure) distance is 15 ft (4.6 m) and the procedure 2 (right side of figure) distance is 12.5 ft (3.8 m).

A lower concentration threshold was considered warranted for procedure 2 because of the potential for the halfway distance interpolation to be non-conservative when the lower concentration is much greater than 100 µg/m^3 and the upper concentration is just less than 100 µg/m^3. The 40 µg/m^3 threshold is subjective, but when the upper benzene vapor concentration is less than this threshold, the halfway interpolation procedure is more accurate. Although more complicated and possibly more accurate interpolation rules could have been developed (such as log-linear plots), procedure 2 was intended as a simple, approximate technique. For any shallow concentration above 40 µg/m^3, the procedure provides for a conservative estimate of the attenuation distance because it uses the full distance to this vapor sample location.

For locations where the measured soil vapor benzene concentration does not attenuate to less than 100 µg/m^3, a clean soil thickness cannot be calculated, but a minimum clean soil thickness is reported as the distance between the shallowest soil gas probe and the top of contamination.

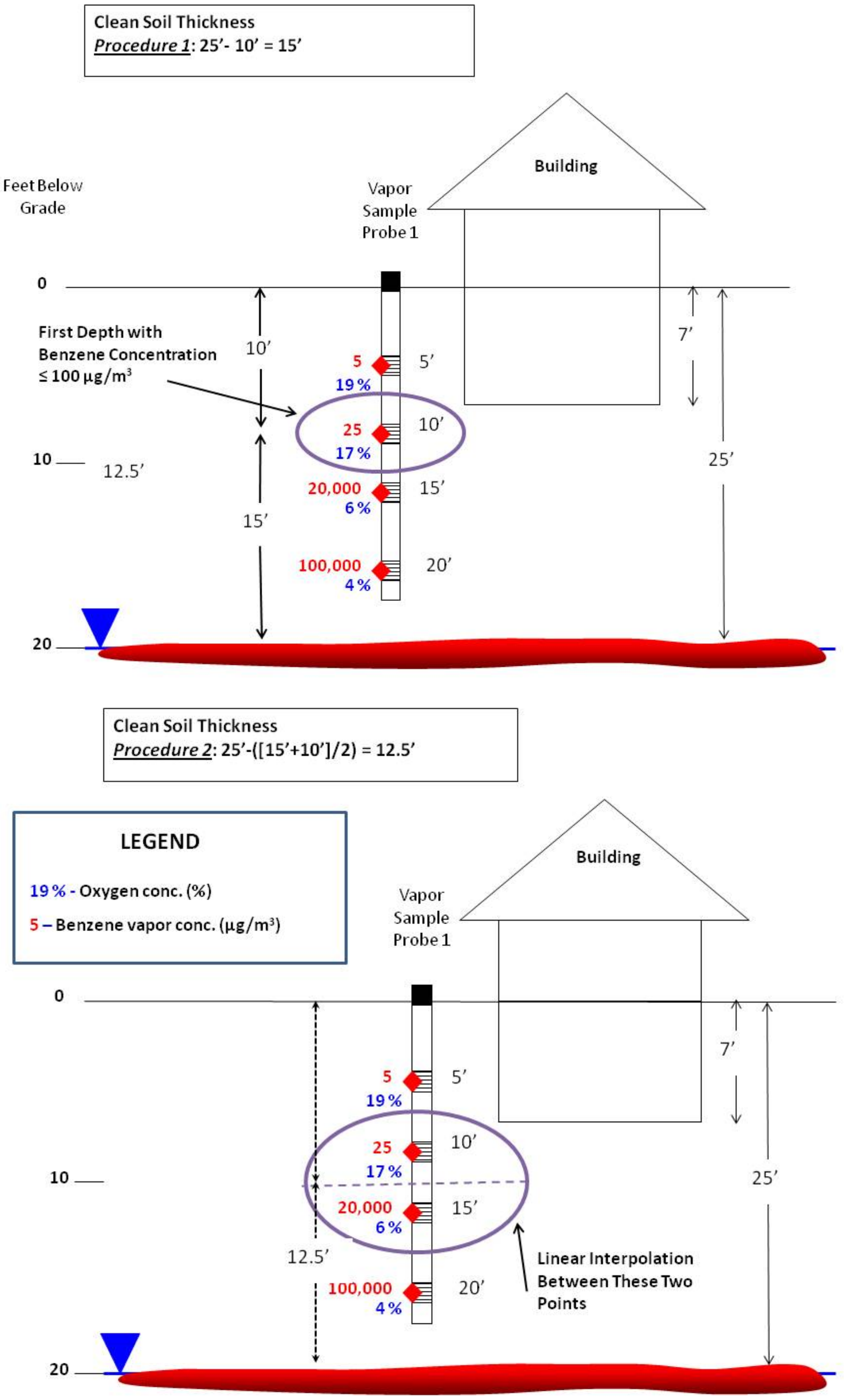


Figure 10. Example calculation of clean soil method distances.

6.3 Soil Vapor Concentration Thresholds

This section describes the development of risk-based soil vapor concentration thresholds for comparison with measured soil vapor concentrations to determine when PVI may be of potential concern. The soil vapor concentration threshold was based on the expected attenuation of vapor concentrations between shallow soil vapor and indoor air and the toxicity of the chemical under consideration.

6.3.1 Sub-slab to Indoor Air Attenuation Factors

The processes that affect the vapor concentration in indoor air for a shallow soil vapor source are primarily soil gas advection and ventilation that causes mixing of the chemical vapor within the enclosed space (Hers et al., 2003; Johnson, 2005). Some additional biodegradation and sorption could also occur between a shallow vapor source and an indoor environment. Several modeling studies provide insight on the attenuation factor[8] for a typical residential house. Yao et al. (2011) reported attenuation factors between 2×10^{-4} and 7×10^{-3} for a numerical modeling study. Johnson (2005) in a modeling study using the Johnson and Ettinger (1991) model calculated attenuation factors between 4.4×10^{-3} and 7.3×10^{-3} for a shallow soil vapor source and representative input parameters for a residential house. A similar study by Hers et al. (2003) included a sensitivity analysis where the maximum attenuation factor for a range of conditions was 9×10^{-3}, and a relatively good comparison (within an order of magnitude) was obtained between Johnson and Ettinger model predictions and measured attenuation factors for chlorinated solvent chemicals. Although this comparison is for chlorinated solvent chemicals, it is relevant here because it identifies typical attenuation factors between shallow or sub-slab vapor and indoor air, irrespective of possible biodegradation processes.

EPA has assembled a database of empirical slub-slab-to–indoor vapor attenuation factors (U.S. EPA, 2012b). Although most of the data in this EPA database is for chlorinated solvents, the sub-slab attenuation factors can be applied to PHCs because little bioattenuation is expected between sub-slab and indoor air. Sub-slab attenuation factors in this U.S. EPA (2012b) database vary over several orders of magnitude because of spatial and temporal variability in both indoor air and sub-slab vapor concentrations and background sources of chemicals in indoor air. In the U.S. EPA (2012b) database, the 50th and 95th percentiles of the sub-slab attenuation factor are 5.0×10^{-3} and 1.8×10^{-1}, respectively, when the data are limited to indoor air concentrations above a 90th percentile background concentration found in the literature. When the data are limited to sub-slab vapor concentrations greater than 100 times the literature background, the 50th and 95th percentiles of the sub-slab attenuation factor are 2.5×10^{-3} and 2.0×10^{-2} respectively (U.S. EPA, 2012b). Therefore, a shallow soil vapor–to–indoor air attenuation factor of 0.01 was considered a reasonably conservative attenuation factor.

6.3.2 Risk-based Concentration Thresholds

Risk-based indoor air concentrations for a residential scenario are provided in **Table 5** for the chemicals of potential concern considered in this analysis. The risk-based indoor air concentrations assume a residential scenario, continuous lifetime exposure to vapors, and no

---

[8] The attenuation factor is defined as the concentration of a chemical in indoor air divided by its concentration in soil gas under a foundation slab (sub-slab attenuation factor) or deeper in the soil beneath the house.

exposure amortization (e.g., calculation of average exposure rate from a less than continuous or lifetime exposure).

For chemicals other than benzene, a risk-based soil vapor concentration (RBC_v) was calculated as 100 times the risk-based air concentration. The thresholds adopted for benzene, 50 and 100 µg/m^3, were based primarily on practical considerations relating to the detection limit (i.e., the frequency of non-detects increases as the benzene concentration decreases) and for consistency with previous database evaluations by Davis (2009) and Lahvis et al. (In prep.). For comparison, assuming a generic sub-slab attenuation factor of 0.01, the calculated benzene threshold is 29 µg/m^3 for an incremental lifetime cancer risk (ILCR) of 1×10^{-6}, and 290 µg/m^3 for an ILCR of 1×10^{-5}. Given the uncertainty in the attenuation factor and benzene toxicity, the adopted threshold of 50 µg/m^3 is not considered substantively different from the 1×10^{-6} ILCR threshold of 29 µg/m^{3}shown in **Table 5**.

Table 5. Risk-based Indoor Air Concentration for Primary Chemicals of Potential Concern

Chemical	Toxicity Endpoint	Risk-Based Indoor Air Concentration (µg/m^3)$^{a, b}$	Source
Benzene	Carcinogenic	2.9 (1×10^{-5} ILCR); 0.29 (1×10^{-6} ILCR)	EPA IRIS
Toluene	Non-carcinogenic	5,000 (RfC)	EPA IRIS
Ethylbenzene	Non-carcinogenic	1,000 (RfC)	EPA IRIS
Xylenes	Non-carcinogenic	100 (RfC)	EPA IRIS
Naphthalene	Non-carcinogenic	3 (RfC)	EPA IRIS
n-Hexane	Non-carcinogenic	700 (RfC)	EPA IRIS
MADEP Aliphatic C5-8	Non-carcinogenic	200	MADEP (2003)
MADEP Aliphatic C9-18	Non-carcinogenic	200	MADEP (2003)
MADEP Aromatic C9-18	Non-carcinogenic	50	MADEP (2003)

[a] The risk-based indoor air concentration assumes a residential receptor and continuous exposure over a lifetime.

[b] The benzene risk-based air concentration is based on the midpoint of the toxicity factor range provided in the EPA IRIS (Integrated Risk Information System) database.

ILCR = Incremental lifetime cancer risk; RfC = reference concentration.

EPA IRIS database accessed February 2012.

MADEP = Massachusetts Department of Environmental Protection TPH method

7. EPA PVI Database Analysis Results

7.1 Exploratory Data Analysis

7.1.1 Comparison of Groundwater and Soil Vapor Concentrations

The cumulative distributions of benzene concentrations in groundwater are plotted in **Figure 11** for hydrocarbon sources classified as dissolved phase and LNAPL. The groundwater benzene concentrations for LNAPL sites are higher than for dissolved sites, but the difference in the distribution between LNAPL and dissolved sites is smaller than expected. This may be due to spatial variability in groundwater concentrations, highly weathered residual-phase LNAPL that is relatively depleted of benzene, variable well screen intervals relative to the water table, and vadose zone LNAPL sources.

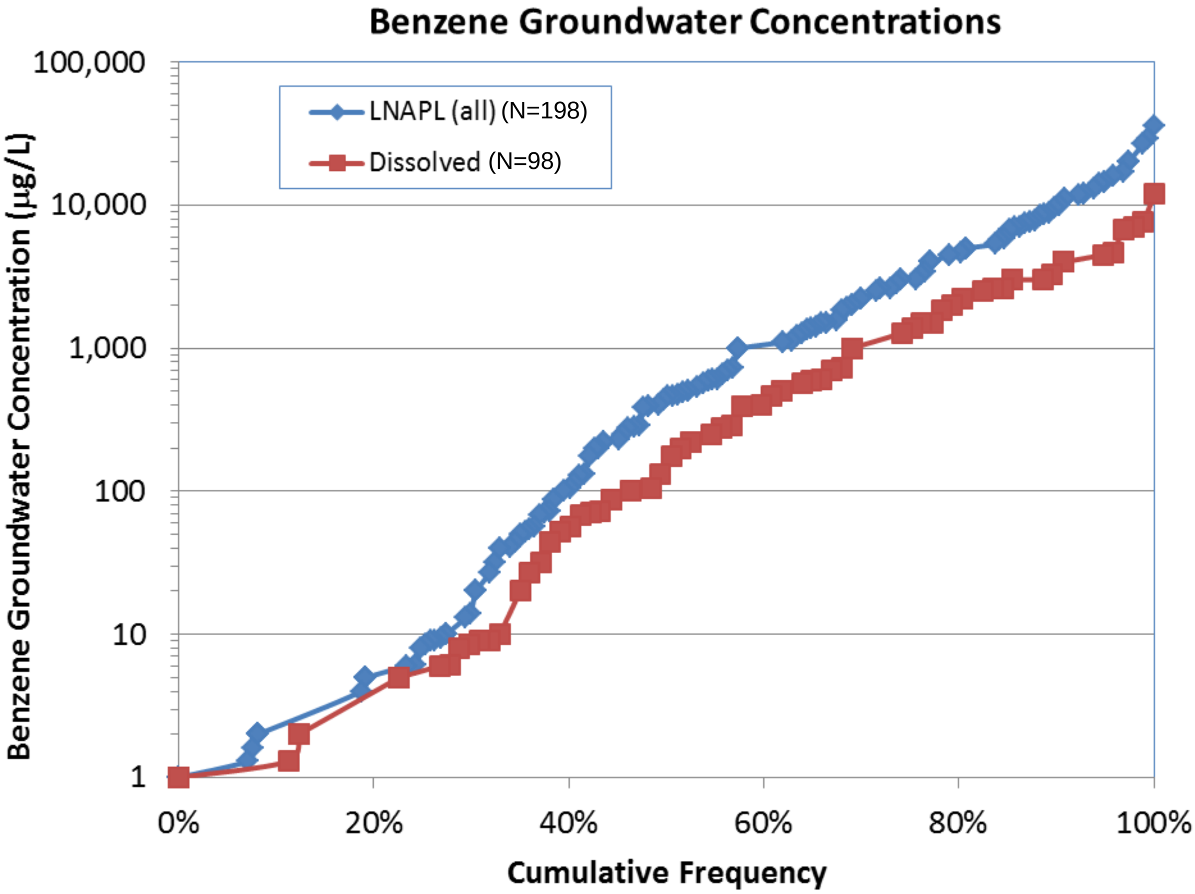


Figure 11. Groundwater concentrations measured near soil vapor sampling locations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites).

The relations between benzene concentrations in groundwater and deep soil vapor probes (within 3 ft [0.9 m] of the contamination source) for dissolved and LNAPL sources are shown in **Figure 12**. There is no apparent correlation for dissolved source data based on visual observation. The reason for the lack of correlation for dissolved source data and relatively consistent, low soil vapor concentrations is consistent with attenuation by biodegradation.

For dissolved-source data, the measured deep benzene vapor concentrations are, in almost all cases, at least an order of magnitude and, in many cases two orders of magnitude, less than the predicted soil vapor concentration based on Henry's Law partitioning and the measured groundwater concentration. This is reasonably attributed to biodegradation. A dimensionless Henry's Law constant of 0.14 was used for benzene, which is based on a groundwater temperature of 15°C, a representative value for the United States based on the groundwater temperature map in U.S. EPA (2004).

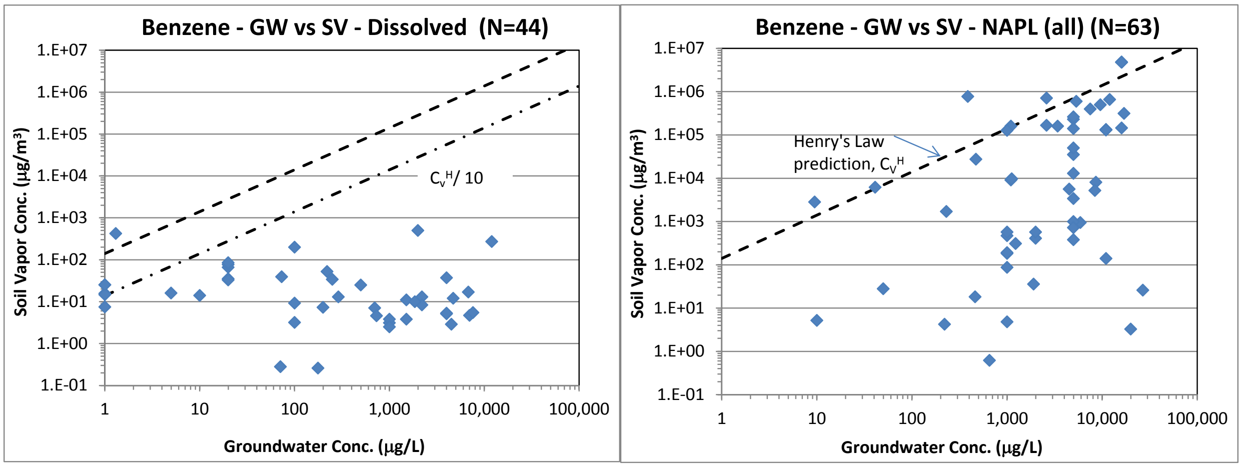


Figure 12. Groundwater concentrations measured near soil vapor sampling locations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites). Only detectable benzene vapor concentrations shown.

A very weak proportional relation based on visual observation (R^2 = 0.08) exists between groundwater and soil vapor concentrations for LNAPL source data. For the LNAPL source data, the measured benzene vapor concentrations are significantly less than predicted for benzene groundwater concentrations less than approximately 1 mg/L. For concentrations greater than 1 mg/L, the benzene vapor concentrations for some data points are close (within a factor of 2 or 3) to the vapor concentrations predicted by Henry's Law multiplied by the groundwater concentration, which is consistent with an LNAPL source and limited attenuation between the source and deep soil vapor sample.

The poor correlation between groundwater and soil vapor concentrations may be due to several factors including variable well screen intervals relative to the water table, variable biodegradation between the groundwater and lowermost soil gas sampling location, spatial variability and differences in dissolved-phase concentrations at groundwater and soil gas sampling locations, and sampling errors.

7.1.2 TPH Vapor versus Oxygen Concentrations

The relation between co-located oxygen and TPH vapor concentrations was evaluated to provide insight on biodegradation processes and a possible lower oxygen limit for occurrence of aerobic biodegradation (Davis et al., 2009; Sweeney, 2012). The expectation is lower oxygen concentrations when there are higher hydrocarbon vapor concentrations and higher oxygen (near atmospheric) concentrations at lower hydrocarbon vapor concentrations (**Figure 1**). An exception to this trend is where there is high natural oxygen demand (e.g., peat sites). As such sites, low concentrations for both PHC vapors and oxygen would be expected. (There are few such sites in the database.) Although a more robust paradigm for interpretation of oxygen and hydrocarbon data would be based on mass fluxes, this requires evaluation of site-specific vertical concentration profiles and soil property data which are more detailed than the data available for many sites in the EPA PVI database.

A plot of co-located oxygen versus TPH vapor concentration data is a useful approximate indicator of trends, and the results shown on **Figure 13** are generally consistent with expected behavior. For dissolved sources, there are no data indicating oxygen depletion, which is consistent with expected low oxygen demand associated with the vapor flux from dissolved sources. The data in the EPA PVI database are consistent in this regard; there are no data indicating depleted oxygen in association with dissolved sources. For LNAPL sources, relatively low oxygen concentrations (defined here as less than 4 percent) occur when TPH vapor concentrations exceed approximately 1 x 10^6 µg/m^3 (1 mg/L), but both oxygen and TPH vapor concentrations are elevated for a few data points. To provide context for interpretation of this data, it is important to recognize that:

- Relatively high TPH vapor concentrations are required before the oxygen depletion is resolvable based on the stoichiometric demand associated with TPH oxidation. Ambient oxygen (21 percent vol/vol or 280 g/m^3) has a measured resolution of about 2 percent vol/vol. With a 0.3 g-hydrocarbon (HC)/g-O_2 consumption ratio based on stoichiometric considerations, this suggests a hydrocarbon level at which significant oxygen consumption should be resolvable of about 280 x (2/21) x 0.3 = 8 g/m^3 or 8 x 10^6 µg/m^3 (defined as the sensitivity threshold on **Figure 13)**.
- Active soil gas sampling results in volume averaging of soil gas because of the dimension of the soil gas probe and sand pack, which often ranges between 0.15 and 0.30 m. Volume averaging can result in elevated TPH vapor and oxygen concentrations.
- Soil gas samples that are obtained either wholly within or that straddle the biodegradation zone may have moderately elevated concentrations of both TPH vapors and oxygen (5 to 10 percent). There are several case studies with detailed soil gas profiles that demonstrate this behavior (Hers et al., 2000; Fischer et al., 1996; Ririe et al., 2002).
- Some leakage of oxygen can occur through the process of sampling or analysis; however, this is not considered to have caused a significant bias for the reasons described below.

The upper right quadrant of **Figure 13,** where TPH vapor concentrations exceed the sensitivity threshold and oxygen concentrations exceed 4 percent, contains only 26 data points (6 percent of the data). Upon closer examination, many of these data were from Hal’s site in Utah (**Figure 13**). Approximately half of the Hal’s site data from this quadrant were determined to be high quality based on internally consistent oxygen versus TPH vertical profile data. The other half were generally deep soil gas probes where oxygen was elevated, suggesting possible leakage (perhaps due to a rise in the water table). Overall, the number of data points with possible concerns relating to leakage was very small. In the case of Hal’s site, the data with possible leakage were for small exclusion distances; thus, they have no bearing on the overall conclusions with respect to distances in this report.

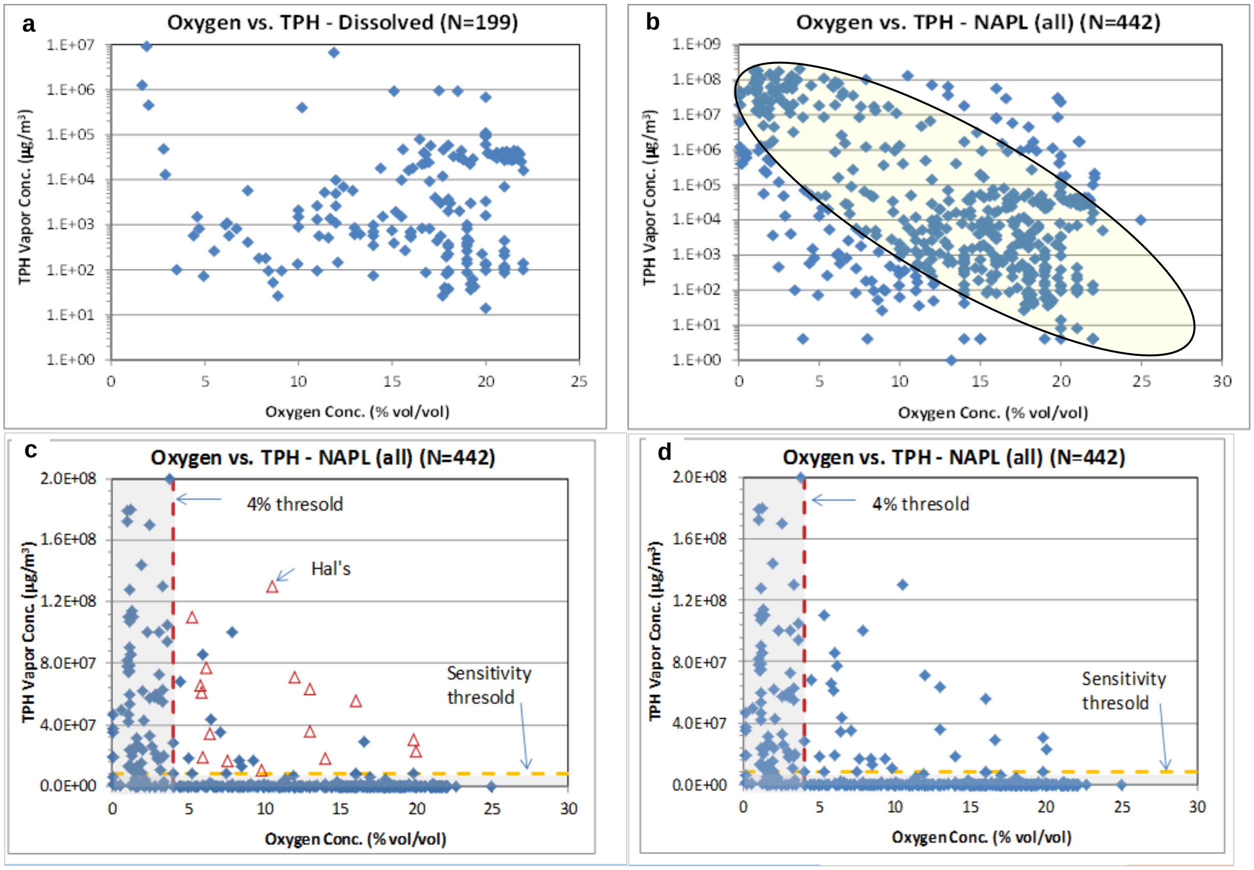


Figure 13. TPH vapor versus oxygen concentrations for dissolved and LNAPL source zones (all refers to UST, fuel terminal, refinery, and petrochemical sites). Data points shown are where both TPH vapor and oxygen concentrations were above detection limits. Shaded areas and ellipse encompass data that generally support the aerobic mineralization paradigm.

7.1.3 Methane Concentrations

The EPA PVI database includes methane data for 27 sites. Methane concentrations exceeded 5 percent (lower explosive limit in air) at five sites (three UST sites and two petroleum refinery sites) but were less than 1 percent at the remaining 22 sites. Three of the five sites with elevated methane concentrations were investigated prior to 2000, so the methane at these sites was probably not associated with ethanol in the gasoline leaked into the subsurface.

A plot of methane versus distance between the LNAPL source and soil gas probe indicates methane concentrations at sites with profile data decreased to below 5 percent within approximately 10 ft of the source (**Figure 14a**). The relationship between methane and benzene vapor concentrations was evaluated because of concern that elevated methane concentrations may result in reduced benzene vapor attenuation because of the oxygen demand represented by methane. As a general relationship, higher benzene concentrations are expected when methane concentrations are elevated because of the oxygen demand represented by methane oxidation (Jewell and Wilson, 2011). There was no apparent correlation between methane and benzene vapor concentrations, possibly because of the limited number of sites with elevated methane concentrations (**Figure 14b**). The data points with co-located elevated benzene vapor (greater than 1,000 µg/m^3) and methane (greater than 1 percent) were found to have distances between the benzene contamination and the soil gas probe of less than 7.5 ft. The relatively small distances do not suggest enhanced benzene vapor transport because of methane.

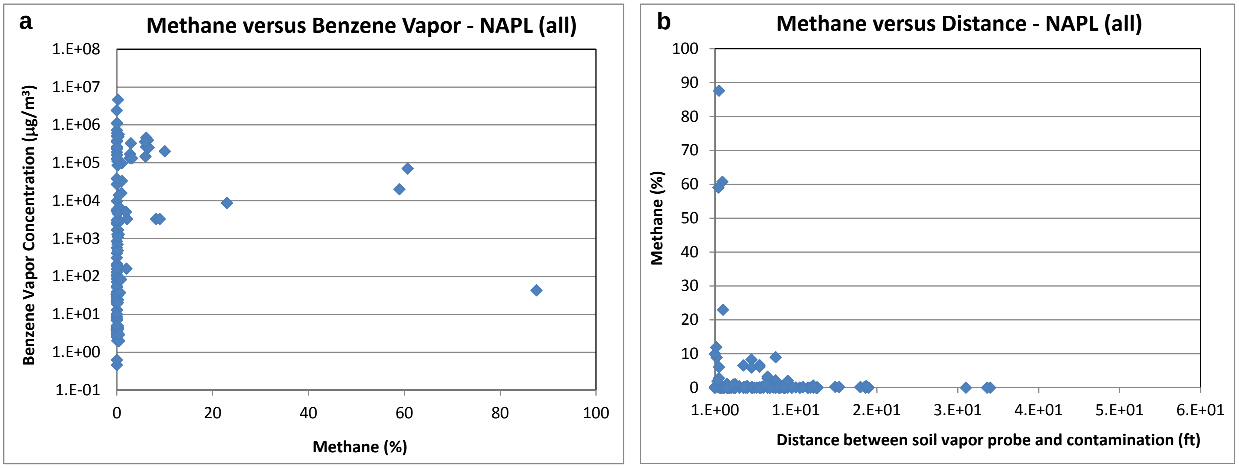


Figure 14. Methane concentrations versus distance and benzene vapor concentrations (all refers to UST, fuel terminal, refinery, and petrochemical sites).

7.1.4 Comparison between Benzene and TEX Vapor Concentrations

As an initial screening step, benzene concentrations were compared with toluene, ethylbenzene, and xylenes (TEX) concentrations to evaluate whether benzene is a risk driver relative to the TEX compounds. The relationships between benzene and ethylbenzene and between benzene and total xylenes concentrations in soil gas are shown in **Figure 15**. Qualitatively, there was a relatively good correlation between these two analyte pairs, although the comparison of benzene to xylenes indicates that concentrations of xylenes were generally up to two orders of magnitude higher than benzene concentrations. The comparison indicated that further analysis of xylenes was warranted and that benzene was a reasonable surrogate for toluene and ethylbenzene.

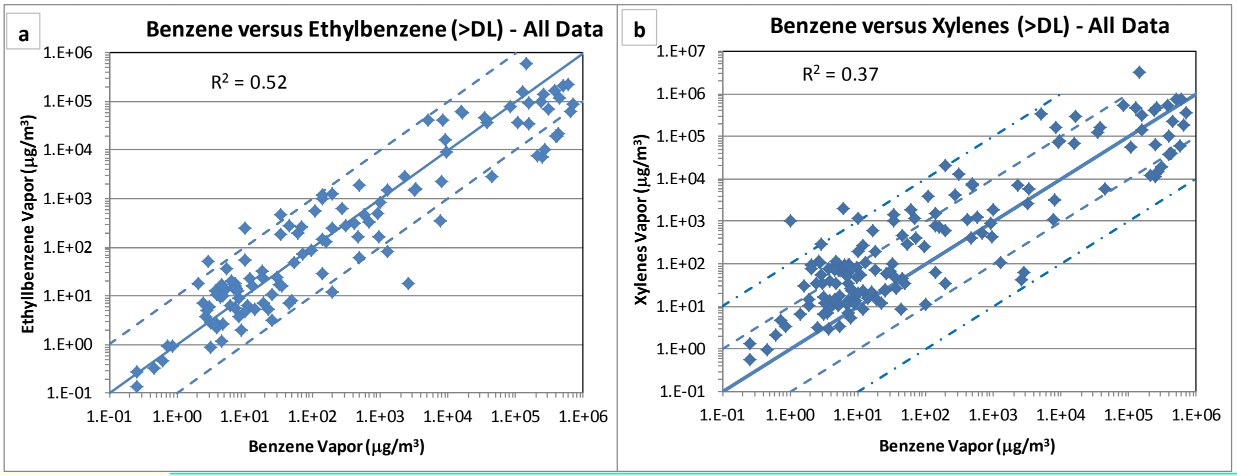


Figure 15. Relationship between benzene and ethylbenzene (left) and benzene and xylenes (right) vapor concentrations. (All refers to UST, fuel terminal, refinery, and petrochemical sites.) Data points are shown where both compounds were above detection limits.

7.2 Vertical Distance Method

For the vertical distance method, the soil vapor concentrations of the PHC compound assessed (excluding benzene) were compared with the risk-based vapor concentration (RBC_v), which is the risk-based indoor air concentration multiplied by a dilution factor of 100 (i.e., attenuation factor of 0.01). For benzene, the probability that the soil vapor concentration is less than a defined threshold (50 and 100 $\mu g/m^3$) for varying source-separation distances was estimated.[9] For definition of inclusion distances, a probability greater than 95 percent was considered a reasonable threshold based on regulatory precedence.

7.2.1 All Data

Data analysis was conducted for dissolved sources, LNAPL sources at UST sites, and LNAPL sources at fuel terminal, petroleum refinery, and petrochemical (non-UST) sites (**Figures 16** through **20**). There are only PHC fraction and hexane data for UST sites; hence, there is not a figure for the all-LNAPL sites category for these compounds. The following compounds were evaluated: benzene, xylenes, hexane, 2,2,4-TMP, 1,2,4-TMB, naphthalene, MtBE, and Massachusetts Department of Environmental Protection (MassDEP) hydrocarbon fractions (C9–10 aromatics, C5–8 aliphatics, and C9–12 aliphatics).

For the benzene analysis, non-detects were addressed both by the common practice of substituting half the detection limit and by using the more statistically robust Kaplan-Meier method. The Kaplan-Meier method resulted in similar or slightly (0 to 7 percent) higher probabilities than the substitution method. The probability of the soil vapor concentration being less than a threshold was estimated for 5 and 30 mg/L groundwater concentration thresholds for benzene and TPH, respectively, which are part of the LNAPL hydrocarbon indicators (presented previously in **Table 4**). A sensitivity analysis was conducted where the threshold for the benzene groundwater concentration was varied between 1 and 10 mg/L and the TPH groundwater concentration was varied between 10 and 50 mg/L. The resulting variation in probability (estimated using the substitution technique) for this range was less than 0.5 percent, indicating the results are not sensitive to the concentration thresholds (possibly because groundwater is a poor predictor of soil vapor concentrations).

---

[9] Negative contamination source–probe distances indicate the soil gas probe was installed below the top of the contamination zone.

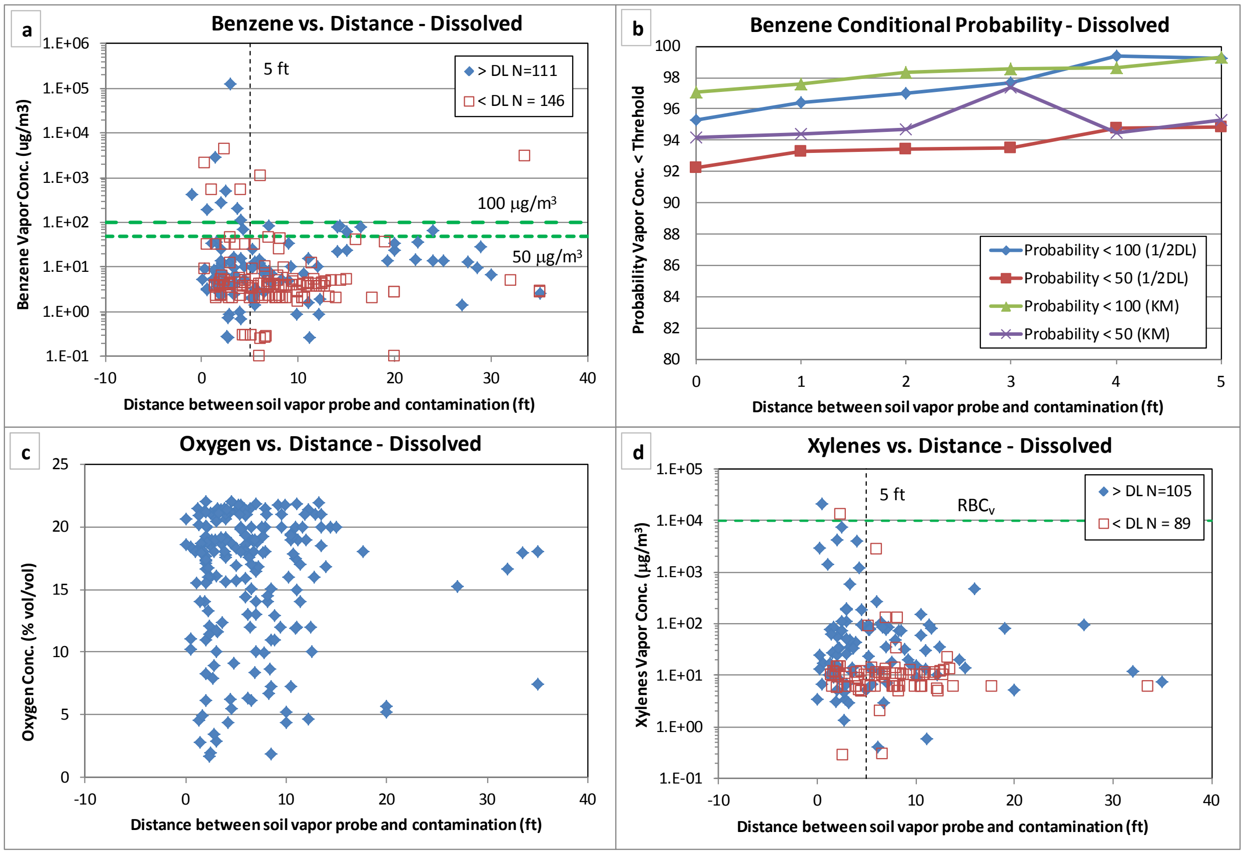


Figure 16. Vertical distance method: benzene (a), oxygen (c), and xylenes (d) data for dissolved-source sites (KM = Kaplan-Meier). Panel b shows the benzene probability data.

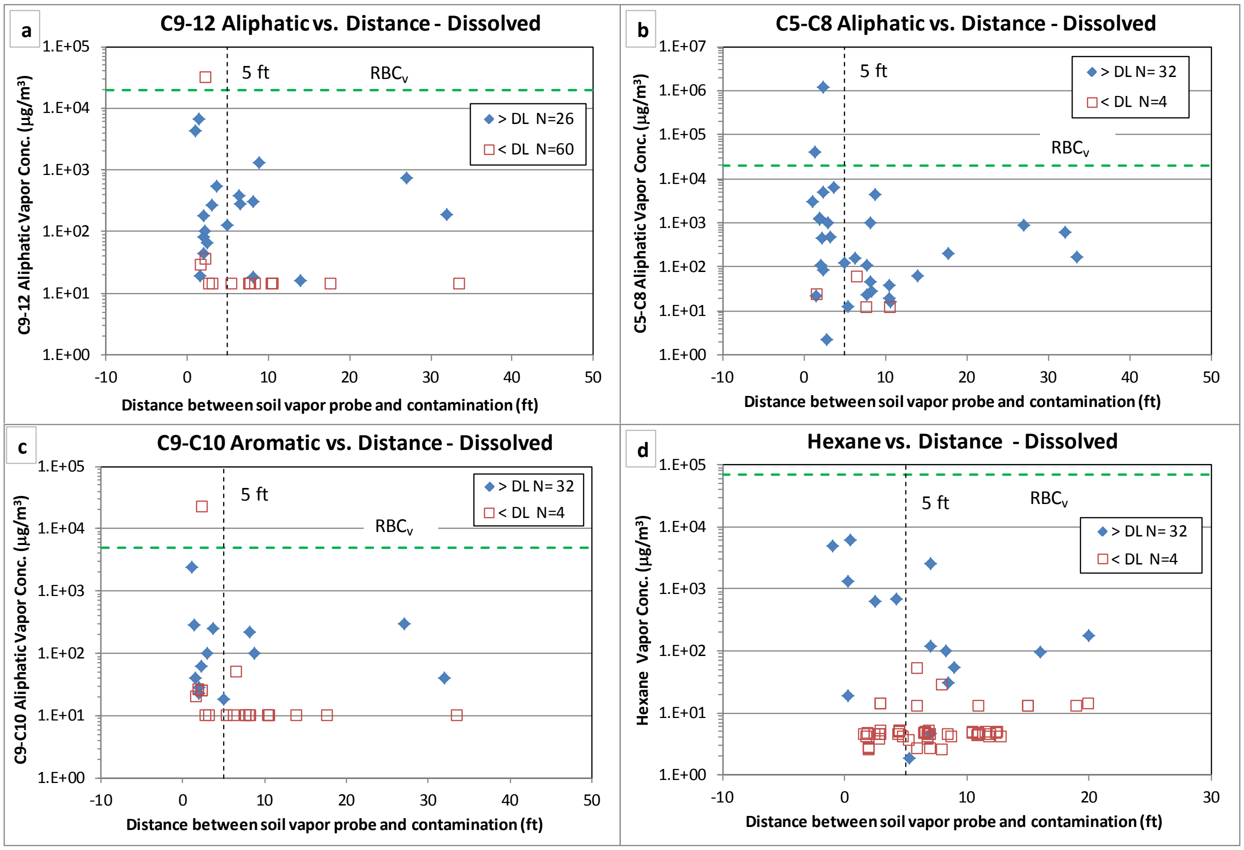


Figure 17. **Vertical distance method: PHC fraction (a–c) and hexane (d) data for dissolved-source sites.**

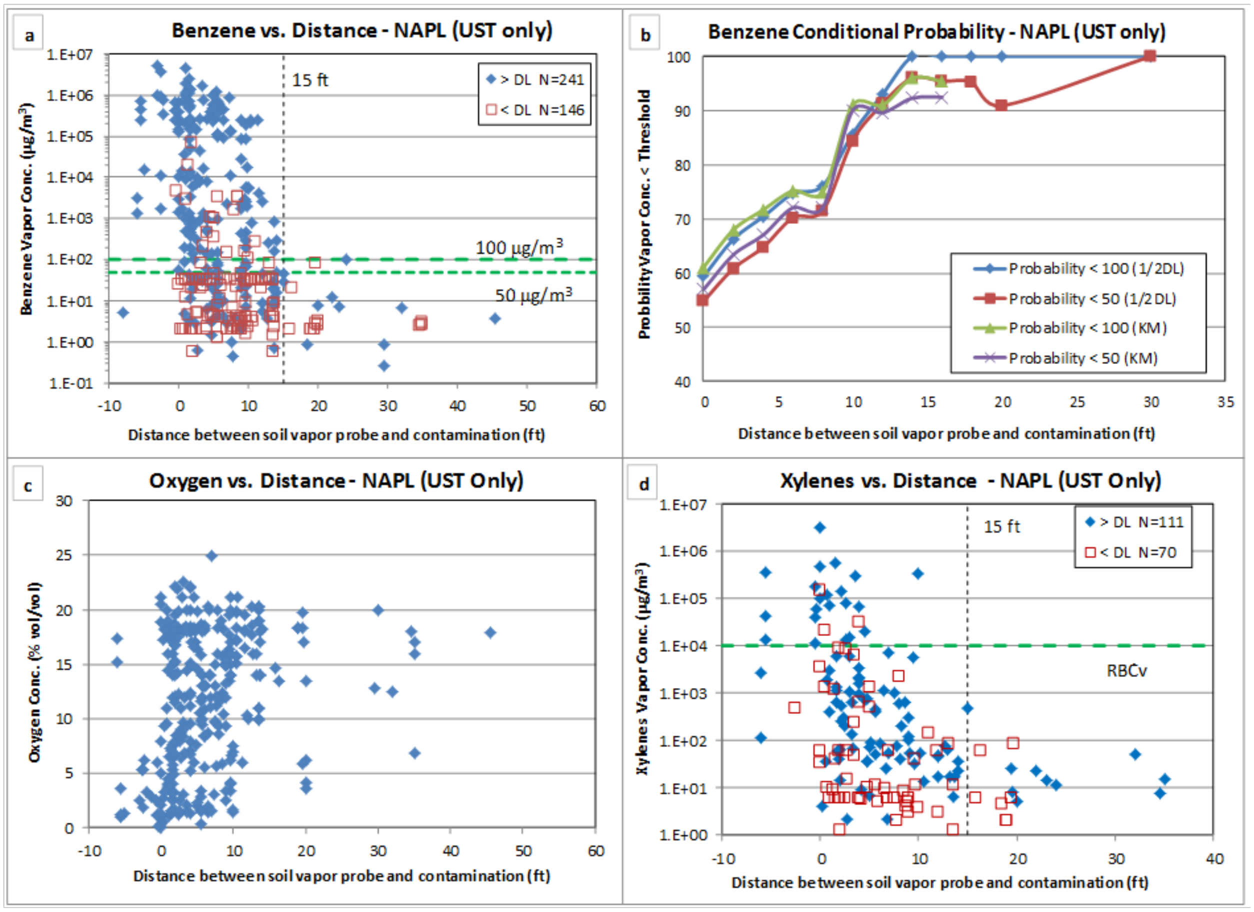


Figure 18. Vertical distance method: benzene (a, b), oxygen (c), and xylenes (d) data for LNAPL sources at UST sites (KM = Kaplan-Meier).

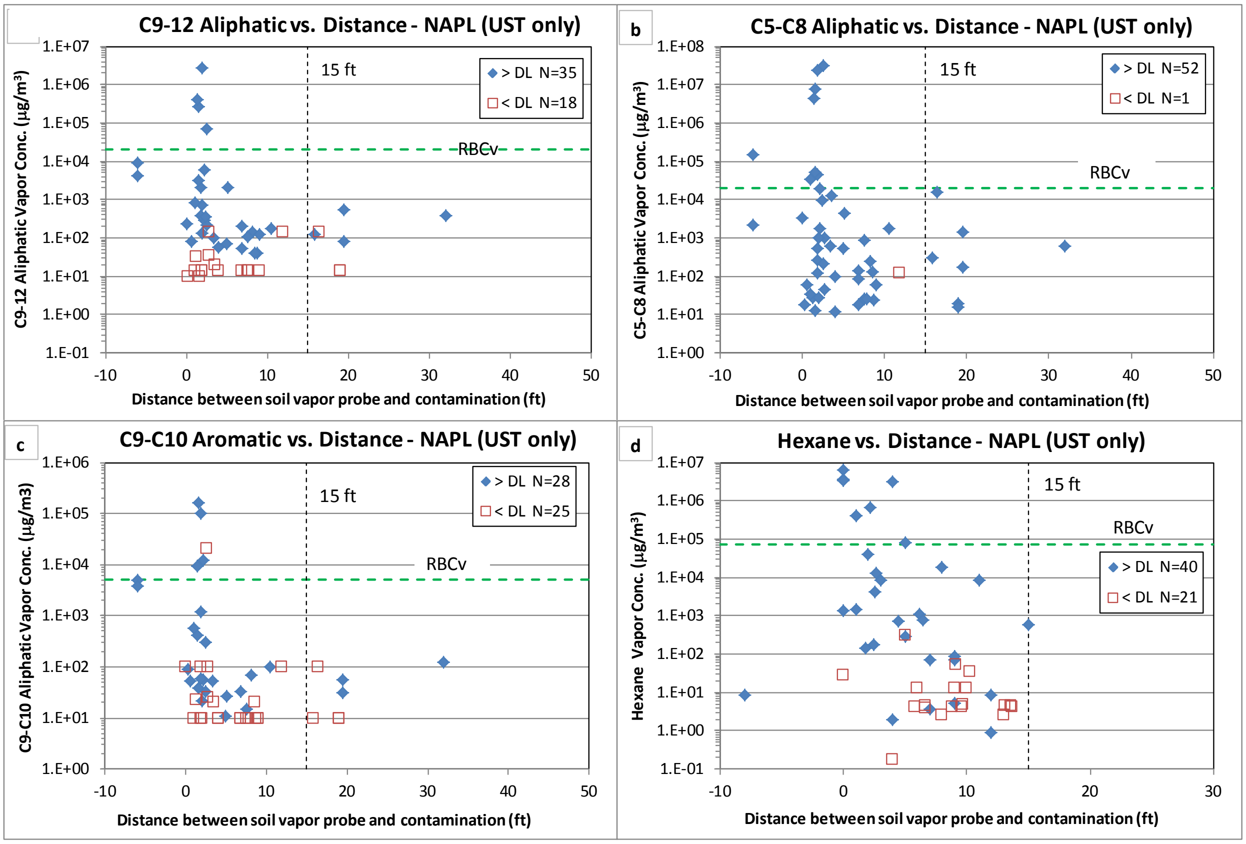


Figure 19. Vertical distance method: PHC fraction (a–c) and hexane (d) data for LNAPL sources at UST sites.

The EPA PVI database was further validated by comparing benzene probabilities for screening distances derived using all data (excluding DQ-1), to a dataset where data ranked as CSM-1 was screened out. The data from the 22 Minnesota sites had a CSM-1 ranking. The difference in the benzene probabilities ranged between 0 and 0.4 percent depending on source-separation distance for dissolved sites and between 0 and 0.8 percent for LNAPL sources at UST sites.

The analysis results show distinct differences between the three scenarios considered, which are 1) dissolved sources, 2) LNAPL sources at UST sites, and 3) LNAPL sources at fuel terminal, refinery, or petrochemical (non-UST) sites (**Table 6**):

- For dissolved sources:
  - Approximately 97 percent of the benzene soil vapor concentrations are less than 100 µg/m^3 and 94 percent are less than 50 µg/m^3 for source-separation distances as small as 0 ft (**Table 6** and **Figures 16** and **17**).
  - For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations for separation distances greater than 3 ft (0.9 m).
  - The analysis indicates there is a low probability of exceeded risk-based thresholds for small separation distances for dissolved sources.

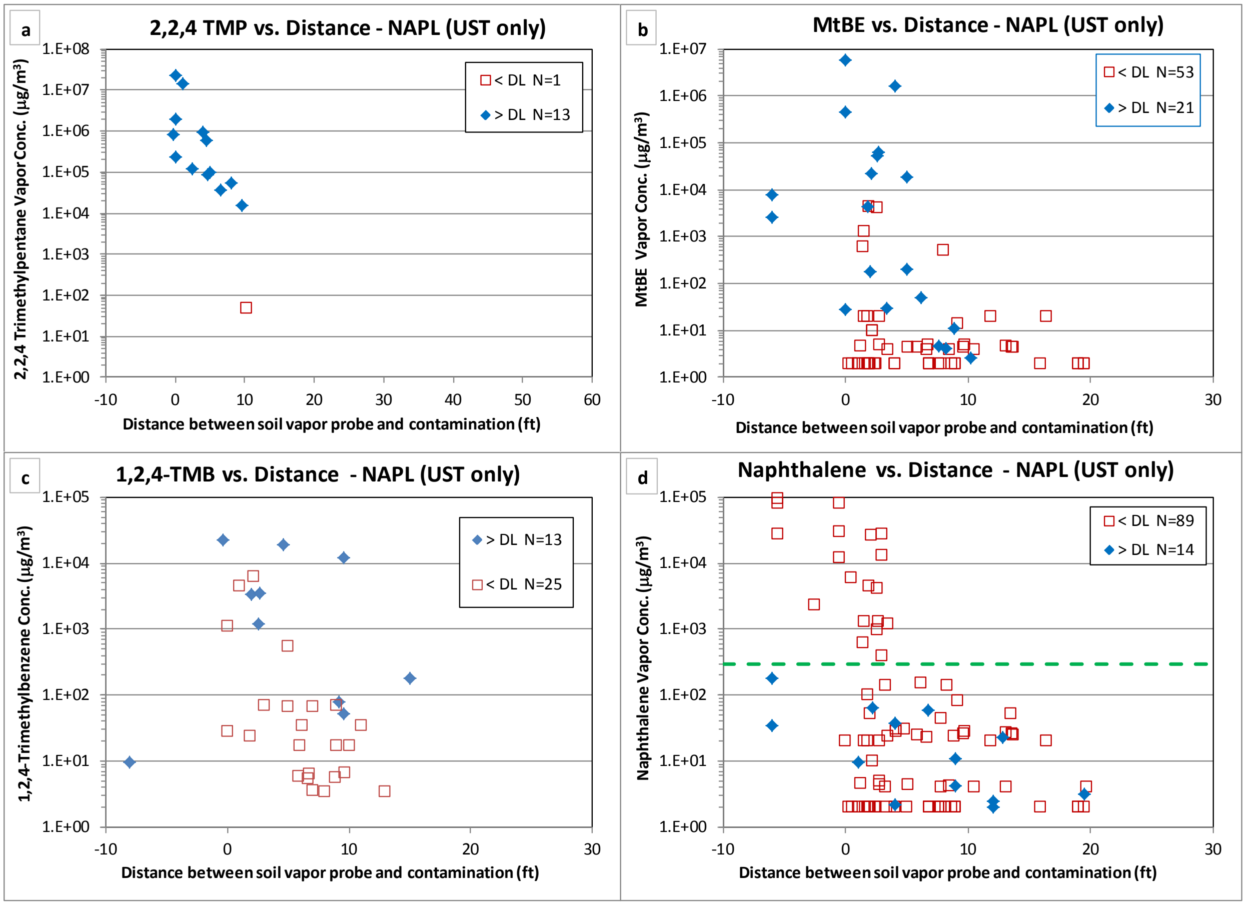


Figure 20. **Vertical distance method: 2,2,4-trimethylpentane (TMP), MtBE, 1,2,4-trimethylbenzene (TMB), and naphthalene data for LNAPL sources at UST sites.**

Table 6. Summary of Results for Vertical Distance Method

	Dissolved Source	LNAPL Source—UST Sites	LNAPL Source — Refinery, Fuel Terminal, Petrochemical Sites
Oxygen	Most O_2 conc. > 4%, and no O_2 < 1%	Many data points with O_2 < 4%, and O_2 < 1% to 6 ft (1.8 m) separation	Many data points with O_2 < 4%, and O_2 < 1% to 11-ft (3.4-m) separation, greater O_2 depletion than UST only
Benzene (100 µg/m^3 threshold)	P_{KM} > 97% for 0 ft separation increasing to 99% at 5 ft (1.5 m)	P_{KM} > 61% for 0 ft separation increasing to ~ 95% at 15 ft (4.6 m)	$P_{1/2DL}$ > 22% for 0-ft separation increasing to ~ 90% at 18 ft (5.5 m)
Benzene (50 µg/m^3 threshold)	P_{KM} > 94% to 95% for 0 ft to 5 ft (1.5 m)	P_{KM} > 57% for 0 ft separation increasing to ~ 93% at 15 ft (4.6 m)	$P_{1/2DL}$ > 22% for 0 ft separation increasing to ~ 90% at 18 ft (5.5 m)
Xylenes	One vapor concentration > RBC_v for separation distance of 3 ft (0.9 m)	>10 vapor concentrations > RBC_v for separation distance up to 11 ft (3.4 m)	>10 vapor concentrations > RBC_v for separation distance up to 12 ft (3.7 m)
Hexane	All vapor concentrations < RBC_v 0 ft	Five vapor concentrations > RBC_v for separation distance up to 4 ft (1.2 m)	N/A

(continued)

Table 6. Summary of Results for Vertical Distance Method (continued)

	Dissolved Source	LNAPL Source—UST Sites	LNAPL Source — Refinery, Fuel Terminal, Petrochemical Sites
C5-8 Aliphatic	Two vapor concentrations > RBC_v for separation distance up to 3 ft (0.9 m)	Five vapor concentrations > RBC_v for separation distance up to 3 ft (0.9 m)	N/A
C9-12 Aliphatic	All vapor concentrations < RBC_v 0 ft	Eight vapor concentrations > RBC_v for separation distance up to 2 ft (0.6 m)	N/A
C9-10 Aromatic	All vapor concentrations < RBC_v 0 ft	Four vapor concentrations > RBC_v for separation distance up to 2 ft (0.6 m)	N/A

P_{KM} = Probability estimated using Kaplan-Meier method for exceeding threshold. $P_{1/2DL}$ = Probability estimated using ½ detection limit substitution method.

- For LNAPL sources at UST sites, the findings were:
  - Approximately 95 percent of the benzene soil vapor concentrations are less than 100 µg/m^3 and 93 percent are less than 50 µg/m^3 at a source-separation distance of approximately 15 ft (4.6 m) (**Table 6** and **Figures 18** to **20**).
  - For all compounds, soil vapor concentrations decrease rapidly between about 5 and 15 ft (1.5 m and 4.6 m).
  - For compounds other than benzene, the available data indicate that measured soil vapor concentrations are less than the risk-based concentrations beyond 11 ft (3.4 m).
  - There are significant differences in source soil vapor concentrations at small source-probe separation distances. The approximate maximum soil vapor concentrations were 3x10^7 µg/m3 for 2,2,4 TMP; 7x10^7 µg/m3 for benzene, hexane, and MtBE; 20,000 µg/m^3 for 1,2,4 TMB; and 180 µg/m^3 for naphthalene.
  - The elevated MtBE vapor concentrations are mostly for one site (Stafford) with residual LNAPL above the water table, and there was evidence for a complete MtBE vapor intrusion pathway at a house with a 6.5-ft LNAPL-basement separation.
- For LNAPL sources at refinery, fuel terminal, or petrochemical (non-UST) sites, the findings were:
  - There are limited data for benzene beyond a 20-ft source-separation distance and limited data at all distances for other compounds.
  - Approximately 90 percent of the benzene soil vapor concentrations are less than the thresholds (50 and 100 µg/m^3) at a source-separation distance of approximately 18 ft (5.5 m). The probability does not substantially increase above 90 percent beyond 18 ft because data are limited for larger separation distances. The benzene vapor concentration versus distance plot indicates benzene vapor concentrations generally decrease by orders of magnitude between 10 and 30 ft (**Table 6** and **Figures 21 and 22**).

- For compounds other than benzene, the available data indicate that measured soil vapor concentrations are less than the risk-based concentrations beyond 12 ft (3.6 m).
- At the Mandan site, a very large diesel release (over 1 million gallons) led to elevated deep, near-source methane concentrations[10] (Breyer and Cowart, 2004). The least attenuation between deep and shallow soil gas (8-ft distance) was observed for methane and naphthalene, for which the ratios of deep to shallow concentrations were 16 and 19, respectively. The greatest attenuation was observed for benzene where the ratio was about 260. Also, deep naphthalene vapor concentrations were up to 20,000 μg/m^3, approximately two orders of magnitude greater than the maximum naphthalene concentration measured at other sites in the database.
- At a refinery with a very large gasoline release (over 1 million gallons) and deep LNAPL source (about 55 ft [16.4 m] depth), the 2,2,4-TMP concentration remained elevated for separation distances as great as 45 ft (15 m).[11]

The analysis results indicate benzene is the risk driver, with exceedances of the risk-based vapor concentrations occurring at larger contamination source–building separation distances compared to other compounds evaluated. There is less attenuation for 2,2,4-TMP compared to benzene, but 2,2,4-TMP is not a risk driver because there is no U.S.EPA toxicity factor for it.

---

[10] There were no oxygen data in the information reviewed.

[11] The reason for the 2,2,4-TMP trend at this site is not known, but the available data indicate significant temporal fluctuations in PHC vapor and oxygen concentrations that may be related to water table fluctuations and operation of a remediation system (ASTDR, 2011). In addition, Mickelski et al. (2010) in a review of data from this site suggests there may also be near surface–contamination sources, although the significance of such possible shallow sources on the 2,2,4-TMP concentrations is not well understood.

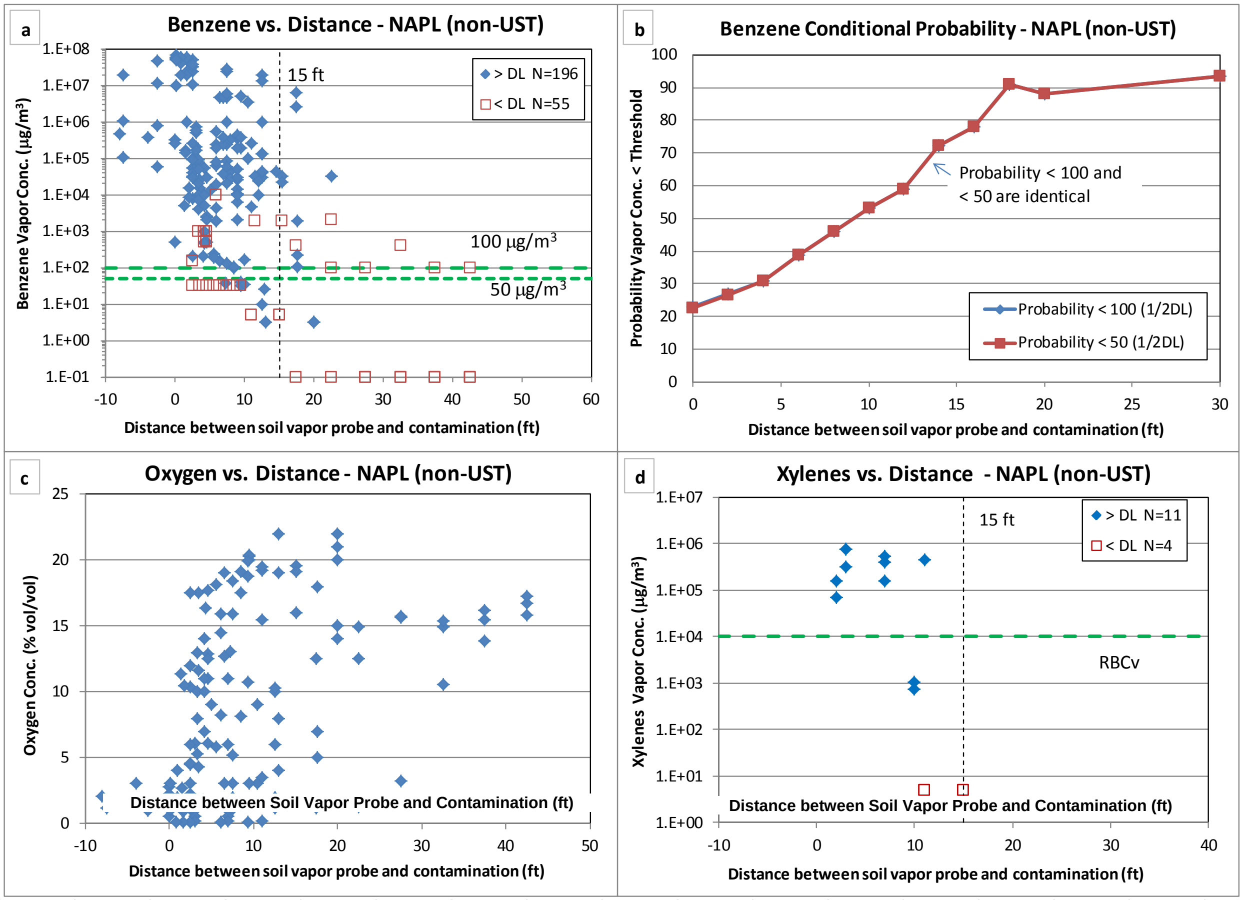


Figure 21. Vertical distance method–benzene, xylenes, and oxygen data for LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites. Red plots over blue.

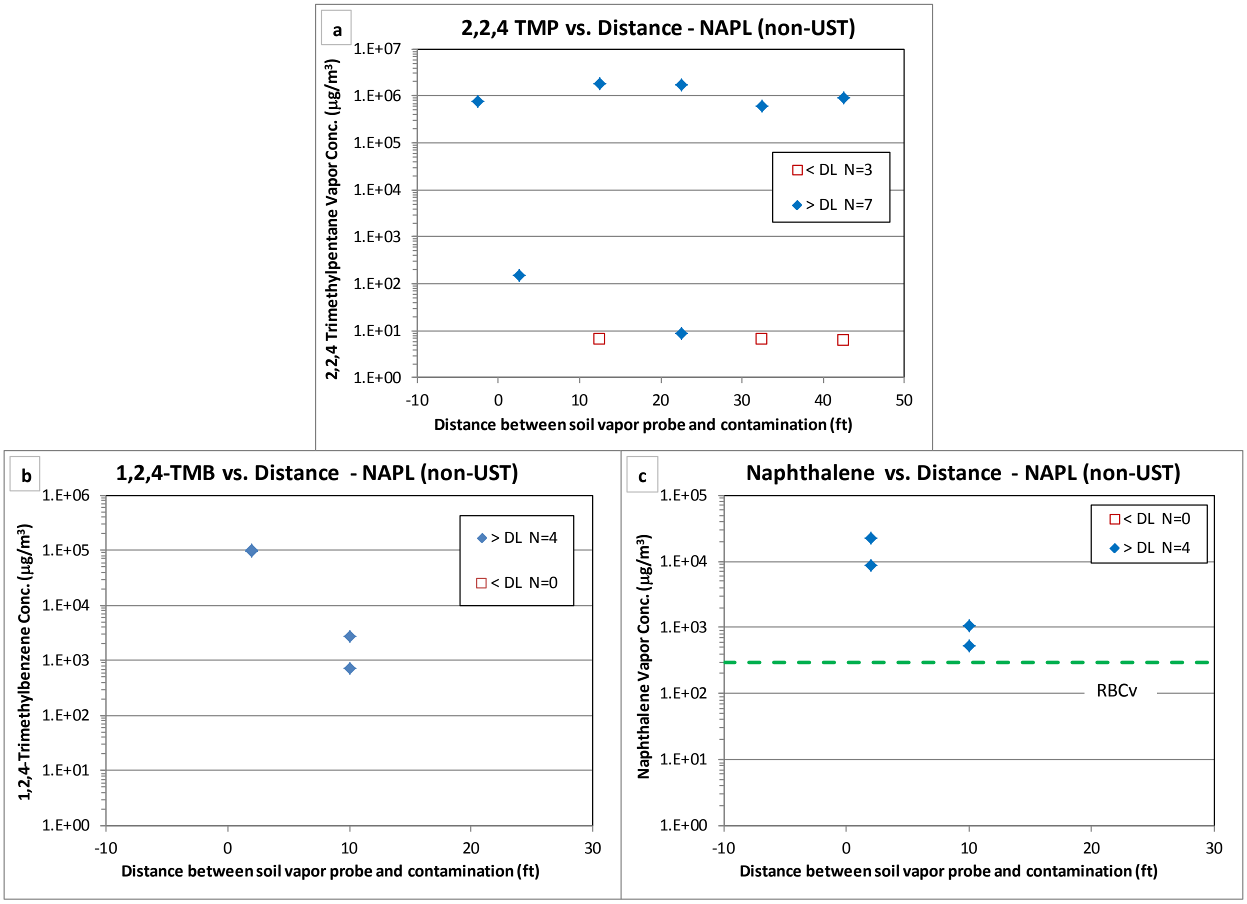


Figure 22. **Vertical distance method–2,2,4-trimethylpentane (TMP), naphthalene, and 1,2,4-trimethylbenzene (TMB) data for LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites.**

7.2.2 Influence of Surface Cover

The potential influence of a surface cover was evaluated through comparison of the probabilities of benzene soil vapor concentrations that are less than 100 µg/m^3 for varying soil-separation distances and through analysis of oxygen concentrations for three different surface covers: (1) building concrete foundation, (2) pavement, and (3) ground cover[12] (**Figures 23 and 24**). The datasets evaluated were limited to LNAPL sources because oxygen is not limiting for dissolved-source sites.

For LNAPL sources at UST sites, the probabilities of benzene soil vapor concentrations less than 100 µg/m^3 were highest for the building scenario, second highest for the ground-cover scenario, and lowest for the pavement scenario (**Figure 23**). Oxygen data are another important indicator of the possible effect of surface cover on aerobic biodegradation. The oxygen concentration trends were qualitatively similar for the pavement and ground-cover scenarios and indicated low (less than 2 percent) oxygen concentrations were limited to small separation distances (less than 10 ft distance). Oxygen concentrations for the below-building scenario were higher than the

---

[12] e.g., ground that is gravel-surfaced, grassy, or dirt-covered

pavement and ground cover scenarios for similar distances, but the dataset was relatively small (N=35).

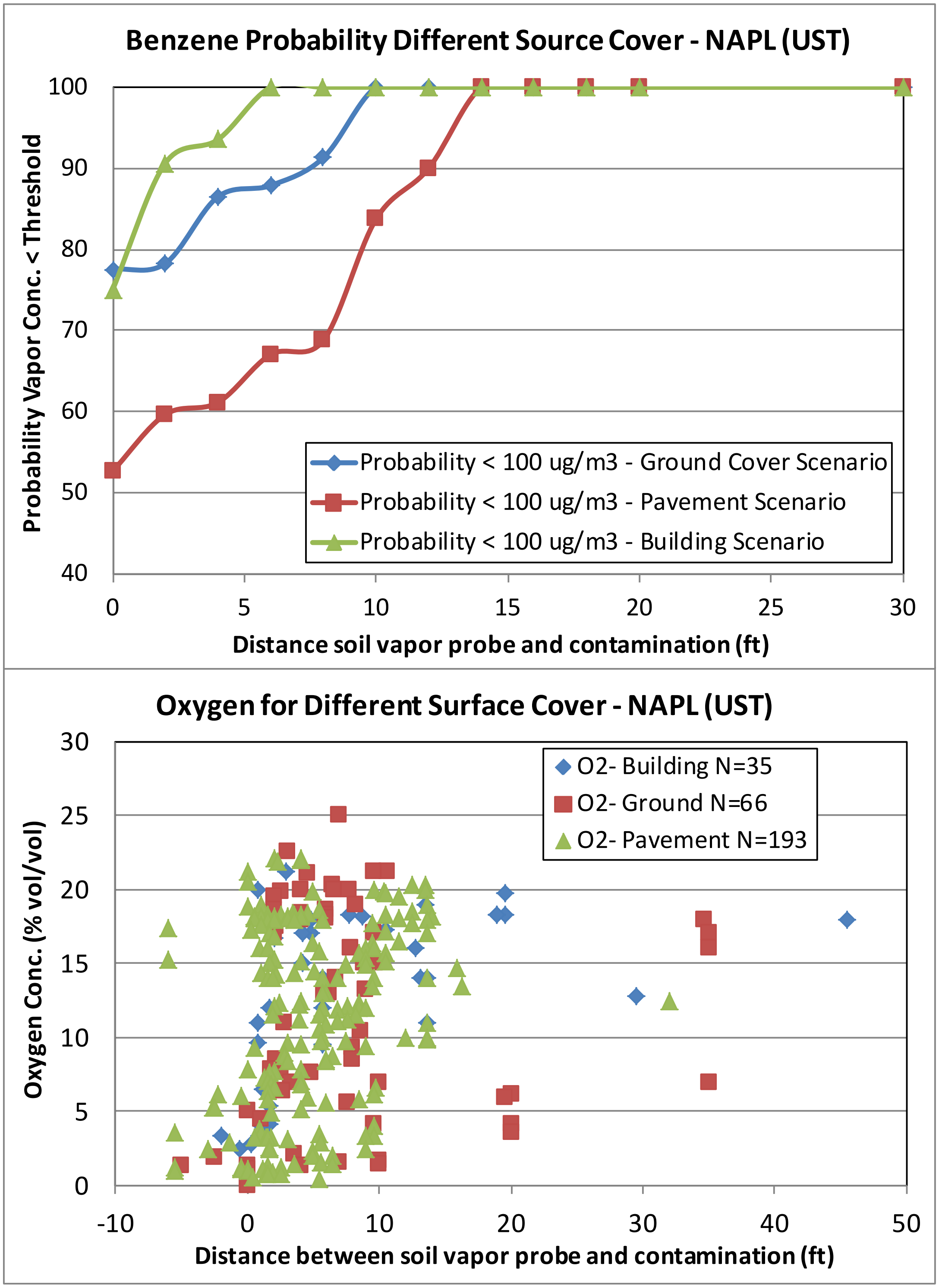


Figure 23. Comparison of probability for benzene soil vapor concentrations to be less than threshold and oxygen concentrations for different surface covers for LNAPL sources at UST sites. Below detection limit concentrations replaced with half the detection limit for analysis.

For LNAPL sources at fuel terminal, refinery, and petrochemical sites, the dataset is relatively small and the benzene probability analysis is variable. Therefore, it is not possible to infer potential differences between the scenarios (**Figure 24**). The oxygen results indicate the lowest concentrations for the building scenario, with seven data points with oxygen concentrations that were below 1 percent between 3 and 11 ft distance. Qualitatively, the oxygen concentrations for the pavement scenario were similar but somewhat higher than for the building scenario, and the concentrations for the ground-cover scenario were significantly higher than for the building scenario.

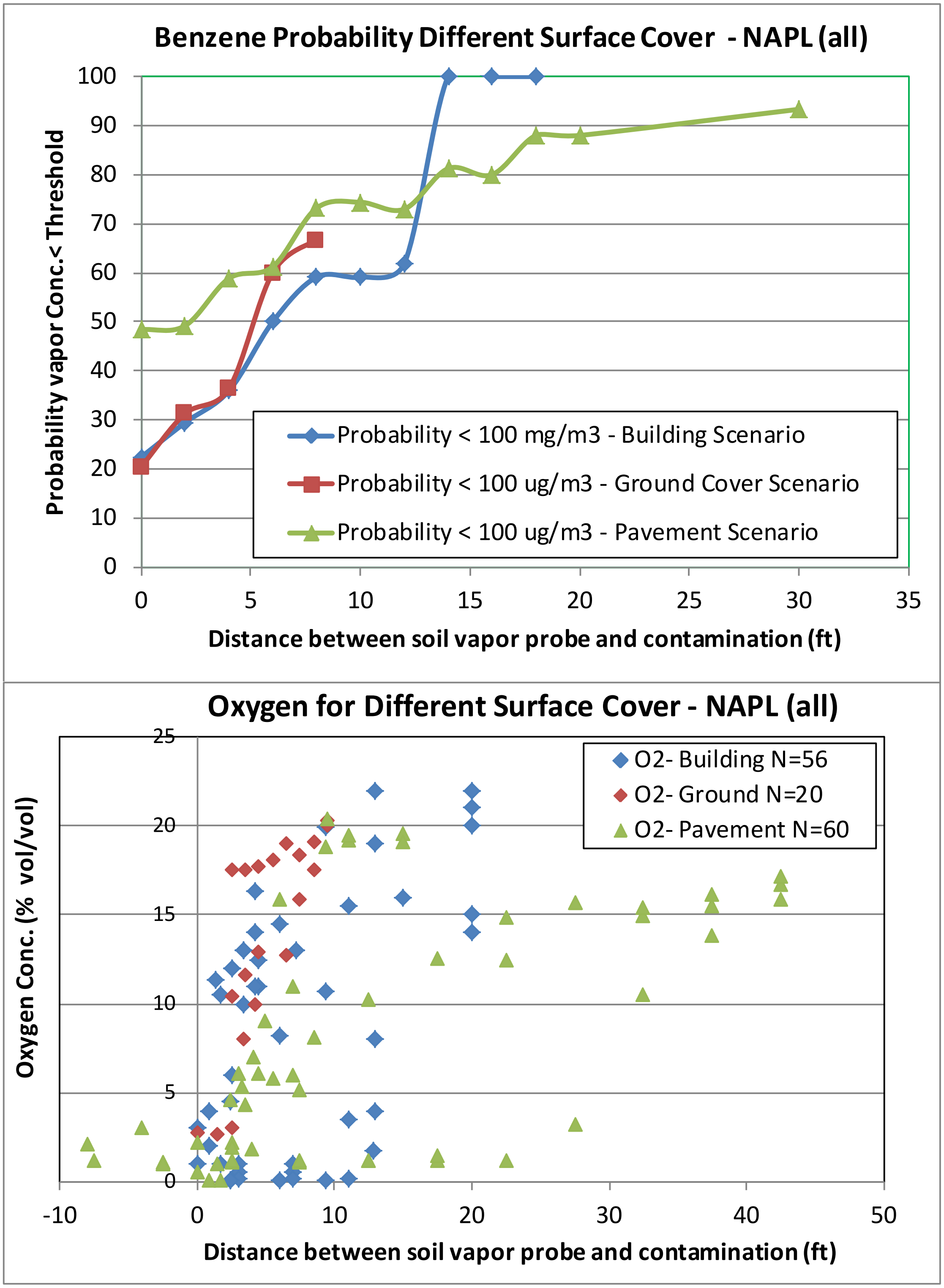


Figure 24. Comparison of probability for benzene soil vapor concentrations to be less than threshold and oxygen concentrations for different surface covers for LNAPL sources at all sites (UST, fuel terminal, refinery, and petrochemical). Below detection limit concentrations replaced with half the detection limit for analysis.

In summary, the type of surface cover did not appear to affect the probability analysis for benzene concentration thresholds (e.g., it did not indicate a consistently lower probability for data obtained below buildings). For UST sites, oxygen concentrations were lower at paved sites but not below buildings. For fuel terminal, refinery, and petrochemical sites, there was greater frequency of depleted oxygen for the below-building scenario, compared to the ground cover and pavement scenarios, which may be a result of larger petroleum releases at such sites and consequent greater oxygen demand, compared to typical releases at UST sites.

7.2.3 Influence of Soil Type

The potential influence of soil type was evaluated through comparison of the probabilities of benzene soil vapor concentrations less than 100 µg/m^3 for varying soil-separation distances and for two general soil types: fine grained and coarse grained (**Figure 25**). The probabilities of benzene soil vapor concentrations less than 100 µg/m^3 were similar for dissolved-source sites for the two soil types. For LNAPL source sites, the probabilities were between 6 and 16 percent greater for coarse-grained soils than those for fine-grained soils for small separation distances, but at larger separation distances, there is a reversal in the trend. The evaluation of data trends is limited by absence of data for fine-grained soils beyond a 14-ft separation distance. The analysis did not identify whether soil type has an influence on benzene soil vapor concentrations and probabilities of exceedances.

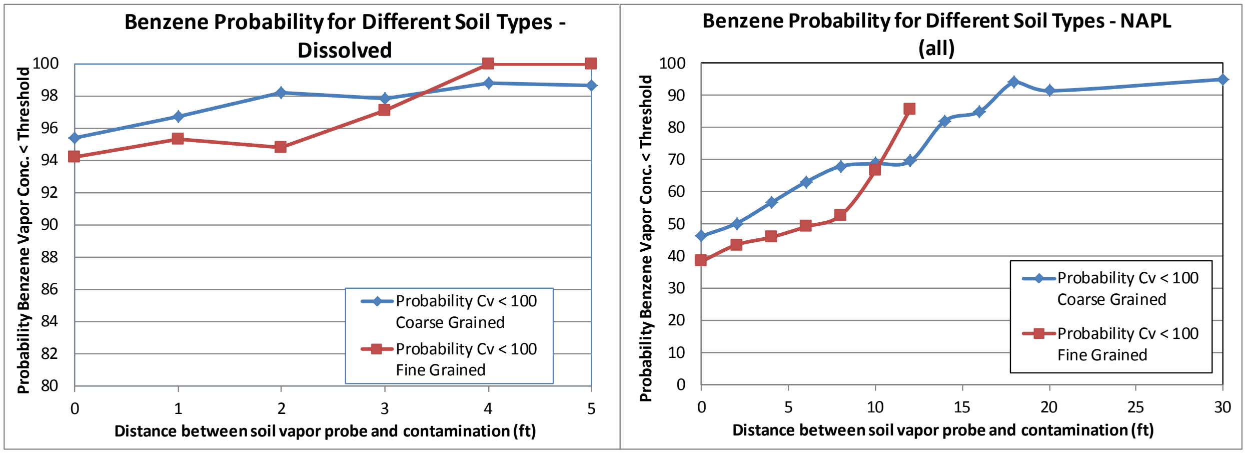


Figure 25. Comparison of probability for benzene soil vapor concentrations to be less than the threshold for different soil types (coarse and fine grained). Below detection limit concentrations replaced with half the detection limit for analysis.

Given the data available, it was not possible to conduct an empirical analysis of the potential effect of layered soil systems where, for example, fine-grained soils (that may be wet) overlie coarse-grained soils. The evaluation of case studies indicated one site where there may have been reduced vertical concentration attenuation of PHC vapors because of a geologic profile where a surficial clay layer overlay coarser-grained soil (Luo et al., 2010).

7.3 Clean Soil Method

The clean soil method (Davis, 2009; 2010) consists of an analysis of the thickness of un-impacted clean soil (i.e., soil not impacted by LNAPL) required for soil vapor benzene concentrations to attenuate to below 100 µg/m^3. As described previously in Section 6, two interpolation procedures were used as part of the estimation process. Procedure 2 is considered a more representative method. The results of the analyses, shown in **Table 7** and **Figures 26** through **28**, are summarized as follows:

- For dissolved-source sites, the 95th percentile clean soil thicknesses (calculated using Excel) for procedures 1 and 2 were 10 ft (3.0 m) and 5.4 ft (1.6 m), respectively (**Figure 26**). There was no trend between clean soil distance and dissolved benzene groundwater concentrations. This result was expected because of the observed poor correlation between groundwater and deep soil vapor concentrations described in Section 7.1.1.
- For LNAPL sources at UST sites, the 95th percentile clean soil thicknesses (incorporating all the data) for procedures 1 and 2 were 13.9 ft (4.2 m) and 13.5 ft (4.1 m), respectively. There was an increase in the clean soil thicknesses for benzene groundwater concentrations greater than approximately 5 mg/L. For a small percentage of the data points (4 percent), an attenuation distance could not be calculated (green symbols on **Figure 27**). However, the omission of that small amount of data was not considered significant to the overall result.
- For LNAPL sources at fuel terminal, refinery, and petrochemical sites, there were insufficient data to estimate percentiles (**Figure 28**).[13] The estimated maximum clean soil thickness was approximately 20 ft (6.1 m). Approximately 26 percent of the data points represent vertical profile data where the shallowest benzene soil vapor concentration was greater than 100 µg/m^3 (green symbols on **Figure 28).**

Table 7. Summary of Results for Clean Soil Method

Source Scenario and Facility Type	Number Sites	Number Data Points	95th Percentile Clean Soil Thickness	
			Procedure 1	Procedure 2
Dissolved	47	170	10.0 ft (3.0 m)	5.4 ft (1.6 m)
LNAPL- UST sites	53	172	13.9 ft (4.2 m)	13.5 ft (4.1 m)
LNAPL – Fuel Terminal, Refinery, and Petrochemical Sites	60	216	*20.0 ft (6.1 m)*[a]	*16.2 ft (4.9 m)*[a]

Note: The above statistics include site data when no benzene groundwater concentration was available.

[a] Values in italics are maximums because percentiles could not be calculated for non-UST LNAPL sites.

---

[13] There were additional data where a clean soil thickness was calculated, but no benzene groundwater data were available near the soil vapor probe, and therefore these data could not be plotted.

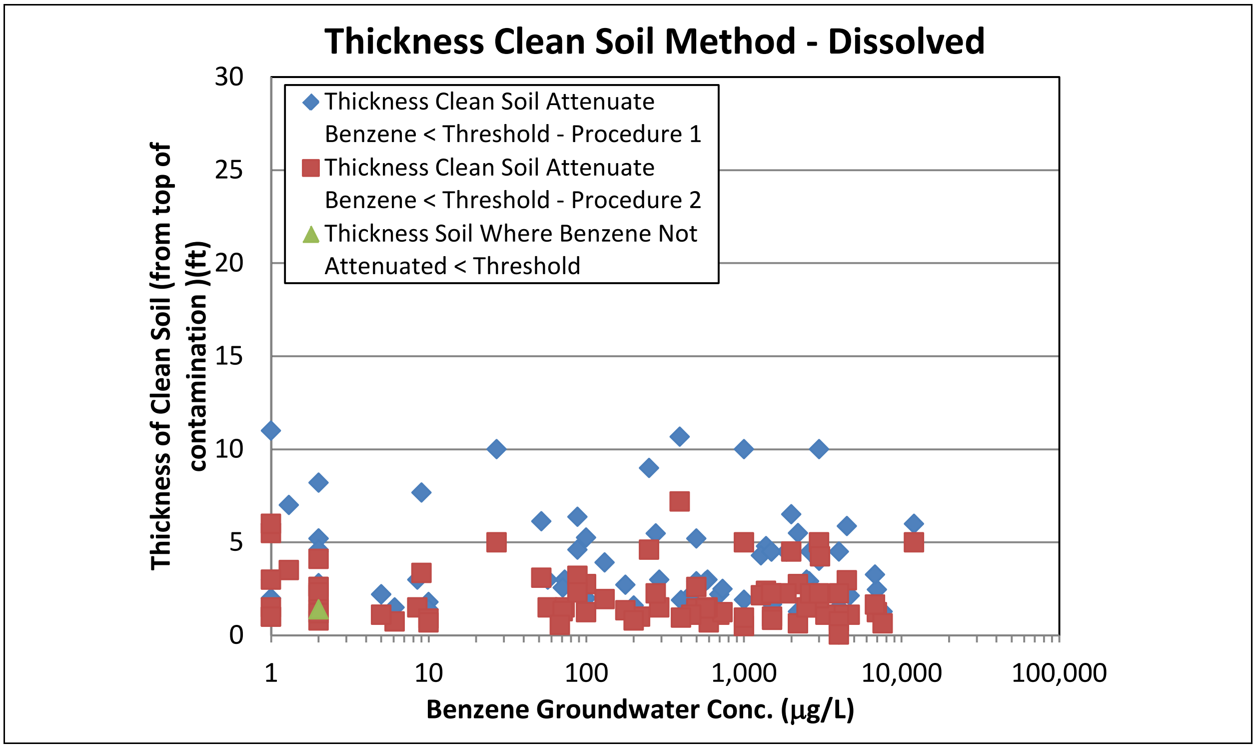


Figure 26. Results of clean soil method for dissolved-source sites. 47 sites, N = 170.

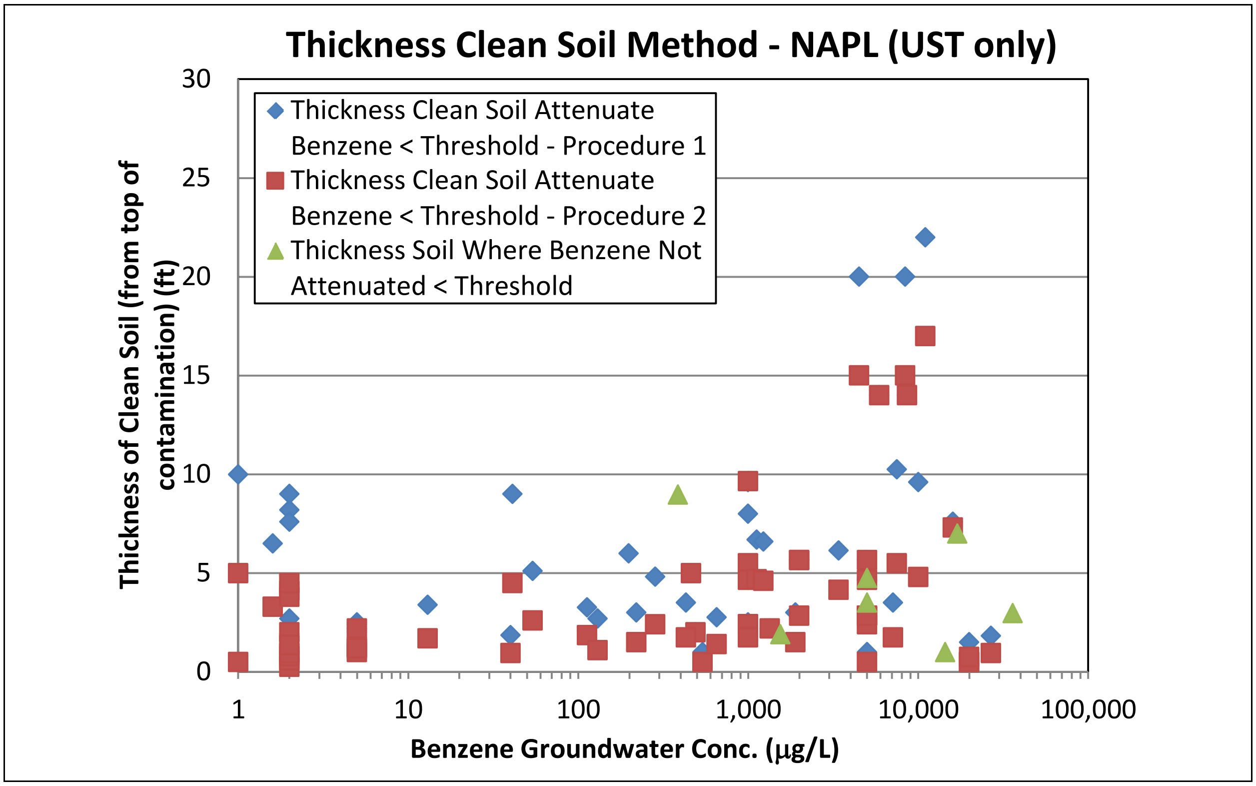


Figure 27. Results of clean soil method for LNAPL sources at UST sites. 53 sites, N = 172.

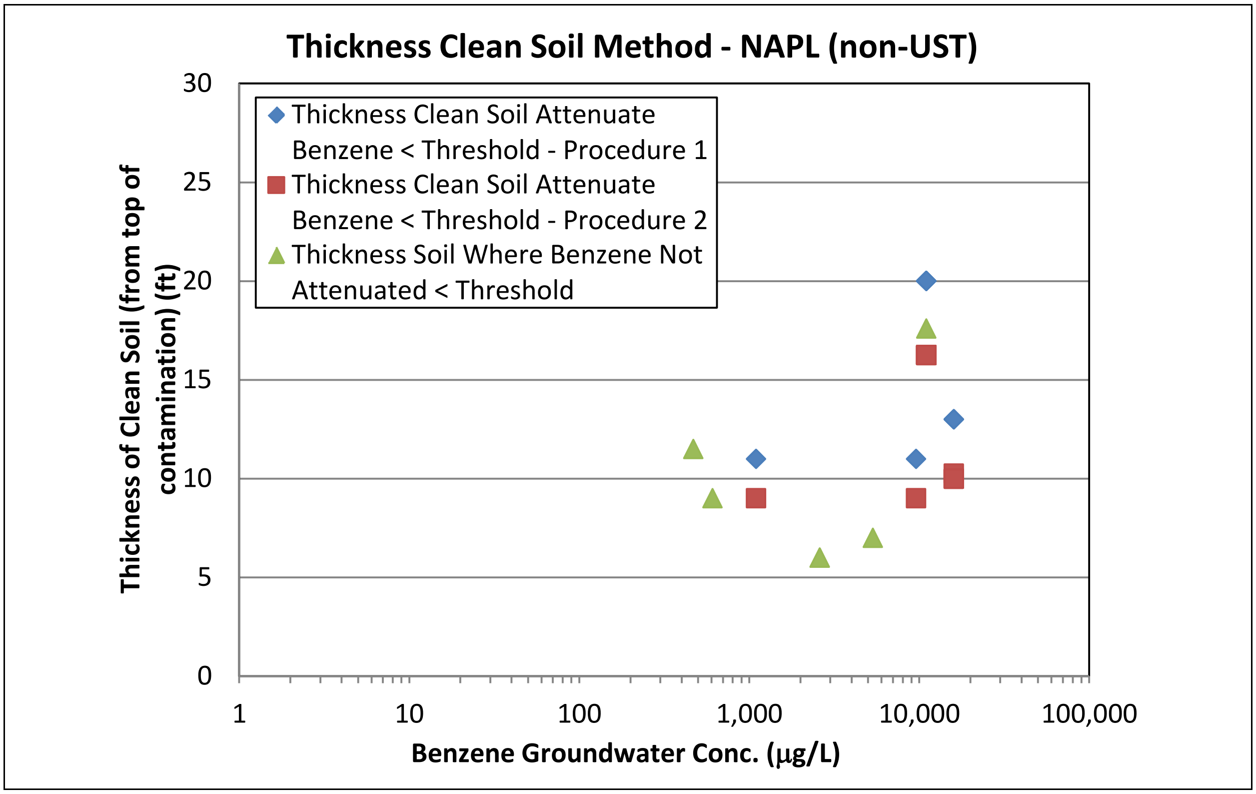


Figure 28. **Results of clean soil method for LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites. 60 sites, N = 216.**

8. Discussion

8.1 Conceptual Site Model and Mathematical Models

The CSM for PHC vapor is the basis for identifying exclusion distances and inclusion behavior criteria. At sites with dissolved PHC contamination in groundwater, aerobic biodegradation is expected to result in the attenuation of PHC vapors, such that there is limited potential for a complete PVI pathway, except for sites with very shallow contamination. For sites with LNAPL contamination, there is greater potential for oxygen limitations below buildings and a complete PVI pathway, depending on site conditions such as source concentrations, depth to source, and building characteristics. Case studies reviewed (Section 2) suggest that the potential for a complete PVI pathway may exist at fuel terminal, petroleum refinery and petrochemical sites (referred to as terminal and refinery sites) with large volume LNAPL releases, particularly where there are large buildings or a capping effect based on geologic conditions. The empirical data analysis of surface type scenario indicated an apparent increase in frequency of depleted oxygen below building foundations for fuel terminal, refinery, and petrochemical sites, but not for UST sites.

The mathematical modeling studies reviewed support the empirical analysis for dissolved PHC sources in that model simulations sources predict very low vapor attenuation factors, except for small separation distances (i.e., less than about 5 ft [1.5 m]) between vapor sources and buildings. For LNAPL vapor sources, three-dimensional model simulations for a residential house scenario and homogeneous soil conditions predict that a vertical separation distance on the order of 23 ft (7.0 m) is required for aerobic reaction front development within the unsaturated zone below the building foundation. There are both potentially conservative aspects associated with the modeling studies reviewed (e.g., simulations did not include oxygen transport through the foundation) and non-conservative aspects (e.g., limited evaluation of layered soil deposits or larger buildings). The modeling results indicate further evaluation of factors potentially influencing oxygen supply and demand, such as source vapor concentration, source size, building size, surface cover, soil layer properties, and natural soil oxygen demand, is warranted for the LNAPL source scenario.

8.2 Methods and Characteristics of the Database

The results of the analysis may be used to derive inclusion distances based on the probability of vapor concentrations being less than defined thresholds for various separation distances between a benzene source and an overlying building and qualitative comparisons of soil vapor concentrations to risk-based soil vapor concentrations for other compounds. The clean soil method is also an acceptable method for defining inclusion distances, but is less accurate when the vertical concentration attenuation is poorly resolved (i.e., when soil gas probes are more than about 5 to 10 ft apart).

The database is representative of a broad range of environmental site conditions, climatic conditions (including relatively dry areas such as Utah), soil types, and land-surface covers that may be found at UST sites. Although the data analysis suggests that the type of surface cover (e.g., building foundation, pavement, open ground) can have an effect on the attenuation of benzene vapor and oxygen concentrations, the database includes sub-slab or vapor data from deeper distances below buildings for 39 sites with small to medium sized buildings. The dataset is considered sufficiently large and robust such that exclusion distances derived from the analysis will include the potential influence of surface cover.

The sources of uncertainty associated with the empirical analysis, and for which additional validation studies should be considered, include the following:

- Influence of methanogenesis on oxygen demand and specifically the effect of ethanol content in gasoline on methane generation rates and aerobic biodegradation of PHC vapors;
- Effect of extensive high organic matter content soils (e.g., peat) with potentially high natural oxygen demand;
- Effect of possible capping through either large buildings and/or certain geologic conditions (wet surface clay underlain by coarse-grained soils) where there may be increased potential for oxygen limitations;
- Limited knowledge of vapor attenuation behavior in fractured bedrocks (although the Australian database appears to indicate less attenuation than for soil geologic settings, as described in Appendix F).
- Limited soil vapor data for fuel terminal, refinery, and petrochemical sites and vapor attenuation behavior of aliphatic compounds such as 2,2,4-TMP; and

- Absence of soil vapor data for lead scavengers, EDB and 1,2-DCA.

8.3 Data Analysis Results

For dissolved sources, the vertical distance method indicates that the probability of benzene vapor concentrations being less than the defined concentration thresholds (50 and 100 µg/m^3) is 94 to 97 percent (Kaplan-Meier statistics) for small source-separation distances (as little as 0 ft), meaning that PVI is unlikely to occur unless a dissolved source is very close to a building foundation. For development of exclusion distances for dissolved sites, allowance should be made for uncertainty in water table elevations due to seasonal variability. For LNAPL sources at UST sites, the vertical distance method indicates that there is a high probability that benzene vapor concentrations will be less than the defined thresholds at distances greater than about 15 ft (4.6 m) when just UST facilities are considered. For fuel terminal, refinery, and petrochemical sites, the data indicate larger distances are required for benzene vapor concentrations to attenuate to similarly low concentrations.

The data indicate a weak correlation between benzene concentrations in groundwater and deep soil vapor for both dissolved and LNAPL sources. However, for the clean soil method, an approximate trend was observed where the clean soil thicknesses needed for benzene vapor attenuation increased when dissolved benzene concentrations were above approximately 5 mg/L (i.e., indicative of LNAPL source zones). The implication of this result is that there is a basis for utilizing groundwater concentrations to identify LNAPL source zones, but that groundwater concentrations cannot be correlated to inclusion distances.

8.4 Exclusion Distance Assessment Framework

The assessment framework for vertical exclusion distances requires identification of the PHC source type (dissolved phase or LNAPL) based on a sufficiently intensive and comprehensive site investigation and multiple lines of evidence approach for LNAPL indicators similar to that described earlier in this report (see **Table 4**), consisting of:

- Collection of continuous soil cores in inferred LNAPL zones;
- Field tests consisting of headspace vapor monitoring, shake and dye tests, visual observations, etc.
- Groundwater monitoring for presence of LNAPL;
- Monitoring of depth to groundwater including seasonal monitoring (needed to identify potential top of the contamination zone);
- Soil and groundwater chemistry testing;
- Geophysical methods such as ultraviolet induced fluorescence where available.
- Soil gas monitoring data where available or warranted.

It is recommended that LNAPL sites be identified primarily by direct indicators (i.e., LNAPL presence). Groundwater and soil concentration thresholds for benzene and potentially other chemical parameters may also be useful, but given the uncertainty in the relation between groundwater and soil vapor concentrations, groundwater and soil chemistry should not be the primary factor for LNAPL indicator screening. If soil gas data are available, elevated aliphatic concentrations (e.g., hexane) may also be indirect indictor for the presence of LNAPL (e.g., see Appendix E and Lahvis et al., In prep.).

Buffer distances to account for uncertainty in the empirical data and site investigation should be considered (i.e., relative to inclusion distances based on this analysis). There is uncertainty for all source scenarios considered, but it is greatest for fuel terminal, refinery, and petrochemical sites. Given that the thickness of clean soil (with no LNAPL present) is an important factor, the assessment framework should address data requirements for LNAPL source zone assessment and collection of data that may affect the inclusion distances, such as water table fluctuations, the height of the capillary fringe, and building location. The inclusion of soil gas testing and minimum oxygen thresholds in the framework would reduce the uncertainty in the assessment process but may not be warranted provided there is sufficient rigor in the site characterization approach to delineate PHC sources, define clean soil zones, and apply robust methods for identifying LNAPL versus dissolved sites.

An inclusion distance approach for LNAPL sources should also include criteria designed to capture sites that fall outside of the findings of the above analysis, including

- fuel terminal, refinery, and petrochemical sites (related to size of petroleum release),
- high organic-rich soils (e.g., peat),
- large building foundations (e.g., associated with apartment complexes or commercial/industrial buildings),
- fractured bedrock, and
- subsurface utilities that act as significant preferential pathways (i.e., where the utility connects a LNAPL-impacted soil zone with the building).

Future research may indicate certain ethanol contents in gasoline may also warrant inclusion and PVI assessments because of their tendency to generate methane, and consume oxygen that is needed for the biodegradation of PHCs.

Because the observed differences in vapor attenuation between UST and non-UST (e.g., fuel terminal, refinery, or petrochemical) sites are inferred to be associated primarily with the volume of the petroleum release, it might seem reasonable to try and define a threshold release volume of concern that would apply to UST sites. However, there are limited data that would enable definition of such a threshold, and a simpler approach based on site type is recommended given that releases at UST sites are typically much smaller than those at fuel terminal, refinery, or petrochemical sites.

8.5 Lateral Inclusion Distances

Greater attenuation of PHC vapors is expected when hydrocarbon sources are offset laterally from buildings compared with sources that are directly below buildings. The modeling studies reviewed in this report indicate greater hydrocarbon vapor attenuation in the lateral compared to vertical direction. In concept, the modeling results suggest similar lateral inclusion distances could be applied as the vertical distances estimated from the current analysis. However, from a practical standpoint, the uncertainty associated with delineating a PHC source near existing or future buildings because of typical data collection density may warrant larger lateral distances than those based on the vertical distance analysis. Recommendation of lateral distances is beyond the scope of this report.

8.6 Comparison with Other Studies

Four different PHC data analysis efforts were conducted in roughly the same time frame as this one:

- Davis [2009],
- Lahvis et al. [In prep.],
- Wright [2011], and
- Peargin and Kolhatkar [2011]).

All five analysis efforts (including this one) support essentially the same inclusion distances for PHC UST sites, in spite of differences in the base data analyzed and each study's approach to the analysis. This suggests an underlying consistency in mechanisms for PHC biodegradation in the subsurface and supports the protectiveness of the use of these distances as inclusion criteria for UST petroleum release sites.

9. Findings and Conclusions

Approaches for assessing PVI that do not account for aerobic biodegradation processes are overly conservative because they do not take into account a proven mechanism for attenuating PHC concentrations in the subsurface. The statistical analysis of soil gas data drawn from the 74 sites[14] presented in this report and accompanying database, along with four similar but distinct efforts, provides an opportunity for developing a screening approach for PHC compounds. The inclusion distance approach is based on the observed attenuation of PHCs over a characteristic separation distance beyond which there is limited potential for a complete PVI pathway. The focus of this analysis was primarily on evaluating PVI at UST sites with petroleum fuel releases, although data from other types of sites (fuel terminals, petroleum refineries, petrochemical facilities) were also considered.

Findings from analysis of dissolved sources in the PVI database include:

- For the vertical distance method, approximately 97 percent of the benzene soil vapor concentrations are less than 100 µg/m^3 and 94 percent of the concentrations are less than 50 µg/m^3 for contamination source-to-building separation distances as small as 0 ft. For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations for separation distances greater than 3 ft (0.9 m).
- For the clean soil method, the 95th percentile vertical clean soil thickness for benzene vapor attenuation to below 100 µg/m^3 is approximately 5.4 ft (1.6 m).

---

[14] Some analyses and findings are based on fewer than 74 sites, see Appendix B for details on data.

- The analysis indicates there is a low probability of exceeding risk-based concentrations even for small separation distances.

Findings from analysis of LNAPL sources at UST sites in the PVI database include:

- Approximately 95 percent of the benzene soil vapor concentrations are less than 100 μg/m^3, and 93 percent of the concentrations are less than 50 μg/m^3 at a contamination source-to-building separation of approximately 15 ft (4.6 m). For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations beyond 11 ft (3.4 m).
- For the clean soil method, the 95th percentile vertical clean soil thickness for benzene vapor attenuation is approximately 13.5 ft (4.1 m).

Findings from analysis of LNAPL sources at fuel terminal, refinery, and petrochemical (non-UST) sites in the PVI database include:

- For the vertical distance method, approximately 90 percent of the benzene soil vapor concentrations are less than the thresholds for a contamination source-to-building separation distance of approximately 18 ft (5.5 m); the probability does not increase beyond 90 percent beyond this distance because data are limited for larger separation distances. For other compounds evaluated, measured soil vapor concentrations are less than the risk-based concentrations beyond 12 ft (3.6 m).
- For the clean soil method, there are insufficient data to estimate percentiles, but the maximum vertical clean soil thickness for benzene vapor attenuation is approximately 20 ft (6.1m).

Other conclusions from this work include:

- The available data indicate benzene is the risk driver for the sites evaluated, with exceedances of the risk-based vapor concentrations for benzene occurring at larger contamination source–building separation distances than observed for the other PHCs with EPA toxicity values.
- There was significantly less attenuation in vapor concentrations for the aliphatic hydrocarbon 2,2,4-TMP compared with benzene, although data were relatively limited. However 2,2,4-TMP does not have a toxicity benchmark and so cannot be evaluated in the vertical distance or clean soil method.
- The data analysis indicates a poor correlation between benzene concentrations in groundwater and deep soil vapor taken above a groundwater source. The implication is that a screening approach for vapor intrusion based on groundwater concentrations is not appropriate for PVI sites. However, groundwater concentrations can be used as an approximation to identify LNAPL sources.
- The analysis of surface cover indicated:
  - For LNAPL sources at UST sites, there were lower oxygen concentrations and less benzene vapor attenuation below paved surfaces, but not below buildings, compared to bare ground cover, and

  - For fuel terminal and refinery sites, there were lower oxygen concentrations below buildings but not below paved surfaces. This finding may result from larger petroleum releases and consequent increased oxygen demand at such sites, compared with typical LNAPL releases at UST sites.

  These results are variable and not conclusive as to the effect of surface cover, but they suggest that there can be reduced oxygen availability below hard surfaces (pavement or building foundations) for the sites evaluated.

- Because the vertical distance method evaluation includes soil vapor concentration data from below buildings at 39 sites, the results are considered reasonably robust with respect to the potential influence of surface cover (although further evaluation of this factor is recommended).

Critical factors affecting PVI, and important metrics for site screening, include:

- The facility type (UST versus fuel terminal, refinery, or petrochemical site), which influences the size of the release;
- The PHC source type (dissolved versus LNAPL); and
- The vertical separation distance between the source and receptor (building foundation).

The mathematical modeling studies reviewed strongly support the empirical analysis and inclusion distances for dissolved sources. For LNAPL sources, the modeling generally supports the empirical analysis, but further evaluation of factors potentially influencing oxygen supply and demand is warranted. These factors include source vapor concentration, source size, building size, surface cover and soil layer properties, and natural soil oxygen demand.

The findings of this report have important implications for PHC screening approaches based on the observed attenuation in PHC vapor concentrations and an inclusion distance approach. Inclusionary criteria or conditions not analyzed in this database, but where more detailed PVI assessment is considered warranted, include non-UST facilities, high organic-rich soils (e.g., peat), large building foundations (e.g., associated with apartment complexes or commercial or industrial buildings), and significant subsurface preferential pathways.

Releases of certain ethanol blends of gasoline may also warrant additional consideration for inclusion and PVI assessments, although further research is required to determine the significance of ethanol content with respect to inclusion distances. Biodegradation of ethanol may generate methane at a greater rate than gasoline without ethanol, consuming oxygen that would otherwise be available for biodegradation of PHCs and thus increasing the potential for PVI.

Inclusion criteria may not apply at sites where there is significant methane generation because of the potential for safety hazards, advective soil gas transport and reduced biodegradation of other PHCs (due to oxygen demand represented by methane). High methane generation potential has been documented at large diesel and gasoline spills at non-UST sites.

10. References

Abreu, L.D., R. Ettinger, and T. McAlary. 2009. Simulated Soil Vapor Intrusion Attenuation Factors including Biodegradation for Petroleum Hydrocarbons. *Ground Water Monitoring and Remediation. 29*:105-177.

Abreu, L.D., and P.C. Johnson. 2005. Effect of Vapor Source, Building Separation and Building Construction on Soil Vapor Intrusion as Studied with a Three-Dimensional Numerical Model. *Environmental Science & Technology*. *39*:4550-4561.

Abreu, L.D., and P.C. Johnson. 2006. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings: Influence of Degradation Rate, Source Concentrations. *Environmental Science & Technology*. *40*:2304-2315.

Alaska Department of Environmental Conservation. 2011. *Hydrocarbon Risk Calculator User Manual*. January 4. Prepared by Lawrence Acomb, Geosphere, Inc.

American Petroleum Institute (API). 2012. BioVapor Indoor Vapor Intrusion Model. Available at http://www.api.org/Environment-Health-and-Safety/Clean-Water/Ground-Water/Vapor-Intrusion/. Accessed February 27, 2012.

ASTM (ASTM International). 2006. *Standard Guide for Development of Conceptual Site Models and Remediation Strategies for Light Nonaqueous-Phase Liquids Released to the Subsurface*. E2531-06e1. ASTM International, West Conshohocken, PA. Available at www.astm.org.

Atlas, R.M. 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiological Reviews*. *45*(1):180-209.

Branco, F.A., and J. de Brito. 2004. *Handbook of Concrete Bridge Management*. American Society of Civil Engineers (ASCE), ASCE Press, Reston, VA.

Breyer, L., and J.B. Cowart. 2004. Attenuation factors for hydrocarbons associated with a diesel spill. Presented at *U.S. EPA Vapor Intrusion Attenuation Workshop: A Study of Observed Vapor Intrusion Attenuation.*14th Annual AEHS West Coast Conference on Soils, Sediments and Water. San Diego, CA. March 15-18.

Bruce, L., T. Miller, and B. Hockman. 1991. Solubility versus Equilibrium Saturation of Gasoline Compounds: A Method to Estimate Fuel/Water Partition Coefficient Using Solubility or Koc. In: *Proceedings of the NWWA/API Conference on Petroleum Hydrocarbons in Ground Water*, p. 571-582, by National Water Well Association, Dublin, OH. Available at http://info.ngwa.org/gwol/pdf/910155295.PDF.

California EPA. 2011. *Final Guidance for the Evaluation and Mitigation of Subsurface Vapor Intrusion to Indoor Air (Vapor Intrusion Guidance)*. Department of Toxic Substances Control. California Environmental Protection Agency. Sacramento, CA. October.

Davis, R.V. 2009. Bioattenuation of Petroleum Hydrocarbon Vapors in the Subsurface: Update on Recent Studies and Proposed Screening Criteria for the Vapor-Intrusion Pathway. *LUSTLine*. *61*:11-14.

Davis, R.V. 2010. Evaluating the Vapor Intrusion Pathway: Subsurface Petroleum Hydrocarbons and Recommended Screening Criteria. 22nd Annual U.S. EPA National Tanks Conference, Boston, MA. September 20-22.

Davis, R.V. 2011a. Evaluating the Petroleum Vapor Intrusion Pathway: Studies of Natural Attenuation of Subsurface Petroleum Hydrocarbons & Recommended Screening Criteria. AEHS 21st Annual West Coast International Conference on Soil, Sediment, Water & Energy, Mission Valley, San Diego, CA. March 15.

Davis, R.V. 2011b. Attenuation of Subsurface Petroleum Hydrocarbon Vapors: Spatial and Temporal Observations. AEHS 21st Annual West Coast International Conference on Soil, Sediment, Water & Energy, Mission Valley, San Diego, CA. March 16.

Davis, G.B., B.M. Patterson, and M.G. Trefry. 2009. Evidence for Instantaneous Oxygen-Limited Biodegradation of Petroleum Hydrocarbon Vapors in the Subsurface. *Groundwater Monitoring and Remediation.* 29:126-137.

DeVaull, G.E. 2007a. Indoor Vapor Intrusion with Oxygen-Limited Biodegradation for a Subsurface Gasoline Source. *Environmental Science & Technology. 41*:3241-3248.

DeVaull, G.E. 2007b. Indoor Air Vapor Intrusion: Predictive Estimates for Biodegrading Petroleum Chemicals. Presented at Air and Waste Management Association (A&WMA) Specialty Conference: Vapor Intrusion: Learning from the Challenges, Providence, RI. September 26-28.

DeVaull, G.E. 2010. Vapor Intrusion from Subsurface to Indoor Air: Biodegradable Petroleum Vapors versus Recalcitrant Chemicals. Presented at Vapor Intrusion 2010: Air & Waste Management Association (A&WMA) Conference, Chicago, IL. September 29-30.

DeVaull, G.E. 2011. Biodegradation Rates for Petroleum Hydrocarbons in Aerobic Soils: A Summary of Measured Data. Presented at International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, NV. June 27-30.

DeVaull, G.E., R.A. Ettinger, J.P. Salinitro, and J.B. Gustafson. 1997. Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) Degradation in Vadose Zone Soils during Vapor Transport: First Order Rate Constants. Presented at NWWA/API Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection, and Remediation, National Water Well Association, Houston, TX. November 12-14.

Fischer, M.L., A.J. Bentley, K.A. Dunkin, A.T. Hodgson, W.W. Nazaroff, R.G. Sextro, and J.M. Daisey. 1996. Factors Affecting Indoor Air Concentrations of Volatile Organic Compounds at a Site of Subsurface Gasoline Contamination. *Environmental Science & Technology. 30*:2948-2957.

Fitzpatrick, N.A., and J.J. Fitzgerald. 2002. An Evaluation of Vapor Intrusion into Buildings through a Study of Field Data. *Soil and Sediment Contamination. 11*:603-623.

Friebel, E., and P. Nadebaum. 2011. *Health Screening Levels for Petroleum Hydrocarbons in Soil and Groundwater: Part 1: Technical Development Document. CRC for Contamination Assessment and Remediation of the Environment*. Technical Report No. 10.

Golder Associates. 2006. *Investigation of Indoor Air Quality in Structures Located above VOC-Contaminated Groundwater. Part 1: Evaluation of Soil Vapor Intrusion at Mount Holly Site, New Jersey*. Submitted to New Jersey Department of Environmental Protection. July.

Grathwohl, P. and U. Maier. 2002. Natural Attenuation of Volatile Hydrocarbons in Unsaturated Soil Zone. *Agricultural Sciences. 7*:9-15.

Helsel, D.R. 2005. *Nondetects and Data Analysis, Statistics for Censored Environmental Data*. John Wiley and Sons, New York.

Helsel, D.R. 2006. Fabricating Data: How Substituting Values for Non-detects Can Ruin Results, and What Can be Done about It. *Chemosphere. 65*:2434-2439.

Hers, I., J. Atwater, L. Li, and R. Zapf-Gilje. 2000. Evaluation of Vadose Zone Biodegradation of BTX Vapours. *Journal of Contaminant Hydrology*. *46*:233-264.

Hers, I., D. Evans, R. Zapf-Gilje, and L. Li. 2002. Comparison, Validation and Use of Models for Predicting Indoor Air Quality from Soil and Groundwater Contamination. *Journal of Soil and Sediment Contamination. 11*(4):491-527.

Hers, I., P. Jourabchi, M. Lahvis, P. Dahlen., E.H. Luo, P. Johnson, and U. Mayer. In preparation. Cold Climate Study of Soil Vapor Intrusion at a Residential House above a Petroleum Hydrocarbon Plume.

Hers, I., R. Zapf-Gilje, P. Johnson, and L. Li. 2003. Evaluation of the Johnson and Ettinger Model of Indoor Air Quality. *Ground Water Monitoring and Remediation. 23*:119-133.

Holden, P.A., L.J. Halverson, and M.K. Firestone. 1997. Water Stress Effects on Toluene Biodegradation by *Pseudomonas putida*. *Biodegradation. 8*:143-151.

Illinois Department of Public Health. 2010. Letter Health Consultation, Vapor Intrusion Event, Hartford Residential Community, Hartford, IL. February 24.

Jewell, K.P. and J.T. Wilson. 2011. A New Screening Method for Methane in Soil Gas Using Existing Groundwater Monitoring Wells. *Groundwater Monitoring and Remediation*. *31*(3): 82-94.

Johnson, P.C. 2005. Identification of Application-Specific Critical Inputs for the 1991 Johnson and Ettinger Vapor Intrusion Algorithm. *Groundwater Monitoring & Remediation. 25*(1):63-78.

Johnson, P.C., and R.A. Ettinger. 1991. Heuristic Model for Predicting the Intrusion Rate of Contaminant Vapors into Buildings. *Environmental Science & Technology*. *25*:1445-1452.

Jourabchi, P., N. Sihota, U. Mayer, I. Hers, and G. DeVaull. 2012. Effects of Ethanol Blended Gasoline Release on Methane Generation and Soil Vapor Transport: Preliminary Results of Biogas Generation Experiments and Soil Vapor Modeling. Presentation at 2012 National Tanks Conference & Expo, March 1-21, St. Louis, MO.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1983. Behavior Assessment Model for Trace Organics in Soil: I. Model Description. *Journal of Environmental Quality*. *12*:558-564.

Kaplan, E.L., and P. Meier. 1958. Nonparametric Estimation from Incomplete Observations. *Journal of the American Statistical Association. 53*:457-481.

Kobayashi, K., and K. Shuttoh. 1991. Oxygen Diffusivity of Various Cementitious Materials, *Cement and Concrete Research*. *21*:273-284.

Lahvis, M.A., and A.L. Baehr. 1996. Estimating Rates of Aerobic Hydrocarbon Biodegradation by Simulation of Gas Transport in the Unsaturated Zone. *Water Resources Research. 32*:2231-2249.

Lahvis, M.A., and A.L. Baehr. 1999. Quantification of Aerobic-Biodegradation and Volatilization Rates of Gasoline Hydrocarbons near the Water Table during Natural-Attenuation Conditions. *Water Resources Research. 35*:753-765.

Lahvis, M.A., I. Hers, R. Davis, J. Wright, and G.E. DeVaull. In preparation. Vapor Intrusion Screening Criteria for Application at Petroleum UST Release Sites.

Leahy, J.G., and R.R. Colwell. 1990. Microbial Degradation of Hydrocarbons in the Environment. *Microbiological Reviews. 54*(3):305-315.

Leeson, A., and R.E. Hinchee. 1996. *Principles and Practices of Bioventing. Volume 1: Bioventing Principles* and Volume 2: *Bioventing Design*. Battelle Memorial Institute. September.

Luo, H., P. Dahlen, and P.C. Johnson. 2010. Hydrocarbon and Oxygen Transport in the Vicinity of a Building Overlying a NAPL Source Zone. Proc. of Air Waste Management Vapor Intrusion Conference, Chicago, IL. September 28-30.

Luo, H., P. Dahlen, P.C. Johnson, T. Peargin, and T. Creamer. 2009. Spatial Variability of Soil-Gas Concentrations Near and beneath a Building Overlying Shallow Petroleum Hydrocarbon–Impacted Soils. *Ground Water Monitoring & Remediation. 29*:81-91.

Luo, H., C. Holton, and P.C. Johnson. 2012. Field Study and Numerical Simulation of Indoor Air Sources Effects on Soil Gas Chemical Concentrations at a Vapor Intrusion Study Site. The 22nd Annual International Conference on Soil, Water, Energy, and Air. March 19-22, San Diego, CA.

McAlary, T., P. Nicholson, D. Bertrand, H. Groenevelt, and R. Ettinger. 2010. A Case Study on the Influence of Aerobic Biodegradation on Vapor Intrusion at a Former Refinery Property. Chapter 13 in *Vapor Emission to Outdoor Air and Enclosed Spaces*, S. Saponaro, E. Sezenna, and L. Bonomo, eds. Nova Science Publishers, Inc., Hauppauge NY.

Madigan, M.T., J.M. Martinko, D.P. Clark, and D.A. Stahl. 2010. *Brock's Biology of Microorganisms*. Prentice Hall, NJ.

Massachusetts Department of Environmental Protection (MADEP). 2003. Updated Petroleum Hydrocarbon Fraction Toxicity Values for the VPH/EPH/APH Methodology. November.

McHugh, T.E., R. Davis, G. DeVaull, H. Hopkins, J. Menatti, and T. Peargin. 2010. Evaluation of Vapor Attenuation at Petroleum Hydrocarbon Sites: Considerations for Site Screening and Investigation. *Soil and Sediment Contamination. 19*:1-21.

McHugh, T., P.C. De Blanc, and R.J. Pokluda. 2006. Indoor Air as a Source of VOC Contamination in Shallow Soils Below Buildings. *Soil & Sediment Contamination. 15*:103-122.

Michalski, P., S. Thompson, C. DeWolf, P. Nicholson, and T. McAlary. 2012. Effects of Alternate Petroleum Hydrocarbon Sources in the Vadose Zone on the Vapor Intrusion Pathway beneath a Residential Community. Proceedings, AWMA Vapor Intrusion Specialty Conference, Denver, CO. October.

Nelson, D.K., T.M. Lapara, and P.J. Novak. 2010. Effects of Ethanol-Based Fuel Contamination: Microbial Community Changes, Production of Regulated Compounds, and Methane Generation. *Environmental Science and Technology. 44*:4525-4530.

NJ DEP (New Jersey Department of Environmental Protection). 2012. *Vapor Intrusion Technical Guidance. Version 2.0*. January. Available at http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig.htm.

Patterson, B., and G. Davis. 2009. Quantification of Vapor Intrusion Pathways into a Slab-on-Ground Building under Varying Environmental Conditions. *Environmental Science and Technology. 43*:650-656.

Peargin, T. and R. Kohlhatkar. 2011. Empirical Data Supporting Groundwater Benzene Concentration Exclusion Criteria for Petroleum Vapor Intrusion Investigations. Proc. of Battelle Presentation at International Symposium on Bioremediation and Sustainable Environmental Technologies, Reno, NV, June 27-30.

Ririe, T. and R. Sweeney. 1995. Fate and Transport of Volatile Hydrocarbons in the Vadose Zone. Proceedings of 1995 Petroleum Hydrocarbon and Organic Chemicals in Groundwater, Houston, TX, pp. 529-542.

Ririe, G.T., R.E. Sweeney, and S.J., Daugherty. 2002. A Comparison of Hydrocarbon Vapor Attenuation in the Field with Predictions from Vapor Diffusion Models. *Soil and Sediment Contamination. 11*:529-544.

Robinson, N.I. and L. Turczynowicz. 2005. One- and Three-Dimensional Soil Transportation Models for Volatiles Migrating from Soils to House Interiors. *Transport Porous Media. 59*:301-323.

Roggemans, S., C.L. Bruce, and P.C. Johnson. 2001. Vadose Zone Natural Attenuation of Hydrocarbon Vapors: An Empirical Assessment of Soil Gas Vertical Profile Data. *Soil and Groundwater Research Bulletin 15*. American Petroleum Institute, Washington, DC, December.

Sanders, P.F., and I. Hers. 2006. Vapor Intrusion into Homes over Gasoline-Contaminated Ground Water in Stafford, New Jersey. *Groundwater Monitoring and Remediation. 26*(1):63-72.

Spalding, R.F., M.A. Toso, M.E. Exner, G. Hattan, T.M. Higgins, A.C. Sekely, and S.D. Jensen. 2011. Long Term Groundwater Monitoring Results at Large, Sudden Denatured Ethanol Releases. *Ground Water Monitoring and Remediation. 31*(3):69-81.

Sweeney, B. 2012. Temporal Effects on Aerobic Biodegradation of Hydrocarbons in Soil Vapor. AEHS West Coast Conference. San Diego, CA. March. Available at https://iavi.rti.org/WorkshopsAndConferences.cfm.

Tittarelli, F. 2009. Oxygen Diffusion through Hydrophobic Cement-Based Materials. *Cement and Concrete Research. 39*:924-928.

U.S. EPA (Environmental Protection Agency). 1996. *Soil Screening Guidance–User's Guide*. EPA Document Number: EPA540/R-96/018. U.S. Environmental Protection Agency, Washington, DC. March.

U.S. EPA (Environmental Protection Agency). 2002. *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance)*. Office of Solid Waste and Emergency Response, Washington, DC. Available at http://www.epa.gov/osw/hazard/correctiveaction/eis/vapor.htm.

U.S. EPA (Environmental Protection Agency). 2004. *Superfund User's Guide for Evaluating Subsurface Vapor Intrusion into Buildings*. Prepared by Environmental Quality Management, Inc. for EPA. Contract Number: 68-W-02-33.

U.S. EPA (Environmental Protection Agency). 2009. *Composition and Behavior of Fuel Ethanol*. EPA/600/R-09/037. U.S. Environmental Protection Agency, Washington, DC. April.

U.S. EPA (Environmental Protection Agency). 2012a. *Petroleum Hydrocarbons And Chlorinated Hydrocarbons Differ In Their Potential For Vapor Intrusion.* U.S. Environmental Protection Agency, Washington, DC. September.

U.S. EPA (Environmental Protection Agency). 2012b. *EPA's Vapor Intrusion Database: Evaluation and Characterization of Attenuation Factors for Chlorinated Volatile Organic Compounds and Residential Buildings.* U.S. Environmental Protection Agency, Washington, DC. Report 530-R-10-002. February.

U.S. EPA (Environmental Protection Agency). 2012c. *Conceptual Model Scenarios for the Vapor Intrusion Pathway.* U.S. Environmental Protection Agency, Washington, DC. Report 530-R-10-003. February.

Wiedemeier, T.H., M.A. Swanson, J.T. Wilson, D.H. Kampbell, R. Miller, and J.E. Hansen. 1996. Approximation of Biodegradation Rate Constants for Monoaromatic Hydrocarbons (BTEX) in Ground Water. *Ground Water Monitoring and Remediation*. Summer:186-194.

Wilson, J.T., J.W. Weaver, and H. White. In press. *An Approach for Developing Site-Specific Lateral and Vertical Inclusion Zones within which Structures Should be Evaluated for Petroleum Vapor Intrusion due to Releases of Motor Fuel from Underground Storage Tanks*. EPA Issue Paper, Office of Research and Development, Ada, OK.

Wisconsin Department of Natural Resources. 2010. Addressing Vapor Intrusion at Remediation & Redevelopment Sites in Wisconsin. Madison, WI: Department of Natural Resources. PUB-RR-800. December.

Wright, J. 2011. Establishing Exclusion Criteria from Empirical Data for Assessing Petroleum Hydrocarbon Vapour Intrusion. *Program and Proceedings of the 4th International*

Contaminated Site Remediation Conference—2011 CleanUP. Adelaide, South Australia, September 11-15. p. 142-143.

Wright, J. 2012. Evaluation of the Australian Petroleum Hydrocarbon VI Database: Exclusion Criteria. Presented at: Recent Advances to VI Application & Implementation—A State-of-the-Science Update. AEHS West Coast Conference. San Diego, CA. March. Available at https://iavi.rti.org/WorkshopsAndConferences.cfm?PageID=documentDetails&AttachID=549.

Yao, Y., R. Shen, K.G. Pennell, and E.M. Suuberg. 2011. Comparison of the Johnson-Ettinger Vapor Intrusion Screening Model Predictions with Full Three-Dimensional Model Results. *Environmental Science & Technology. 45*(6):2227-35.

Zobell, C.E. 1946. Action of Microorganisms on Hydrocarbons. *Bacteriological Reviews. 10*(1-2):1-49.

Zwick, T.C., A. Leeson, R.E. Hinchee, L. Hoeppel, and L. Bowling. 1995. Soil Moisture Effects During Bioventing in Fuel-Contaminated Arid Soils. Third International In-Situ and On-Site Bioreclamation Symposium. In-Situ Aeration, v. 3, Batelle Press, San Diego, CA.

Appendix A. Review of Exclusion/Inclusion Distances in Existing Vapor Intrusion Guidance

Many state regulatory approaches exclude sites from the need for PVI assessments if they are more than a specified distance from the source of vapor contamination. Distances applied in this context are referred to as inclusion distances in this report.[15] A default distance adopted by many states is 100 ft (30 m) in the lateral, and in some cases, vertical direction. However, guidance for New Hampshire, New Jersey, Connecticut, and Massachusetts specifies a 15- to 30-ft (4.6- to 9.1-m) exclusion or inclusion distance for aerobically biodegradable chemicals.[16] New Hampshire and New Jersey specify this distance applies laterally and vertically, whereas Connecticut more generically indicates inclusion distances as extending from contaminated groundwater. The criterion for Massachusetts is dependent on whether volatile LNAPL is present. The technical justification for exclusion distance criteria is relatively limited or not provided in the guidance by these jurisdictions. This is understandable given that detailed evaluations of empirical data and/or modeling studies to support inclusion or exclusion distances are a recent development.

Several states are in the process of developing or have recently developed guidance for PHCs based on a pathway exclusion or inclusion distance approach. A summary of guidance from New Jersey, California, and Wisconsin follows:

- The New Jersey Department of Environmental Protection (NJ DEP, 2012) recommends a PVI investigation based on a 30-ft (9.1-m) critical distance criterion for PHC-related groundwater contamination and a 100-ft (30-m) criterion for PHC-related free product contamination. As an alternative approach, NJ DEP (2012) allows for an exclusion distance approach based on benzene concentrations for gasoline contamination. A PVI investigation is not necessary if the vertical separation distance between the water table (all references to water table are for seasonal high conditions) and building slab is:
  - At least 10 ft (3.0 m) for a benzene groundwater concentration ≤ 1,000 μg/L;
  - At least 5 ft (1.5 m) for a benzene groundwater concentration ≤ 100 μg/L; or
  - At least 5 ft (1.5 m) for oxygen ≥ 2 percent (v/v) in the unsaturated zone and a benzene groundwater concentration ≤ 1,000 μg/L.

    The gasoline exclusion criteria apply only when all of the following four conditions are met: 1) The building is relatively small, 2) The area around the building is not extensively paved, 3) Clean soil exists between the water table and

---

[15] States may use the term "inclusion distance" or "exclusion distance" in their guidance. Either term defines a safe distance between the petroleum source and likely receptors in buildings. In the main body of this document, we use inclusion distance, but in this appendix we may use either exclusion or inclusion, depending on which term was used in the state guidance we are discussing.

[16] The U.S. EPA's 2002 *Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils* specified vertical and lateral exclusion distances of 100 ft (30 m), based on empirical observations of the approximate distance from the interpolated edge of chlorinated solvent plumes where indoor vapor detections were observed. This guidance did not address vapor intrusion from petroleum releases.

the building, and 4) NAPL is not present within 30 ft (9.1 m) of the building (vertically and horizontally) (see NJ DEP [2012] for additional details).

- The California EPA (2011) presents an exclusion distance approach to managing retail petroleum sites, characterized as a low-threat closure scenario. The exclusion distances were based on a review of empirical data (primarily Lahvis [2011] and Davis [2009]) and modeling studies (primarily Abreu et al. [2009]). Four scenarios are defined with the following benzene exclusion distance criteria:
  - **Scenario 1—Unweathered LNAPL on groundwater:**
    - A 30-ft (9.1-m) vertical bioattenuation zone between an unweathered LNAPL (residual or free-phase) source and a building foundation.
  - **Scenario 2—Unweathered LNAPL in soil:**
    - A 30-ft (9.1 m) lateral and vertical separation distance between an unweathered LNAPL (residual or free-phase) source in soil and a building foundation.
  - **Scenario 3—Dissolved phase benzene concentrations in groundwater:**
    - With no oxygen measurements:
      - A 5-ft (1.5 m) vertical separation distance between a dissolved-phase benzene source < 100 µg/L and a building foundation.
      - A 10-ft (3.0 m) vertical exclusion distance for a dissolved-phase benzene source < 1,000 µg/L and a building foundation.
    - With oxygen > 4 percent:
      - A 5-ft (1.5 m) vertical separation distance between a dissolved-phase benzene source < 1,000 µg/L and a building foundation.
  - **Scenario 4—Direct measurement of soil gas concentrations:**
    - Application of a bioattenuation (additional attenuation) factor of 1,000 times to risk-based soil gas criteria (i.e., vapor sources) located within 5 ft (1.5 m) of a building foundation.
- Wisconsin’s Department of Natural Resources (2010) in their guidance states that where no petroleum odors are detected, PVI can be ruled out at most petroleum release sites with low source concentrations where there is 5 ft (1.5 m) in the horizontal and vertical directions of clean, unsaturated soil with an oxygen content ≥ 5 percent between the residual petroleum and the building. Larger exclusion distances are specified when free product is present (30 ft [9.1 m]) or benzene concentrations in groundwater exceed 1 mg/L (20 ft [6.1 m]). When these distance thresholds and other criteria (e.g., no preferential pathways, no fractured bedrock) are met, a PVI assessment is not required.

Appendix B. Data Quality and Database Content

Table B-1 provides data quality information by site in the PVI database. Each site was scored considering conceptual site model (CSM) robustness using a three-point ranking (3 highest, 1 lowest) and data quality (DQ) using a five-point ranking (5 highest, 1 lowest). CSM robustness rankings included:

- **CSM-3**: Well-developed CSM, appropriately located soil gas probes, vertical soil gas profiles, well-characterized contamination source (NAPL and dissolved), and available ancillary data (e.g., soil properties).
- **CSM-2**: Less well-developed CSM with well-located probes but with more limited soil gas locations (e.g., single location), and a reasonably well characterized contamination source.
- **CSM-1**: Limited data to develop CSM and to evaluate appropriateness of soil gas probe locations and results, generally a single soil gas location, limited or no CSM-related information, and/or inadequate data to perform clean soil thickness analyses.

DQ rankings were defined as follows:

- **DQ-5**: Very high quality data, with fully documented QA/QC, permanent probes, leak tracer and/or pneumatic testing, and fixed gas data consistent with hydrocarbon vapor concentrations. In some cases, a site’s data have been given a 5 ranking when not all of these aspects were met, but when there is well-developed CSM and the research is peer reviewed.
- **DQ-4**: High quality data, with QA/QC mostly documented, generally permanent probes and leak tracer testing, and fixed gas data that are consistent with hydrocarbon vapor concentrations.
- **DQ-3**: Moderate quality data, with some QA/QC documentation and fixed gas data that may be limited in quantity or inconsistent with hydrocarbon vapor concentration data.
- **DQ-2**: Low to moderate data quality, limited QA/QC documentation (but typically still collected under state program oversight), limited data documentation, no fixed gas results. Minimum data quality for inclusion in database analysis.
- **DQ-1**: Low quality data, unacceptable data quality indicators or methods. Data excluded from all analyses.

A detailed data quality table can also be found in the PVI database that accompanies this report.

The PVI database contents are summarized in **Tables B-2** and **B-3**. Table B-2 provides basic site information, including facility type, the type of release, soil type, building information, and what media were sampled (e.g., soil, groundwater, soil gas, indoor air). Table B-3 provides counts of by site and analyte of soil vapor analyses in PVI database.

Table B-1. Data Quality and Conceptual Site Model Robustness Information in PVI Database

Site Name	State	CSM Rank[a]	Data Quality Rank[b]	Probe Type	Leak Tracer[c]	Purging Procedure?	Pneumatic Testing?	Fixed Gas Data?	Fixed Gas and HC Vapor Data Consistent?	Acceptable VOC Analysis Method?	VOC Analysis Method	Laboratory QA/ QC?	Peer Review or Research Program	Federal or State Program	Comment
Alameda Naval Air Station	CA	3	5	Permanent	N	Y	Y	Y	Y	Y	GC/PID/FID/TCD	Y	Journal	N	
Coachella	CA	3	4	Driven	N	Y	Y	Y	Y	Y	Field GC/PID	N	Journal	N	
Huntington Beach	CA	3	4	Driven	N	Y	Y	Y	Y	Y	Field GC/PID	N	Journal	N	
Mission Valley Terminal	CA	2	4	Driven/ Permanent	Y	Y	N	Y	Y	Y	EPA 8260B/TO-15	N	N	CA DTSC	Geoprobe method used for driven probes
Newport Beach	CA	3	4	Driven	N	Y	Y	Y	Y	Y	Field GC/PID	N	Journal	N	
Port Hueneme	CA	3	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Journal	N	
Former Chevron Station	CA	3	5	Permanent	Y	Y	N	Y	Y	Y	TO-15	N	N	CA DTSC	
Dave's Amoco	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
NYM	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Jacobsen Residence	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Larsons 66	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
D&E Sales	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Moen Oil	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Johnsons Auto	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Midtown Service	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
John's Garage	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Buchannon Nursing	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation

(continued)

Table B-1. Data Quality and Conceptual Site Model Robustness Information in PVI Database (continued)

Site Name	State	CSM Rank[a]	Data Quality Rank[b]	Probe Type	Leak Tracer[c]	Purging Procedure?	Pneu-matic Testing?	Fixed Gas Data?	Fixed Gas and HC Vapor Data Con-sistent?	Accept-able VOC Analysis Method?	VOC Analysis Method	Labor-atory QA/ QC?	Peer Review or Research Program	Federal or State Program	Comment
Red & White Service	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Side Lake Store	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Ossippe Store	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
AC Oil	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Schmunks	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Kennys Oil	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Settes Garage	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Tilson Auto	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Rogers Mobile	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Rub-a-Dub	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Long Shot Trucking	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Eggens Oil	MN	1	2	Unknown	N	N	N	N	NA	Y	TO-15	N	N	MN PCA	Data from MN PCA; limited documentation
Chillum	MD	2	2	Permanent	N	N	N	N	NA	Y	TO-15	N	N	EPA R3	
Reuben's Market	ME	3	3	Permanent	N[d]	Y	Y	Y	N	Y	TO-15	Y	N	ME DEP	Elevated TPH vapor conc. and O2 conc.
Cumberland Farm 1803	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1817	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	

(continued)

Table B-1. Data Quality and Conceptual Site Model Robustness Information in PVI Database (continued)

Site Name	State	CSM Rank[a]	Data Quality Rank[b]	Probe Type	Leak Tracer[c]	Purging Procedure?	Pneumatic Testing?	Fixed Gas Data?	Fixed Gas and HC Vapor Data Consistent?	Acceptable VOC Analysis Method?	VOC Analysis Method	Laboratory QA/ QC?	Peer Review or Research Program	Federal or State Program	Comment
Twin Bridge Market	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1806	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1805	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1839	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1822	ME	3	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
7-Eleven	ME	3	3	Permanent	N[d]	Y	Y	Y	N	Y	TO-15	Y	N	ME DEP	Elevated TPH vapor conc. and O2 conc.
Cumberland Farm 1836	ME	2	4	Permanent	Y	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1829	ME	2	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	
Cumberland Farm 1842	ME	1	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	Site not analyzed; soil gas data are limited
Cumberland Farm 1834	ME	1	4	Permanent	N[d]	Y	Y	Y	Y	Y	TO-15	Y	N	ME DEP	Site not included; soil gas data are limited
Mandan	ND	2	4	Permanent	Y	Y	N	Y	Y	Y	TO-15, TO-13	Y	Conference	N	AEHS presentation; good notes
BP Paulsboro	NJ	3	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Thesis	N	
Hulme Street	NJ	3	4	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	NJDEP	NJ DEP	
Stafford	NJ	3	5	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	NJDEP	NJ DEP	
BP Akron	OH	2	3	Permanent	N	N	N	Y	N	Y	TO-15, ASU GC/FID	N	Thesis	N	
BP Columbiana	OH	2	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Thesis	N	
BP Conneaut	OH	2	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Thesis	N	
BP Kent	OH	2	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Thesis	N	

(continued)

Table B-1. Data Quality and Conceptual Site Model Robustness Information in PVI Database (continued)

Site Name	State	CSM Rank[a]	Data Quality Rank[b]	Probe Type	Leak Tracer[c]	Purging Procedure?	Pneumatic Testing?	Fixed Gas Data?	Fixed Gas and HC Vapor Data Consistent?	Acceptable VOC Analysis Method?	VOC Analysis Method	Laboratory QA/ QC?	Peer Review or Research Program	Federal or State Program	Comment
Former Refinery	OK	3	4	Permanent	Y	Y	N	Y	Y	Y	TO-15, TO-3, Landtec	Y	Book	N	Chapter in peer-reviewed book
Beaufort	SC	3	4	Permanent	N	Y	N	Y	Y	Y		N	Journal	N	
Bountiful Bicycle	UT	3	4	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
Gas & Go #7	UT	3	4	Permanent	Y[e]	N	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
Gold Cross Ambulance	UT	3	3	Permanent	N	Y	N	N	N/A	Y	TO-15	Y	N	UT DEQ	
Hal's Chevron	UT	3	5	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	USEPA ORD	UT DEQ	
Handi Mart	UT	1	2	Driven	N	N	N	Y	Y	Unknown	Unknown	N	Thesis	UT DEQ	Utah State Univ, Ryan Dupont
#102 Chevron	UT	3	4	Permanent	Y	Y	N	Y	Y	Y	EPA 8260B	Y	N	UT DEQ	
Logan Food Mart	UT	3	3	Permanent	N	Y	N	N	N/A	Y	TO-15	Y	N	UT DEQ	
Price Rental Property	UT	2	3	Permanent	N	Y	N	N	N/A	Y	TO-15	Y	N	UT DEQ	
Salina Cash Saver	UT	3	5	Permanent	Y	N	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
Jenkins	UT	3	5	Permanent	N	Y	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
Wheel-In Market	UT	3	3	Permanent	N	N	N	N	N/A	Y	TO-15	Y	N	UT DEQ	
Teasdale Country Store	UT	3	2	Driven	N	N	N	Y[f]	N/A	Y	TO-15	Y	N	UT DEQ	
Tesoro #40	UT	3	5	Permanent	N	Y	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
7-Eleven #23387	UT	3	4	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	N	UT DEQ	
Refinery Site	na	3	4	Permanent	N	N	N	Y	Y	Y	TO-15, ASU GC/FID	N	Thesis	N	
Chatterton Research Site	BC	3	5	Permanent	N	Y	Y	Y	Y	Y	Field GC/PID	Y	Thesis	N/A	
Ottawa	ON	1	1	Permanent	N	N	N	N	N/A	N	Field detector	N	N	N/A	
North Battleford	SK	3	5	Permanent	Y	Y	Y	Y	Y	Y	TO-15	Y	Journal	N/A	

(continued)

Table B-1. Data Quality and Conceptual Site Model Robustness Information in PVI Database (continued)

Site Name	State	CSM Rank[a]	Data Quality Rank[b]	Probe Type	Leak Tracer[c]	Purging Procedure?	Pneumatic Testing?	Fixed Gas Data?	Fixed Gas and HC Vapor Data Consistent?	Acceptable VOC Analysis Method?	VOC Analysis Method	Laboratory QA/ QC?	Peer Review or Research Program	Federal or State Program	Comment
Peace River	AB	3	5	Permanent	Y	Y	Y	Y	Y	Y	TO-15	Y	N	N/A	
Fort Ware	BC	3	4	Permanent	Y	Y	N	Y	Y	Y	TO-15	Y	N	N/A	
Perth	AUWA	3	4	Permanent	N	N	N	Y	Y	Y	GC/MS/TCD	N	Journal	N/A	

Notes

[a] CSM-3: Well-developed CSM, appropriately located soil gas probes, vertical soil gas profiles, well characterized contamination source (NAPL vs. dissolved) and ancillary data (e.g., soil properties)

CSM-2: Less well-developed CSM with well located probes, but with more limited soil gas locations (e.g., single location), reasonably well characterized contamination source

CSM-1: Limited data to develop CSM on and to evaluate appropriateness of soil gas probe locations, generally single soil gas location

[b] DQ-5: Very high quality data, QA/QC is fully documented, includes permanent probes, leak tracer and pneumatic testing, and fixed gas data that is consistent with hydrocarbon vapor concentrations. In some cases, site data has been given a 5 ranking when not all aspects met, but when there is well-developed CSM and peer-reviewed research program.

DQ-4: High quality data, QA/QC is mostly documented, generally includes permanent probes and leak tracer testing, includes fixed gas data that is consistent with hydrocarbon vapor concentrations.

DQ-3: Moderate quality data, some QA/QC documentation, generally fixed gas data, but may be limited in quantity or inconsistent with hydrocarbon vapor concentration data.

DQ-2: Low to moderate data quality, limited QA/QC documentation (but typically still collected under state program), limited data, no fixed gas results. Minimum data quality for inclusion in database analysis.

DQ-1: Low quality data, unacceptable data quality indicators or methods. Data excluded from all analysis.

[c] Leak test results acceptable except as noted.

[d] While Maine sites did not include leak tracer testing, relatively extensive fixed gas analyses were performed. In addition, the fixed gas concentrations before and after collection of the Summa canisters were obtained and reviewed for consistent concentrations

[e] One in seven samples failed the leak tracer test (iso-propanol>10,000 $\mu g/m^3$)

[f] Limited data (one sample).

CA DTSC = California Department of Toxic Substances Control; ME DEP = Maine Department of Environmental Protection; MN PCA = Minnesota Pollution Control Authority;

EPA R3 = U.S. EPA Region 3; NJ DEP = New Jersey Department of Environmental Protection; UT DEQ = Utah Department of Environmental Quality;

Y = yes; N = no; N/A = not applicable; na = not available

Table B-2. Summary of Site Information in PVI Database

								Building Use					Foundation Type			Media Sampled			
Site Name	City	Country	State or Province	Contamination Source	Vapor Source Type	Soil Type	Site Type	Number Buildings	Residential	Smaller Commercial	Larger Commercial	Building Footprint (ft.^{2})	Basement	Slab on Grade	Crawlspace or Dirt Floor	Groundwater	Soil Vapor	Sub-slab Vapor	Soil
Alameda Naval Air Station	Alameda	USA	CA	G	LNAPL	Coarse	UST	1		o		538		o		o	O	o	
Coachella	Coachella	USA	CA	G	LNAPL	Coarse	Terminal										O		
Huntington Beach	Huntington Beach	USA	CA	G	LNAPL	Coarse	UST										O		o
Mission Valley Terminal	San Diego	USA	CA	G, D, J, E	LNAPL	Coarse/Fine	Terminal	2		o	o	1,500–7,200		o		o	O	o	
Newport Beach	Newport Beach	USA	CA	G	LNAPL/Dis	Coarse	UST										O		
Port Hueneme	Port Hueneme	USA	CA	G	LNAPL/Dis	Coarse	UST									o	O		o
Former Chevron Station #9-5669	South San Francisco	USA	CA	G	LNAPL/Dis	Coarse	UST									o	O		o
Dave's Amoco	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
NYM	N/A	USA	MN	G*	Dis	Coarse	UST									o	O		o
Jacobsen Residence	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST									o	O		o
Larsons 66	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
D&E Sales	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
Moen Oil	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
Johnsons Auto	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
Midtown Service	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	O		o
John's Garage	N/A	USA	MN	G*	LNAPL/Dis	N/A	UST										O		

(continued)

Table B-2. Summary of Site Information in PVI Database (continued)

								Building Use					Foundation Type			Media Sampled			
Site Name	City	Country	State or Province	Contami-nation Source	Vapor Source Type	Soil Type	Site Type	Number Buildings	Residential	Smaller Commercial	Larger Commercial	Building Footprint (ft.^{2})	Basement	Slab on Grade	Crawlspace or Dirt Floor	Groundwater	Soil Vapor	Sub-slab Vapor	Soil
Buchannon Nursing Home	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	o		o
Red & White Service	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									o	o		o
Side Lake Store	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									O	o		o
Ossippe Store	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									O	o		o
AC Oil	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									O	o		o
Schmunks	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									O	o		o
Kennys Oil	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST									O	o		o
Settes Garage	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST										o		
Tilson Auto	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST										o		
Rogers Mobile	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST									O	o		o
Rub-a-Dub	N/A	USA	MN	G*	LNAPL/Dis	Coarse	UST									O	o		o
Long Shot Trucking	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST									O	o		
Eggens Oil	N/A	USA	MN	G*	LNAPL/Dis	Fine	UST									O	o		o
Chillum site	Maryland	USA	MD	G	LNAPL/Dis	Coarse	UST									O	o		
Reuben's Market	Milo	USA	ME	G	LNAPL/Dis	Coarse/Fine	UST	1		o		N/A		o		O	o	o e	o
Cumberland Farm 1803	Sandford	USA	ME	G	LNAPL	Coarse	UST	1	O			N/A	o			O	o	o	

(continued)

Table B-2. Summary of Site Information in PVI Database (continued)

Site Name	City	Country	State or Province	Contamination Source	Vapor Source Type	Soil Type	Site Type	Building Use					Foundation Type			Media Sampled			
								Number Buildings	Residential	Smaller Commercial	Larger Commercial	Building Footprint (ft.^{2})	Basement	Slab on Grade	Crawlspace or Dirt Floor	Groundwater	Soil Vapor	Sub-slab Vapor	Soil
Cumberland Farm 1817	Berwick	USA	ME	G	LNAPL/Dis	V.Coarse	UST									O	o		
Twin Bridge Market	Leeds	USA	ME	G	LNAPL/Dis	Coarse	UST									O	o		o
Cumberland Farm 1806	South Portland	USA	ME	G	LNAPL	Coarse	UST									O	o		o
Cumberland Farm 1805	Portland	USA	ME	G	LNAPL/Dis	V.Coarse/Coarse	UST	1			o	3,900		o		O	o	o e	o
Cumberland Farm 1839	Portland	USA	ME	G	LNAPL/Dis	Coarse/Fine	UST									O	o		
Cumberland Farm 1822	Saco	USA	ME	G	LNAPL/Dis	Coarse	UST	1								O	o	o	
7-Eleven	Lewiston	USA	ME	G	LNAPL/Dis	Coarse/Fine	UST	2	O	o		1,500–2,000	o	o		O	o	o e	
Cumberland Farm 1836	North Windham	USA	ME	G	LNAPL/Dis	Coarse	UST	1			o	5,000		o		O	o	o	
Cumberland Farm 1829	Augusta	USA	ME	G	Dis	V.Coarse	UST									O	o		
BP Paulsboro	Paulsboro	USA	NJ	G	LNAPL	Coarse	Terminal	1	O			N/A	o			O	o	o	o
Hulme Street	Mount Holly	USA	NJ	G	Dis	Coarse	UST	3	O			400	o		o	O	o	o	o
Stafford	Stafford	USA	NJ	G	LNAPL/Dis	Coarse	UST	5	O			600–800	o			O	o	o	o
Mandan	Mandan	USA	ND	D	LNAPL	Fine	Refinery	13	O	o	o	varies	o		o	o	o		o

(continued)

Table B-2. Summary of Site Information in PVI Database (continued)

								Building Use					Foundation Type			Media Sampled			
Site Name	City	Country	State or Province	Contami-nation Source	Vapor Source Type	Soil Type	Site Type	Number Buildings	Residential	Smaller Commercial	Larger Commercial	Building Footprint (ft.^{2})	Basement	Slab on Grade	Crawlspace or Dirt Floor	Groundwater	Soil Vapor	Sub-slab Vapor	Soil
BP Akron	Akron	USA	OH	G	LNAPL/Dis	Coarse	UST										O		o
BP Columbiana	Columbiana	USA	OH	G	LNAPL	Fine	Terminal										o		o
BP Conneaut	Conneaut	USA	OH	G	LNAPL	Coarse	UST										o		o
BP Kent	Kent	USA	OH	G	LNAPL	V.Coarse	UST										o		o
Former Refinery	not specified	USA	OK	G	LNAPL	Fine	Refinery	1		o		775		o			o	o	
Beaufort	Beaufort	USA	SC	G	LNAPL	Fine	UST									O	o		
Bountiful Bicycle	Bountiful	USA	UT	G	LNAPL	Fine	UST												o
Gas & Go #7	North Salt Lake	USA	UT	G	LNAPL/Dis	Fine	UST									o	o		
Gold Cross Ambulance	Salt Lake City	USA	UT	G	Dis	Fine	UST	2	O		o	1,500–10,000		o		O	o	o	o
Hal's Chevron	Green River	USA	UT	G	LNAPL/Dis	Fine	UST	2		o		625–2,500	o			O	o	o	o
Handi Mart	Midvale	USA	UT	G	LNAPL	Coarse	UST										o		o
#102 Chevron	Jacksons	USA	UT	G	Dis	Coarse	UST	4	O	o		N/A	o	o		O	o	o	
Logan Food Mart	Logan	USA	UT	G	Dis	Fine	UST	1		o		N/A		o		O		o	o
Price Rental Property	Price	USA	UT	G	LNAPL	Coarse	UST	1		o		N/A							
Salina Cash Saver	Salina	USA	UT	G	LNAPL	Coarse	UST	1			o	2,700		o			o	o	o
Jenkins Oil	Santa Clara	USA	UT	G	LNAPL/Dis	Fine	UST	1		o		1,350		o		O	o	o	
Wheel-In Market	Salt Lake City	USA	UT	G	LNAPL	Fine	UST	1		o		N/A		o		O		o e	

(continued)

Table B-2. Summary of Site Information in PVI Database (continued)

Site Name	City	Country	State or Province	Contamination Source	Vapor Source Type	Soil Type	Site Type	Building Use					Foundation Type			Media Sampled			
								Number Buildings	Residential	Smaller Commercial	Larger Commercial	Building Footprint (ft.^{2})	Basement	Slab on Grade	Crawlspace or Dirt Floor	Groundwater	Soil Vapor	Sub-slab Vapor	Soil
Teasdale Country Store	Teasdale	USA	UT	G	LNAPL	Coarse	UST	1		o		N/A	o			O		o	o
Tesoro #40	Salt Lake	USA	UT	G	Dis	Fine	UST	2	O			2,200	o 1/2			O		o	
7-Eleven #23387	Murray	USA	UT	G	LNAPL	Fine	UST									O	O		
Refinery Site	Hooven	USA	-	G,D	LNAPL	Coarse	Refinery									O	O		
Peace River	Peace River	Canada	AB	G	LNAPL	Fine/Coarse	UST	0								o	O		
Chatterton Research Site	Delta	Canada	BC	BTX	LNAPL	Coarse	Refinery	1	O			610		o		O	O	o	
Fort Ware	Fort Ware	Canada	BC	D	LNAPL	V. Coarse	UST	0								o	O		
Ottawa	Ottawa	Canada	ON	G,D	Dis	Fine	UST									O	O		
North Battleford	North Battleford	Canada	SK	G	LNAPL/Dis	Coarse	UST	1	O						o	O	O	o	o
Perth	Perth	Australia	WAus	K	LNAPL	Coarse	Refinery	1			o	2,700		o					

For contamination type: G = gasoline, D = diesel, J = jet fuel, E = ethanol, K = kerosene; G* for MN sites inferred to be gasoline-impacted sites, but no confirmatory data provided.

Dis = dissolved. An arbitrary threshold for smaller versus larger building was set as 2,500 ft^2.

Table B-3. Soil Vapor Analyses in PVI Database

Site Name	City	Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	224-Trimethylpentane	Hexane	Heptane	MtBE	1,3-Butadiene	TPH	TPH Method	MADEP TPH Fractions	Oxygen	Carbon	Methane
Alameda Naval Air Station	Alameda	2	0	0	0	0	0	0	0	0	0	12	Iso-pentane	0	12	12	8
Coachella	Coachella	27	0	0	0	0	0	0	0	0	0	0	N/A	0	26	25	26
Huntington Beach	Huntington Beach	26	0	0	0	0	0	0	0	0	0	0	N/A	0	26	26	26
Mission Valley Terminal	San Diego	84	0	0	0	0	0	0	0	0	0	84	TPHg 8260	0	24	22	0
Newport Beach	Newport Beach	20	0	0	0	0	0	0	0	0	0	0	N/A	0	20	20	20
Port Hueneme	Port Hueneme	0	0	0	0	0	0	0	0	0	0	62	GC/FID	0	55	47	0
Former Chevron Station #9-5669	South San Francisco	27	18	18	18	0	0	0	0	0	0	9	Modified TO-3 GC/FID	0	18	18	9
Dave's Amoco	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
NYM	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Jacobsen Residence	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Larsons 66	N/A	4	4	4	4	0	0	3	4	0	0	4	TPH as Gas	0	0	0	0
D&E Sales	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Moen Oil	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Johnsons Auto	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Midtown Service	N/A	10	0	0	0	0	0	10	10	0	0	10	TPH as Gas	0	0	0	0
John's Garage	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Buchannon Nursing Home	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Red & White Service	N/A	4	4	4	4	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Side Lake Store	N/A	5	2	2	2	0	0	5	5	0	0	5	TPH as Gas	0	0	0	0
Ossippe Store	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0

(continued)

Table B-3. Soil Vapor Analyses in PVI Database (continued)

Site Name	City	Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	224-Trimethylpentane	Hexane	Heptane	MtBE	1,3-Butadiene	TPH	TPH Method	MADEP TPH Fractions	Oxygen	Carbon	Methane
Ossippe Store	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
AC Oil	N/A	4	0	0	0	0	0	0	0	0	0	4	TPH as Gas	0	0	0	0
Schmunks	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Kennys Oil	N/A	4	0	0	0	0	0	0	0	0	0	4	TPH as Gas	0	0	0	0
Settes Garage	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Tilson Auto	N/A	3	0	0	0	0	0	0	0	0	0	3	TPH as Gas	0	0	0	0
Rogers Mobile	N/A	3	3	3	3	0	0	0	0	0	0	3	TPH as Gas	0	0	0	0
Rub-a-Dub	N/A	4	0	0	0	0	0	4	4	0	0	4	TPH as Gas	0	0	0	0
Long Shot Trucking	N/A	4	2	2	2	0	0	0	0	0	0	4	TPH as Gas	0	0	0	0
Eggens Oil	N/A	3	1	3	3	0	0	0	0	0	0	3	TPH as Gas	0	0	0	0
Chillum site	Maryland	18	0	0	0	0	0	0	0	0	0	0	N/A	0	0	0	0
Reuben's Market	Milo	7	7	7	7	7	0	0	0	7	7	7	MADEP APH	7	7	7	7
Cumberland Farm 1803	Sandford	3	3	3	3	3	0	0	0	3	3	3	MADEP APH	3	5	5	5
Cumberland Farm 1817	Berwick	6	6	6	6	6	0	0	0	5	6	6	MADEP APH	6	6	6	4
Twin Bridge Market	Leeds	4	4	4	4	4	0	0	0	4	4	4	MADEP APH	4	4	4	4
Cumberland Farm 1806	South Portland	1	1	1	1	1	0	0	0	1	1	1	MADEP APH	1	1	1	1
Cumberland Farm 1805	Portland	28	28	28	28	28	0	0	0	28	28	28	MADEP APH	28	28	28	28
Cumberland Farm 1839	Portland	9	9	9	9	9	0	0	0	9	9	9	MADEP APH	9	9	9	9
Cumberland Farm 1822	Saco	2	2	2	2	2	0	0	0	2	2	2	MADEP APH	2	2	2	2
7-Eleven	Lewiston	17	17	17	17	17	0	0	0	17	17	17	MADEP APH	17	17	17	17
Cumberland Farm 1836	North Windham	5	5	5	5	5	0	0	0	5	5	5	MADEP APH	5	5	5	4
Cumberland Farm 1829	Augusta	5	4	5	5	5	0	0	0	5	5	5	MADEP APH	5	5	5	5

(continued)

Table B-3. Soil Vapor Analyses in PVI Database (continued)

Site Name	City	Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	224-Trimethylpentane	Hexane	Heptane	MtBE	1,3-Butadiene	TPH	TPH Method	MADEP TPH Fractions	Oxygen	Carbon	Methane
Mandan	Mandan	4	0	4	4	4	0	0	0	0	0	0		0	0	0	2
BP Paulsboro	Paulsboro	11	11	11	11	0	0	0	0	0	0	7	GRO (8015)	0	18	18	7
Hulme Street	Mount Holly	8	8	8	8	0	6	0	0	0	0	0	N/A	0	2	1	0
Stafford	Stafford	14	14	14	14	0	14	12	12	12	0	0	N/A	0	4	0	0
BP Akron	Akron	9	0	0	0	0	0	0	0	0	0	9	GRO (8015)	0	9	9	0
BP Columbiana	Columbiana	4	0	0	0	0	0	0	0	0	0	4	GRO (8015)	0	4	4	0
BP Conneaut	Conneaut	3	0	0	0	0	0	0	0	0	0	3	GRO (8015)	0	3	3	0
BP Kent	Kent	4	0	0	0	0	0	0	0	0	0	4	GRO (8015)	0	4	4	0
Former refinery	OK (not specified)	4	0	0	0	0	0	0	0	0	0	4	TO-3, TO-15	0	4	3	2
Beaufort	Beaufort	9	6	3	6	0	0	0	0	0	0	7	Select C6-9 ali & aro cmpd's	0	9	9	0
Bountiful Bicycle	Bountiful	14	14	14	14	8	0	6	6	0	0	14	TO-15	0	6	7	0
Gas & Go #7	North Salt Lake	15	15	15	15	15	0	0	0	0	0	15	TPH (relative to MW=100 TMB)	0	15	15	15
Gold Cross Ambulance	Salt Lake City	5	0	0	0	0	0	0	0	0	0	5	TO-15	0	0	0	0
Hal's Chevron	Green River	127	14	14	14	0	0	0	0	0	0	127	Modified TO-3 GC/FID	0	68	66	31
Handi Mart	Midvale	0	0	0	0	0	0	0	0	0	0	3	N/A	0	3	3	0
#102 Chevron	Jacksons	55	44	44	56	42	0	0	0	0	0	56	Modified TO-3 GC/FID	0	56	56	56
Logan Food Mart	Logan	1	0	0	0	0	0	0	0	0	0	0	N/A	0	0	0	0
Price Rental Property	Price	1	1	1	1	0	0	0	0	0	0	0	N/A	0	0	0	0
Salina Cash Saver	Salina	14	14	14	14	14	0	0	0	0	0	14	GRO as TMB	0	14	14	0
Jenkins Oil	Santa Clara	63	63	63	63	63	0	50	50	23	0	63	TO-15 GRO at MW=100	0	63	62	63

(continued)

Table B-3. Soil Vapor Analyses in PVI Database (continued)

Site Name	City	Benzene	Toluene	Ethylbenzene	Xylenes	Naphthalene	224-Trimethylpentane	Hexane	Heptane	MtBE	1,3-Butadiene	TPH	TPH Method	MADEP TPH Fractions	Oxygen	Carbon	Methane
Wheel-In Market	Salt Lake City	1	0	0	0	0	0	0	0	0	0	1	TO-15	0	0	0	0
Teasdale Country Store	Teasdale	3	0	0	0	0	0	0	0	0	0	3	N/A	0	2	2	0
Tesoro #40	Salt Lake	4	4	4	4	4	4	4	4	0	0	4	TO-15 (C5-11)	0	2	2	0
7-Eleven #23387	Murray	5	5	5	5	3	0	0	0	0	0	5	Modified TO-3 GC/FID	0	5	5	5
Refinery Site	Unknown	53	0	0	0	0	10	0	0	0	0	53	N/A	0	31	31	0
Peace River	Peace River	3	3	3	3	0	3	3	3	0	0	3	CCME F1+F2	0	3	3	3
Chatterton Research Site	Delta	63	0	0	0	0	0	0	0	0	0	0	N/A	0	24	0	0
Fort Ware	Fort Ware	3	3	3	3	3	0	0	0	0	0	3	CCME F1+F2	0	3	3	3
Ottawa	Ottawa	0	0	0	0	0	0	0	0	0	0	7	Gastector	0	7	7	0
North Battleford	North Battleford	9	9	9	9	0	9	5	0	0	0	9	TO-15 C6-10	0	9	9	5
Perth	Perth	1	0	0	0	0	0	0	0	0	0	13	0	0	17	8	0
Number Sites with Data		69	39	40	40	20	6	22	21	13	11	62	N/A	11	44	42	27
Total Number Analyses		893	368	372	387	243	46	150	146	121	87	782	N/A	87	655	603	367

[This page intentionally left blank.]

Appendix C. Analysis of Australian PVI Database

C.1 Introduction

Wright (2011, 2012) compiled a database of paired petroleum hydrocarbon soil vapor and groundwater source concentrations over 3 years from sites in Australia, as summarized in **Table C-1**. The data were obtained from 124 sites across Australia as geographically located in **Figure C-1**. The contents of the Australian database are summarized in Table C-1.

Table C-1. Summary of petroleum hydrocarbon data within Australian database

Information sources	1083 paired soil vapor and groundwater source concentrations from 124 sites Vapor data from single and nested wells, 12% of which are sub-slab
Site types	120 USTs, 1 refinery, 2 pipeline leak sites, 1 fuel terminal
Data reported	Benzene, toluene, ethylbenzene and xylenes (BTEX); volatile total petroleum hydrocarbon fractions (TPH); and hexane (soil vapor only); measurements of oxygen, carbon dioxide, and methane in the soil profile; source type and site characteristics include type of surface cover (building, pavement, ground)
Geographic Locations	43% of sites from Victoria (VIC), 29% from New South Wales (NSW), 10% from South Australia (SA), 7% from Australian Capital Territory (ACT), 4% from Queensland (QLD), 3% from Western Australia (WA), and remaining 4% from Tasmania (TAS) and the Northern Territory (NT)
Contamination Sources	Dissolved phase (28% data) and NAPL (72% data) from petrol and/or diesel sources
Soil types	The dominant soil types comprise sand (13%), clay (42%), and sandy clay (45%). 41% of all data sites include groundwater within a fractured rock system and where at least one soil vapor probe was completed within fractured rock.

Figure C-1. **Geographical Distribution of Sites in Australian Database.**

C.2 Climatic Information

Victoria (VIC): The majority of the sites are located in suburbs of Melbourne, the capital city of Victoria. Temperatures in Melbourne range from an average of 43 to 55°F (6 to 13°C) in winter to 54 to 79°F (12 to 26°C) in summer. Melbourne can experience extreme heat, because of the movement of hot dry air from central Australia, resulting in temperatures above 104°F (40°C). Mean rainfall in Melbourne is 26 inches (650 mm) per year.

New South Wales (NSW): The majority of the sites are located in suburbs of Sydney, the capital city of NSW. Sydney's weather is temperate, with the city's temperatures moderated by its location close to the ocean. Temperatures in Sydney range from an average of 8 to 16°C in winter to 43 to 77°F (13 to 25°C) in summer. Sydney's weather can be influenced by the movement of warm/hot moist air from the north (Queensland) or from the movement of hot dry air from central Australia. Mean rainfall in Sydney is 48 inches (1,213 mm) per year. Regional areas of NSW experience hotter, drier conditions than Sydney.

Australian Capital Territory (ACT): The ACT, which largely comprises Canberra and urban suburbs, is located within NSW, inland and south of Sydney. The climate has warm to hot summers and cool to cold winters. Temperatures in Canberra range from an average of 32 to 55°F (0 to 13°C) in winter to 46 to 82°F (8 to 28°C) in summer. Mean precipitation in Canberra is 24 inches (616 mm) per year.

Queensland (QLD): The majority of the sites are located in suburbs of Brisbane, the capital city of QLD, located in the southeast corner of the state. Brisbane has a humid subtropical climate with warm to hot humid summers and dry to moderately warm winters. Temperatures in Brisbane range from an average of 48 to 70°F (9 to 21°C) in winter to 64 to 86°F (18 to 30°C) in summer. Mean rainfall in Melbourne is 39 inches (986 mm) per year.

South Australia (SA): The majority of the sites are located in suburbs of Adelaide, the capital city of SA. Adelaide has a hot Mediterranean climate resulting in cool, wet winters and hot, dry summers. Temperatures in Adelaide range from an average of 45 to 59°F (7 to 15°C) in winter to 57 to 84°F (14 to 29°C) in summer. Adelaide can experience extreme heat and extended heat wave conditions, because of the movement of hot dry air from central Australia, resulting in temperatures above 104°F (40°C). Adelaide is the driest capital city in Australia, with highly variable and unreliable rainfall. Mean rainfall in Adelaide is 21 inches (546 mm) per year. North of Adelaide, in regional inland areas, the climate is hotter and drier.

Western Australia (WA): The majority of the sites are located in suburbs of Perth, the capital city of WA. Perth has a temperate to Mediterranean climate resulting in cool, wet winters and hot, dry summers. Temperatures in Perth range from an average of 45 to 57°F (7 to 14°C) in winter to 61 to 88°F (16 to 31°C) in summer. Mean rainfall in Perth is 33 inches (850 mm) per year. East, north, and northeast of Perth are drier desert areas that experience a more significant and distinctive wet (winter) season and dry (summer) season.

The database includes some areas of Australia that are dry:

- Loxton, SA—mean annual rainfall is 10 inches (264 mm);

- Barham NSW—mean annual rainfall is 15 inches (373 mm); and
- Cleve SA—mean annual rainfall is 16 inches (400 mm).

Note that from 2000 to 2010 Australia was in drought with most locations experiencing rainfall much lower than average. All data in the Australian PVI database were collected between 2004 and 2010.

C.3 Data Evaluation and Filters

The criteria and filters applied by Wright (2011, 2012) for the data evaluation were

- presence of overlying clean soil,
- determination of the presence of NAPL,
- conceptual model qualifier, and
- data quality (DQ) qualifier.

The criteria used for determining the presence of overlying clean soil were the following:

- Available data do not suggest the presence of petroleum contamination in overlying soil.
- Insufficient data are available to determine whether the overlying soil is contaminated, so these locations may be affected by petroleum hydrocarbons in overlying soil.
- Overlying soil is known to be affected by the presence of petroleum hydrocarbons or the location is directly adjacent to operational fuel infrastructure where impacts are present.

The following criteria were used to determine the presence of NAPL:

- Field observations noted as phase-separated hydrocarbon, free product or a sheen;
- Near effective solubility: consisting of benzene groundwater concentrations greater than 3 to 10 mg/L, sum of BTEX greater than 20 mg/L (for petrol (gasoline) sites); TPH (C6-14) greater than 30 mg/L (for petrol sites; value selected to account for BTEX up to 20 mg/L and aliphatics concentrations of approximately 10 mg/L); and TPH(C10-14) greater than 5 mg/L (for diesel sites);
- Methane in soil gas greater than 10 percent;
- Aliphatics (hexane) in soil gas >1,000 $\mu g/m^3$; and
- Aliphatics (TPH) in soil gas >50,000 $\mu g/m^3$ (where no hexane is reported).

Data characterized as LNAPL based solely based on elevated aliphatics in soil gas were not included in the assessment where source concentrations are considered because these sites have poor source (groundwater) data.

The CSM Qualifier consisted of a five-point ranking (5-highest, 1-lowest) based on the following criteria:

- 3–5: Data collected from appropriate locations on the site using nested soil gas (SG) wells (preferred) or single point wells that include locations close to the source and through the profile, with the further ranking between 3 and 5 based on quantity and other factors (e.g., soil property data, hydrogeologic data).
- 2: Data collected from appropriate locations on the site using single or nested SG wells that do not extend close enough to the source to enable an understanding of subsurface attenuation.
- 1: Data collected either from inappropriate locations on the site or from depths that are so shallow that no understanding of subsurface attenuation can be determined.

The DQ Qualifier consisted of a five-point ranking (5 = highest, 1 = lowest) based on the following criteria:

- 3–5: Data quality considered to be moderate to high based on appropriate methods, passing of tracer tests, appropriate documentation, appropriate QA/QC, and the dataset included the measurement of fixed gases (some allocated level 3 lacked fixed gases data).
- 2: Data quality was considered low because of limited QA/QC, limited analysis of VOCs and/or no fixed gases.
- 1: Data quality was considered poor because of failure of the tracer test, breakthrough of sample tubes, incorrect/inappropriate methodology used, no QA/QC, and/or no/poor documentation.

C.4 Data Importation and Compilation Process

The Australian data received were incorporated into the PVI database but were analyzed separately from the U.S. sites in this study. After importation into the Access version of the PVI database, the Australian data were examined with respect to internal consistency and inconsistencies and errors were corrected through communications with the database originator. The data were then were exported in spreadsheet format for the analyses discussed in this appendix.

C.5 Data Analysis

The Australian data analysis was conducted for dissolved and LNAPL sites, and different filters were applied as described below. All analyses were conducted with data removed where there was known petroleum hydrocarbon contamination in overlying soil. The data analyses scenarios were as follows:

1. Scenario 1: All data (excluding where known petroleum contamination in soil).

2. Scenario 2: Fractured bedrock and non-UST sites filtered out.

3. Scenario 3: Fractured bedrock, non-UST sites, and data with lower quality (DQ-1) and confidence (CSM-1 and 2) filtered out.

Scenario 3 is considered most appropriate for use in estimating exclusion criteria.

The vertical distance method was employed to evaluate vertical separation distances in relation to toxicity-based thresholds as described in the main body of this report for the above scenarios. For Scenario 3, a further analysis was conducted to evaluate the effect on surface cover on the results.

C.6 Data Results

The data analysis for key parameters (benzene, hexane, xylenes) is presented in **Figures C-2** through **C-4** for dissolved sites and Scenarios 1 through 3 and **Figures C-5** through **C-7** for LNAPL sites and Scenarios 1 through 3. In addition, for benzene, the probability that the soil vapor concentration is less than a defined threshold (50 and 100 μg/m^3) for varying source-separation distances was estimated. For the benzene analysis, non-detects were addressed by the common practice of substituting half the detection limit for non-detects.

The results for Scenario 3 (scenario appropriate for exclusion distance analysis) are summarized in **Table C-2**. The results indicate significant differences between dissolved and LNAPL sites and for different scenarios. The probability of benzene vapor concentration less than 100 μg/m^3 for dissolved sites is 93 percent at 0 ft separation, increasing to 95 percent at 5 ft (1.5 m); while the probability of benzene vapor concentration less than 100 μg/m^3 for NAPL (UST) sites is 66 percent at 0 ft, increasing to 94 percent at 15 ft (4.6 m) separation.

A comparison of the U.S. EPA to Australian database indicates slightly lower probabilities for both dissolved and NAPL sites (1 to 5 percent) for the Australian database for equivalent source-separation distances. For NAPL sites, the oxygen concentrations were also depleted (less than 1 percent) for greater source-separation distances.

The analysis of the effect of surface cover on conditional probabilities for benzene concentrations to exceed the 100 μg/m^3 threshold and oxygen concentrations versus separation distance did not suggest surface cover (building, pavement) resulted in an oxygen shadow. The analysis also showed reduced attenuation for buildings and pavement compared with the ground-cover scenario, although it is recognized that the number of sub-slab data points below buildings were limited (**Figure C-8**).

Table C-2. Summary of Results for Vertical Distance Method for Scenario 3

	Dissolved Source—UST Sites	LNAPL Source—UST Sites
Oxygen	Most O_2 conc. > 4%, and no O_2 < 0.5%	Many data points with O_2 < 4%, and O_2 < 1% to 25 ft (7.6 m) separation
Benzene (100 μg/m^3 threshold)	$P_{/2DL}$ > 93% for 0 ft separation increasing to 95% at 5 ft (1.5 m)	$P_{1/2DL}$ > 66% for 0 ft separation increasing to ~ 94% for 15-ft (4.6-m) separation
Benzene (50 μg/m^3 threshold)	$P_{1/2DL}$ > 90% for 0 ft separation increasing to 95% at 5 ft (1.5 m)	$P_{1/2DL}$ > 60% for 0 ft separation increasing to ~ 88% for 15-ft (4.6-m) separation
Xylenes	All vapor concentrations < RBC_v at 0 ft	Vapor concentrations > RBC_v for separation distance up to 12 ft (3.7 m)
Hexane	All vapor concentrations < RBC_v at 0 ft	Vapor concentrations > RBC_v for separation distance up to 12 ft (4 m)

$P_{1/2DL}$ = Probability estimated using half detection limit method for exceeding threshold.

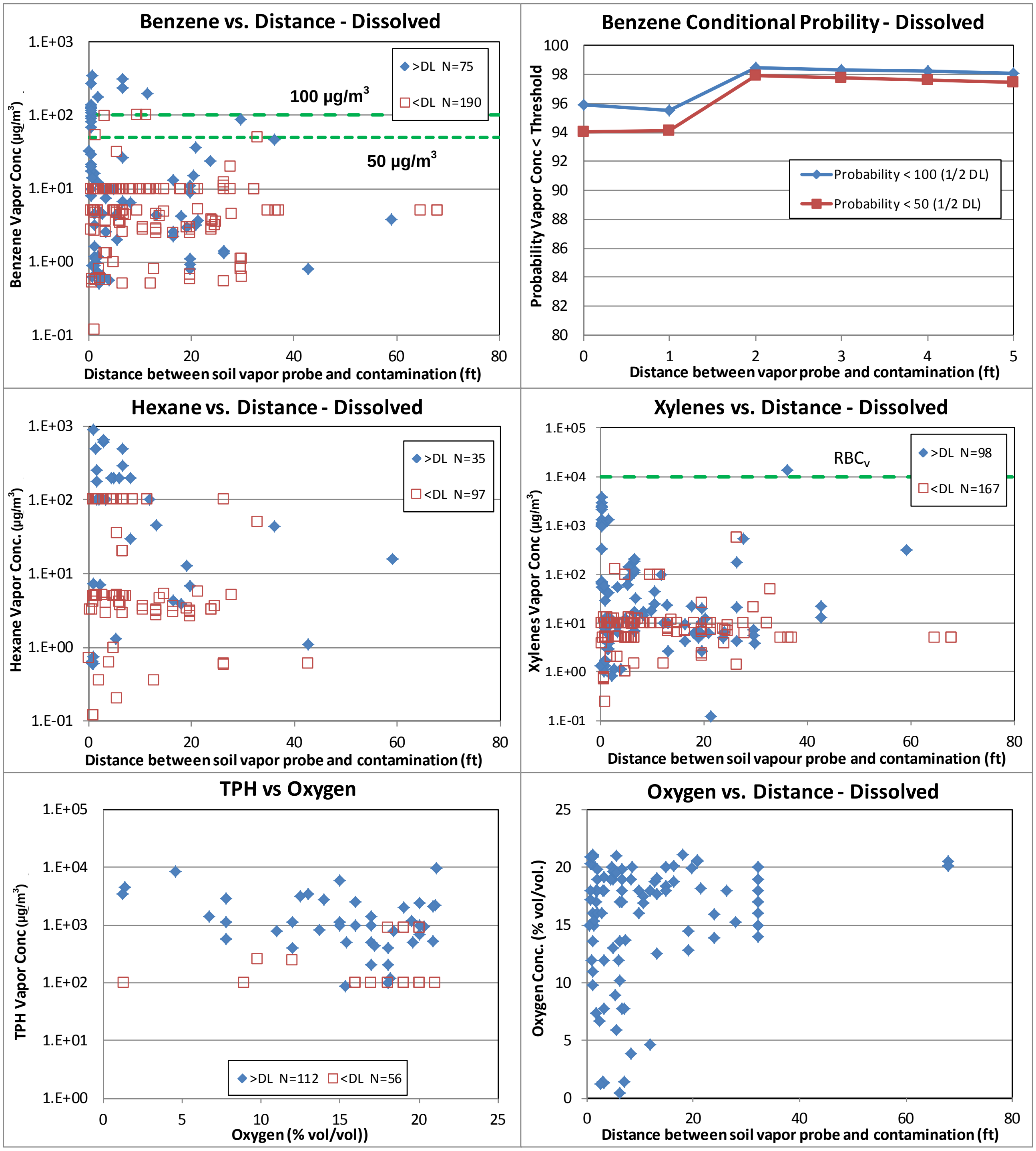
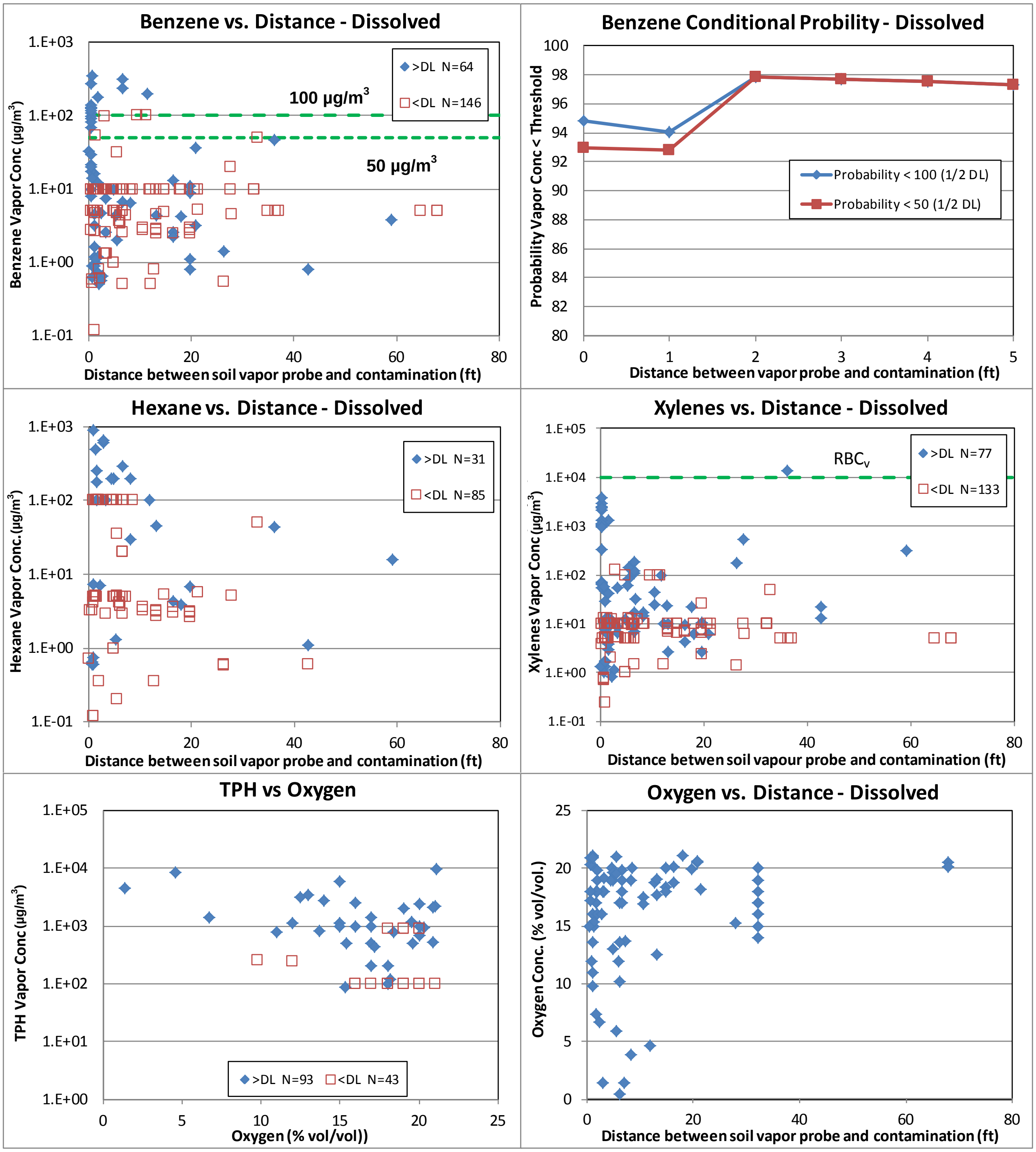


Figure C-2. Vertical distance methods for dissolved sites—all data (Scenario 1)



Benzene vs. Distance - Dissolved

Benzene Conditional Probility - Dissolved

Hexane vs. Distance - Dissolved

Xylenes vs. Distance - Dissolved

TPH vs Oxygen

Oxygen vs. Distance - Dissolved

Figure C-3. Vertical distance method for dissolved UST sites—fractured bedrock and non-UST sites filtered out (Scenario 2)

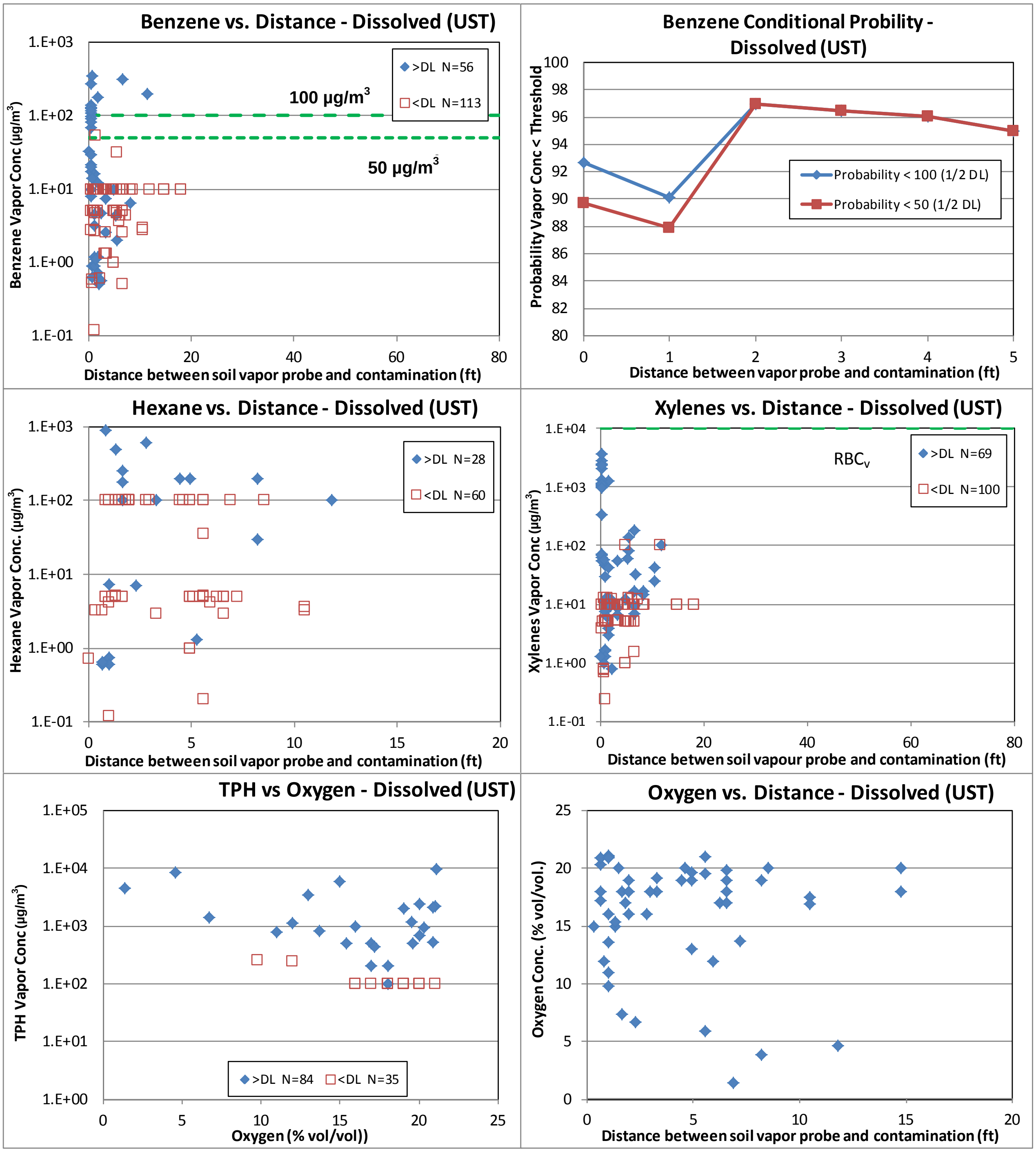


Figure C-4. Vertical distance method for dissolved UST Sites—fractured bedrock, non-UST Sites and lower data quality and confidence (DQ-1 and CSM-1&2) filtered out (Scenario 3)

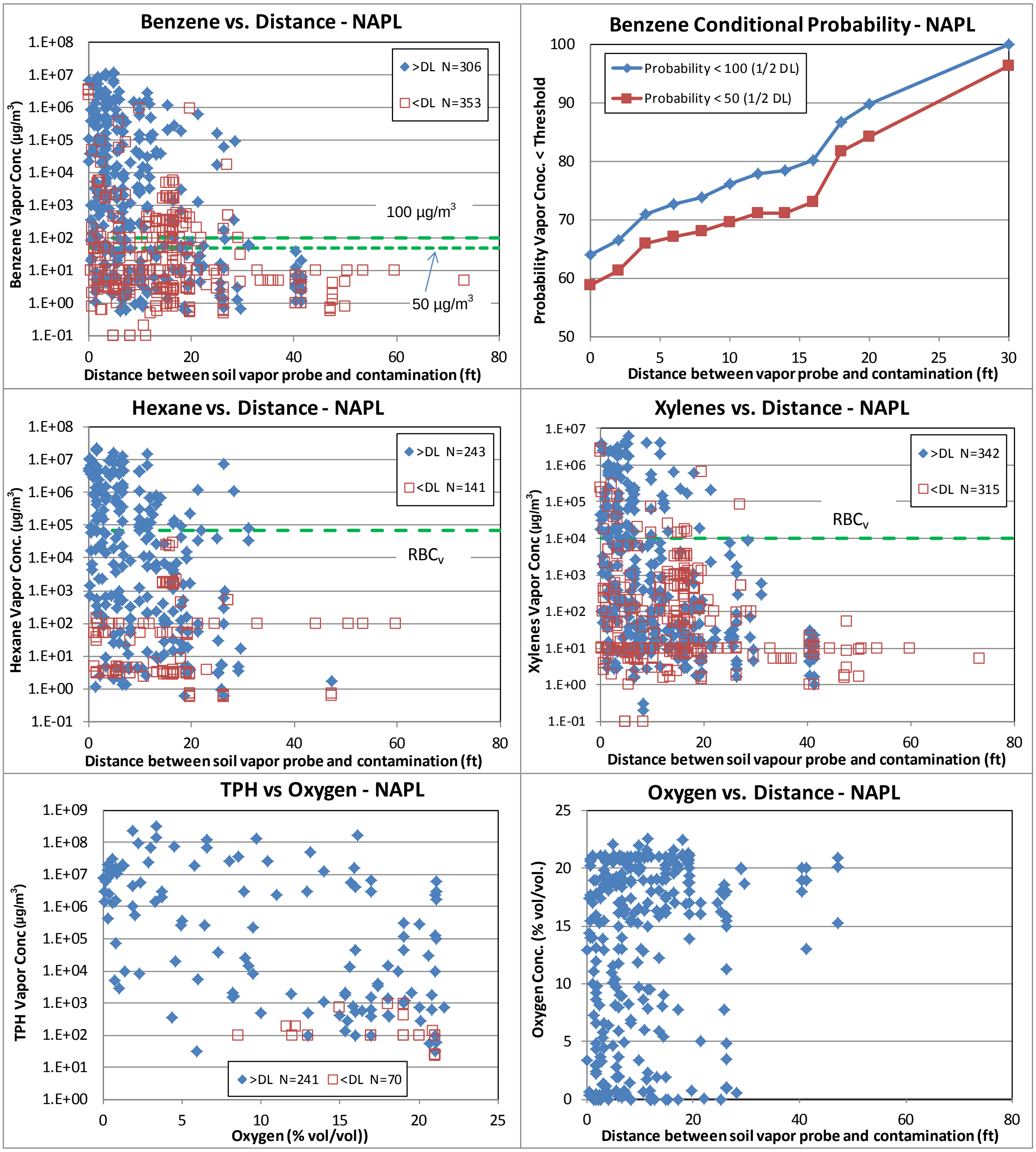


Figure C-5. Vertical distance methods for NAPL Sites—all data (Scenario 1)

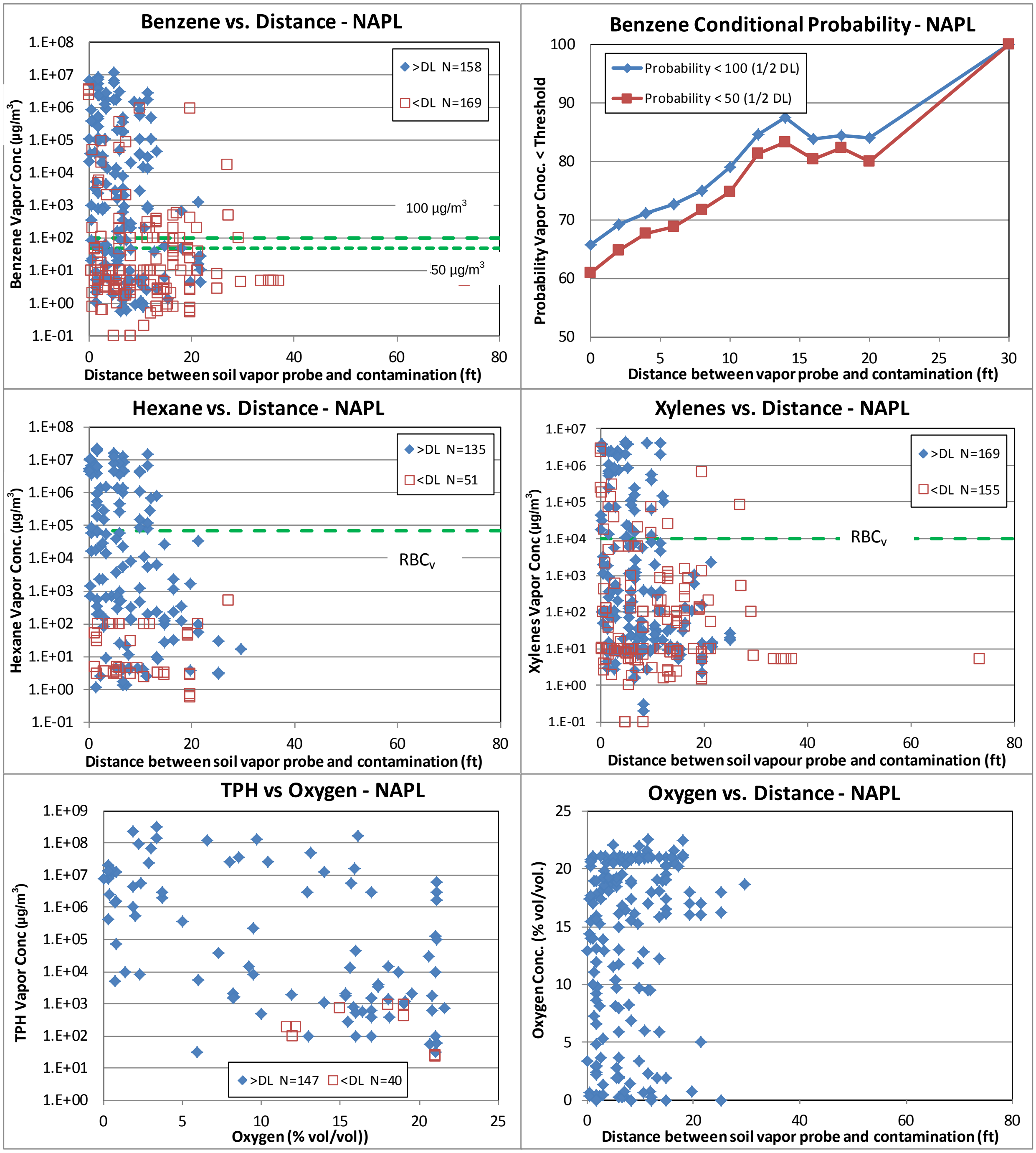


Figure C-6. Vertical distance method for NAPL UST sites—fractured bedrock and non-UST sites filtered out (Scenario 2).

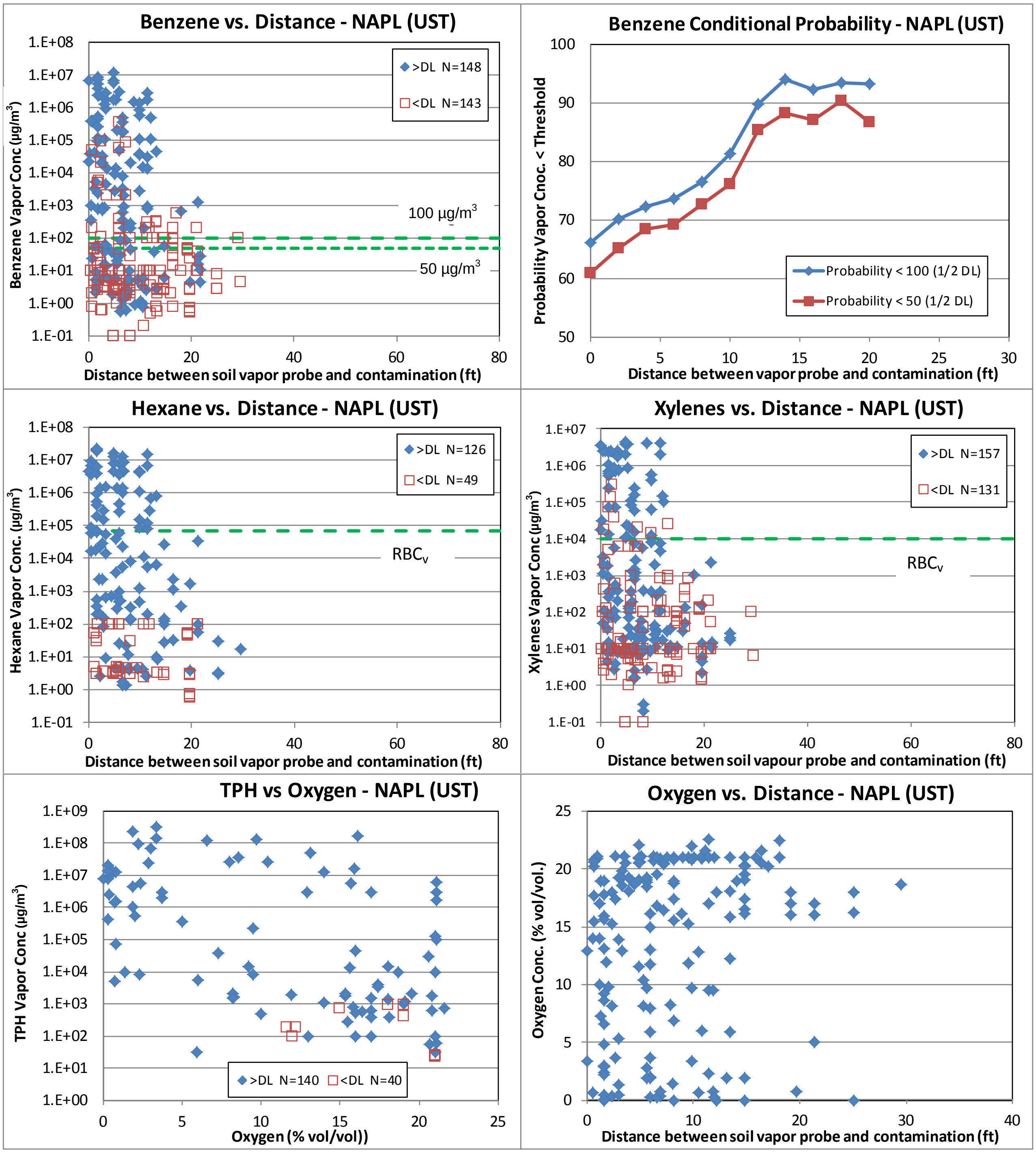


Figure C-7. Vertical distance method for NAPL UST sites—fractured bedrock, non-UST sites and lower data quality and confidence (DQ-1 and CSM-1&2) filtered out (Scenario 3)

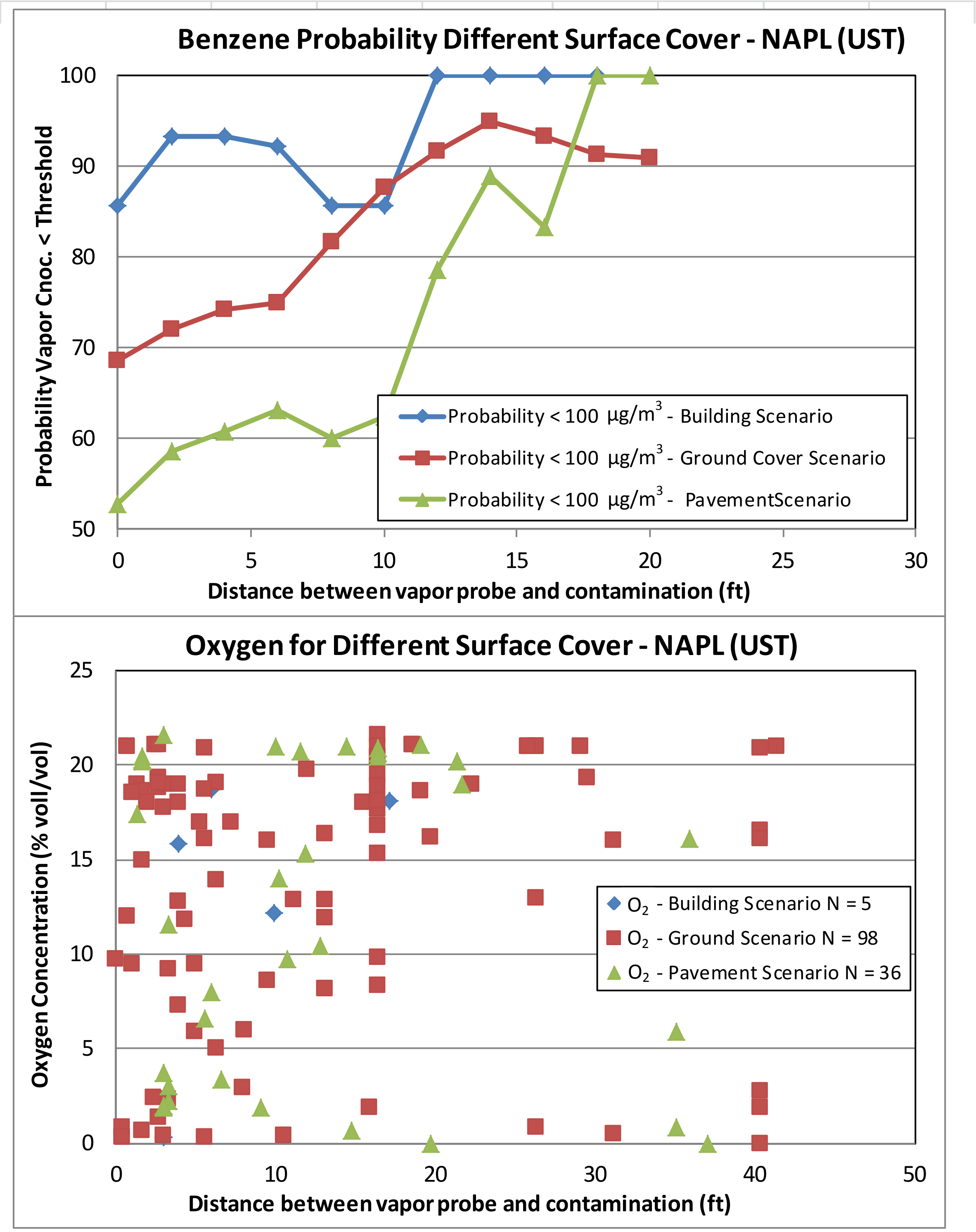


Figure C-8. **Comparison of probability for benzene soil vapor concentrations to be less than 100 µg/m^3 threshold (top panel) and oxygen concentrations for different surface covers for NAPL UST sites (bottom panel). Below detection limit concentrations replaced with half the detection limit for analysis.**

References

Wright, J. 2011. Establishing Exclusion Criteria from Empirical Data for Assessing Petroleum Hydrocarbon Vapour Intrusion. *Program and Proceedings of the 4th International Contaminated Site Remediation Conference—2011 CleanUP*. Adelaide, South Australia, September 11-15. p. 142-143.

Wright, J. 2012. Evaluation of the Australian Petroleum Hydrocarbon VI Database: Exclusion Criteria. Presented at: Recent Advances to VI Application & Implementation—A State-of-the-Science Update. AEHS West Coast Conference. San Diego, CA. March. Available at https://iavi.rti.org/WorkshopsAndConferences.cfm?PageID=documentDetails&AttachID=549.

Appendix D. PVI Database Data Dictionary

Attachment D-1. Data Structure as of Nov 30, 2012

Field Name	Type	Size	Description
Table: Building_Distances			
building_id	Long Integer	4	Link to Buildings table
location_id	Long Integer	4	Link to Locations table
horz_dist_to_bldg	Double	8	Closest horizontal distance from sampling location to building (not applicable for indoor samples)
horz_dist_to_bldg_unit	Text	20	Measurement unit for horizontal distance from sample location to building
horz_dist_comment	Text	255	Comment about building-to-location link
time_stamp	Date	8	Date/time record was created
Table: Buildings			
building_id	Long Integer	4	Building identifier (aka, subsite)
orig_bldg_id	Text	50	Original ID number for building
site_id	Long Integer	4	Link to Sites
bldg_name	Text	60	Name of building
bldg_type	Text	50	Physical description of building (links to lt_Building_Types)
bldg_use	Text	50	Use of building (residential, commercial, industrial, school, etc.)
footprint_area	Double	8	Footprint area of the building
footprint_area_unit	Text	20	Unit of measurement for footprint_area
foundation_type	Text	50	Type of building foundation (lookup values in lt_Foundation_Types)
fnd_depth_to_base	Double	8	Depth to base of foundation (below ground surface)
fnd_depth_to_base_unit	Text	20	Unit of measurement for depth to base of foundation
bldg_comment	Memo	0	Comment field
time_stamp	Date	8	Date/time record was created
Table: Data_Provider			
data_provider_id	Long Integer	4	Unique ID for data provider; links to Site table
data_provider	Text	60	Company, agency, or individual responsible for submittal of PVI data
data_contact_name	Text	30	Name of contact associated with data_provider
data_contact_address1	Text	40	Contact street address and/or box number
data_contact_address2	Text	40	Site address, part two. Box number or other info.
data_contact_city	Text	20	City
data_contact_state	Text	2	Postal abbreviation for State
data_contact_zipcode	Text	10	Zip code
data_contact_email	Text	60	Contact e-mail address
data_contact_phone	Text	60	Contact phone number

Field Name	Type	Size	Description
time_stamp	Date	8	Date/time record was created
Table: Documents			
doc_id	Long Integer	4	Unique ID for document
site_id	Long Integer	4	Link to Sites table
ref_id	Long Integer	4	Link to Reference table
doc_name	Text	255	Document descriptive name
file_name	Text	255	physical file name
doc_year	Text	4	Document year (for bibliography)
doc_desc	Text	255	Description for the document
doc_date	Date	8	Document creation date
doc_source	Text	255	Document source
author_org	Text	100	Document author's organization
author_citation	Text	255	Author name in citation formats
author_name	Text	50	Document author's name
Journal	Text	255	Journal name in citation format
Volume	Text	20	Journal volume in citation format
Pages	Text	20	Journal pages in citation format
author_phone	Text	20	Document author's phone number
doc_links	Memo	0	Website address (i.e., URL) for documents available on the Internet
doc_comments	Memo	0	Other comments about the document (e.g., use, applicability)
public_yn	Text	1	Can this information be made available to the public? (Y=yes, N=no)
doc_original_format	Text	100	Original format of document
date_QC_completed	Date	8	Date that QC was completed
time_stamp	Date	8	Date/time record was created
Table: DQ_Table			
site_id	Long Integer	4	Unique ID for site
CSM_Rank	Integer	4	Conceptual site model rank (1–3), 3 is best (see lt_CSM_Rank table)
DQ_Rank	Integer	4	Data quality rank (1–5), 5 is best (see lt_DQ_rank table)
Probe_Type	Text	25	Type of soil gas probe (permanent, driven, unknown)
Leak_Tracer	Text	3	Was leak tracer test conducted? (Y/N) NOTE: ME used extensive fixed gas data instead.
Purging_Procedure	Text	3	Was the probed purged before sampling? (Y/N)
Pneumatic_Test	Text	3	Was a pneumatic test conducted? (Y/N)
Fixed_Gas_Data	Text	3	Was fixed gas data collected? (Y/N)
FG-HC_Consistent	Text	3	Are the fixed gas and VOC data consistent? (Y/N)
Acceptable_VOC_Method	Text	10	Is the VOC method acceptable? (Y/N)

Field Name	Type	Size	Description
VOC_Method	Text	25	VOC analytical method (TO-15, EPA 8260, GC, PID, FID, TCD, unknown, etc.)
Lab_QAQC	Text	3	Is laboratory QA/QC documented and acceptable? (Y/N)
Peer_Review	Text	25	Was study peer reviewed? (journal, thesis, state/fed. research, N)
Reg_Program	Text	25	Regulatory program oversight of study (reg. program, NA)
DQ_Comment	Text	255	Comment on data quality
Table: Links			
Link_ID	Long Integer	4	Unique ID for the links of the specificed two location_xy_id.
location_xy_id1	Long Integer	4	First location of the linkage: probe location_xy_id
location_xy_id2	Long Integer	4	Second location of the linkage: non-probe location_xy_id
distance_xy	Double	8	Lateral distance between the two linked xy locations
distance_xy_units	Text	10	Unit of the lateral distance
Table: Locations			
sample_location_id	Long Integer	4	Location ID where sample was taken at 3 D level (including depth z)
site_id	Long Integer	4	Link to Sites table
building_id	Long Integer	4	Link to Buildings table
location_xy_id	Long Integer	4	Unique ID for each location at 2D level, used for linking locations laterally in the Links table
import_loc_id	Text	25	3D location XY ID assigned by RTI for import (Example: M129-M130, M207, M208)
loc_name	Text	100	Location xy name at 2D level
samp_loc_name	Text	255	More specific name of sampling location (e.g., port A on Probe SV-2 or SV-2a); may vary by depth
sample_depth	Double	8	Sample depth, below land surface
sample_depth_unit	Text	20	Unit of measurement for sample depth
loc_type	Text	50	Location type (Indoor air, outdoor air, probe, bulk soil, or well)
loc_int/ext	Text	20	Interior or exterior location
loc_desc	Text	255	Additional description of location (e.g., floor, designated use of room)
vz_soil_text_code	Text	10	Vadose zone soil texture (Links to lt_Soil_Textures) in code
vz_alt_soil_desc	Text	255	Alternate soil description (may be more specific than vz_soil_txt_code)
vz_alt_soil_desc_src	Text	255	Description of soil between the sampling point and the source
fractured_rock	Text	20	Indicates if there is fractured rock
vz_alt_soil_grade	Text	255	Site soil gradation (V.Coarse, Coarse, Fine)
vz_porosity	Double	8	Vadose zone porosity

Field Name	Type	Size	Description
vz_porosity_unit	Text	20	Unit of measurement for vadose zone porosity
loc_comment	Memo	0	Comment about latitude, longitude and vertical elevation. Store information about the collection method, post processing of the data (if GPS were involved), or description of feature of the facility represented by the coordinates.
time_stamp	Date	8	Date/time record was created
Table: lt_Building_Types			
bldg_type	Text	50	Physical description of building
Table: lt_Countries			
Country	Text	5	Country short name
country_name	Text	25	County name
Table: lt_CSM_Rank			
CSM_Rank	Integer	4	Conceptual site model rank (1–3), 3 is best
CSM_Description	Text	255	Conceptual site model rank description
Table: lt_DQ_Rank			
DQ_Rank	Integer	4	Data quality rank (1–5), 5 is best
DQ_Description	Memo	0	Data quality rank description
Table: lt_Foundation_Types			
foundation_type	Text	50	Building foundation types (lookup values for Buildings table)
Table: lt_Hydrogeologic_Settings			
hydro_setting_desc	Text	255	General Hydrogeologic setting description
Table: lt_Parameters			
parameter_id	Long Integer	4	Unique ID for each measurement parameter
parameter_abbrev	Text	10	Short abbreviation for measurement parameter (e.g., MEK, BP)
parameter_name	Text	50	Measurement parameter name (e.g., 2-butanone, barometric pressure)
cas_number	Text	15	Chemical Abstract System number (where applicable)
parameter_class	Text	50	Parameter class or grouping
organic_yn	Text	1	Must be "Y" for organic constituents or "N" for inorganic constituents
HLC25	Double	8	Henry's Law Constant at 25 degrees C (unitless)
DeltaH	Double	8	Enthalpy of vaporization at the normal boiling point (cal/mol)
Tc	Double	8	Critical temperature (degrees Kelvin)
Tb	Double	8	Normal boiling point (degrees Kelvin)
Comment	Text	255	
sort_name	Text	50	parameter name used for sorting
Table: lt_Sample_Media			
Media	Text	50	Media sample type

Field Name	Type	Size	Description
Table: lt_Soil_Textures			
soil_txt_code	Text	10	soil texture code (links to Locations table)
soil_txt_name	Text	50	soil texture name
soil_txt_desc	Text	255	Description of soil texture from IAVI guidance document Table 4, p. 35
Table: lt_Stat_Types			
stat_type	Text	20	Statistic type
Table: lt_States			
state_fips	Text	2	State fips code
state_name	Text	50	State name
state_abbrev	Text	4	State abbreviation
Table: lt_Units			
unit_type	Text	20	Type or category for which the units are applicable (used to limit list in forms)
unit_code	Text	20	Reported unit (abbreviation)
unit_desc	Text	100	Description of unit (unabbreviated)
unit_pref	Boolean	1	Indicates which is the preferred unit for the unit_type (used for setting default value)
Table: References			
ref_id	Long Integer	4	Unique id for references
References_text	Text	255	Description for the document
time_stamp	Date	8	Date/time record was created
Table: Results			
test_result_id	Long Integer	4	Unique ID for test result
import_result_id	Text	25	Result ID assigned by RTI for data imports
sample_id	Long Integer	4	Sample ID that this test result is for - linked to Samples
parameter_id	Long Integer	4	Link to lt_Parameters. Measurement parameter that result measures.
parameter_name	Text	50	Measurement parameter name (e.g., 2-butanone, barometric pressure)
result_value	Double	8	Analytical result, field measurement, or statistical calculation
result_unit	Text	15	Units of measurement for the result (and result_error_delta)
result_comment	Text	255	Result-specific comments
lab_anl_method_code	Text	35	Laboratory analytical method code
report_detection	Text	20	report detection limit
detect_flag_yn	Text	1	Must be either "Y" for detected analytes or "N" for non_detects
value_type	Text	12	Value type for result_value ("actual", "estimated", "interpolated", or "calculated").

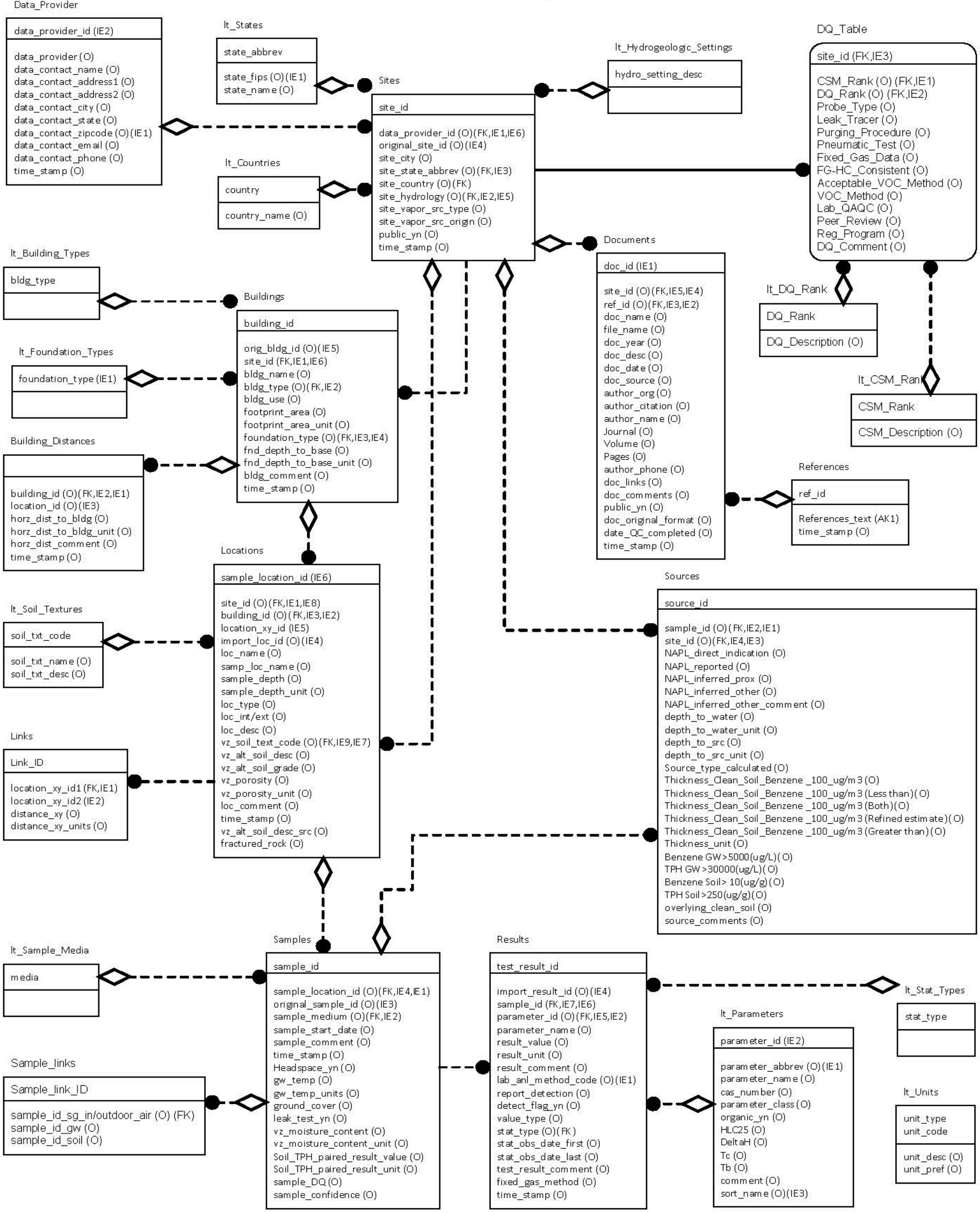
Field Name	Type	Size	Description
stat_type	Text	20	Statistic type reflected in the result_value (links to lt_Stat_Types)
stat_obs_date_first	Date	8	Earliest date of sample used to determine result_value
stat_obs_date_last	Date	8	Latest date of sample used to determine result_value
test_result_comment	Memo	0	Comment field
fixed_gas_method	Text	255	Method for fixed gases
time_stamp	Date	8	Date/time record was created
Table: Sample_links			
Sample_link_ID	Long Integer	4	Unique ID for each sample link; used to pair samples
sample_id_sg_in/outdoor_air	Long Integer	4	Sample ID for soil gas, indoor air, or outdoor air sample
sample_id_gw	Long Integer	4	Sample ID for groundwater sample
sample_id_soil	Long Integer	4	Sample ID for soil sample
Table: Samples			
sample_id	Long Integer	4	Unique ID for each sample
sample_location_id	Long Integer	4	Location ID where sample was taken at 3 D level (including depth z)
original_sample_id	Text	40	Sample ID in original source
sample_medium	Text	20	Medium within which measurement was taken (links to lt_Sample_Media)
sample_start_date	Date	8	Date sample collection began in (MM/DD/YYYY) format
sample_comment	Memo	0	Comments related to the sample
time_stamp	Date	8	Date/time record was created
Headspace_yn	Text	1	Soil sample only: is this a headspace measurement?(Y, N)
gw_temp	Double	8	Groundwater samples only: groundwater temperature at time of sampling
gw_temp_units	Text	10	Groundwater samples only: units for groundwater temperature
ground_cover	Text	50	Soil Gas samples only: Surface cover (paved, grassy, etc.)
leak_test_yn	Text	1	Soil Gas samples only: Has the vapor probe been leak tested? (Y, N)
vz_moisture_content	Double	8	Vadose zone moisture content (measured value)
vz_moisture_content_unit	Text	20	Unit of measurement for vadose zone moisture content
Soil_TPH_paired_result_value	Double	8	Paired soil TPH analytical results (links by 3D location and sample date)
Soil_TPH_paired_result_unit	Text	15	Units of measurement for the paired soil TPH result (and result_error_delta)
sample_DQ	Text	20	Sample data quality (1 to 5): 1 = poor quality and 5 = high quality (Aus. data)
sample_confidence	Text	20	Conceptual site model qualifier confidence (1 to 5): 1 = inappropriate locations and 5 = appropriate locations (Aus. data)

Field Name	Type	Size	Description
Table: Sites			
site_id	Long Integer	4	Unique ID for site
data_provider_id	Long Integer	4	Links site to the Data_Provider table.
original_site_id	Text	45	Site identifier in original source
site_city	Text	20	City of site
site_state_abbrev	Text	4	State abbreviation for State of site (links to lt_States)
site_country	Text	50	Country name (links to lt_Countries)
site_hydrology	Text	255	Hydrogeologic Setting (links to lt_Hydrogeologic_Settings)
site_vapor_src_type	Text	50	Type of contamination (e.g., gasoline)
site_vapor_src_origin	Text	255	Origin of the vapor source (UST, spill, landfill, etc.)
public_yn	Text	1	Can this information be made available to the public? (Y=yes, N=no)
time_stamp	Date	8	Date/time record was created
Table: Sources			
source_id	Long Integer	4	Unique ID for sources
sample_id	Long Integer	4	Link to Sample table
site_id	Long Integer	4	Link to Sites table
NAPL_direct_indication	Boolean	1	NAPL based on direct indication
NAPL_reported	Boolean	1	NAPL based on report
NAPL_inferred_prox	Boolean	1	NAPL inferred from proximity
NAPL_inferred_other	Boolean	1	NAPL inferred from other references
NAPL_inferred_other_comment	Text	255	Comments on NAPL inferred from other references
depth_to_water	Double	8	Depth to water table (below land surface) at time of sampling
depth_to_water_unit	Text	20	Unit of measurement for depth to water
depth_to_src	Double	8	Depth to vapor source at time of sampling (= GW depth for GW samples)
depth_to_src_unit	Text	20	Unit of measurement for depth to src
Source_type_calculated	Text	255	Source type (NAPL or Dissolved)
Thickness_Clean_Soil_Benzene _100_ug/m3	Double	8	Method 1: Thickness Clean Soil Benzene 100 $\mu g/m^3$ Criteria
Thickness_Clean_Soil_Benzene _100_ug/m3 (Less than)	Double	8	Method 1: Thickness Clean Soil Benzene 100 $\mu g/m^3$ Criteria (less than)
Thickness_Clean_Soil_Benzene _100_ug/m3 (Both)	Double	8	Method 1: Thickness Clean Soil Benzene 100 $\mu g/m^3$ Criteria (both)
Thickness_Clean_Soil_Benzene _100_ug/m3 (Refined estimate)	Double	8	Method 2: Thickness Clean Soil Benzene 100 $\mu g/m^3$ Criteria (refined estimate)
Thickness_Clean_Soil_Benzene _100_ug/m3 (Greater than)	Double	8	Thickness Clean Soil Benzene 100 $\mu g/m^3$ Criteria (greater than)
Thickness_unit	Text	20	Unit of measurement for thickness

Field Name	Type	Size	Description
Benzene GW>5000(ug/L)	Boolean	1	Calculated Benzene GW indicator by 3D and date linkages
TPH GW>30000(ug/L)	Boolean	1	Calculated TPH GW indicator by 3D and date linkages
Benzene Soil> 10(ug/g)	Boolean	1	Calculated Benzene Soil indicator by 3D and date linkages
TPH Soil>250(ug/g)	Boolean	1	Calculated TPH Soil indicator by 3D and date linkages
overlying_clean_soil	Text	20	Indicates if there is overlying clean soil between the source and the sample
source_comments	Text	255	Comments related to the source

Appendix E. PVI Database Entity Relationship Diagram

PVI Database Diagram
November 21, 2012



Appendix F. Analysis of Lead Scavengers: Ethylene Dibromide and 1,2-Dichloroethane

F.1 Historical & Current Uses

F.1.1 Gasoline Additives

Ethylene dibromide (EDB or 1,2-dibromoethane) and 1,2-dichloroethane (1,2-DCA) are synthetic organic chemicals that were historically used as gasoline additives to prevent lead deposits that foul internal combustion engines. For this reason, they are commonly referred to as lead scavengers. Addition of EDB and 1,2-DCA to gasoline began in significant amounts from the mid-1920s and continued until leaded gasoline was phased out beginning in late 1980s.

The U.S Environmental Protection Agency (EPA) began a phase-down program in 1973 to reduce the lead content in gasoline. Since the early 1940s and until that phase-down, leaded gasoline contained EDB and 1,2-DCA with molar portions of Pb:Cl:Br of 1:2:1. On-road uses of leaded gasoline were banned in 1996 (Falta, 2004; U.S. EPA, 2006).). Prior to 1974, the average EDB and 1,2-DCA concentrations in U.S. automotive gasoline were as high as about 0.320 g/L, which decreased to about 0.180 g/L in late 1970s and further down to about 0.060 g/L by early 1980s. Use of leaded gasoline in on-road vehicles has been banned since 1996 (U.S. EPA, 2006).

Lead scavengers are still used as additives to aviation gasoline (avgas) and automobile racing fuel. Avgas, however, does not use 1,2-DCA and has twice the amount of bromine with a molar ratio Pb:Br of 1:2. Use of EDB as an additive to leaded gasoline accounted for more than 80 percent of its consumption in 1981. However, there are also other industrial and agricultural uses of both EDB and 1,2-DCA.

F.1.2 Other Industrial & Agricultural Uses

EDB was used in agricultural applications as a soil fumigant and a pesticide from 1948 to 1983. Its use as a pesticide was suspended in 1984 (Falta, 2004). According to U.S. EPA (2006), EDB is currently used as a nonflammable solvent for resins, gums, and waxes and as a chemical intermediate in synthesis operations. It is used most commonly to make vinyl bromide, which is a flame retardant in modacrylic fibers. Other current applications of EDB are as an intermediate in the preparation of dyes and pharmaceuticals.

U.S. EPA (2006) lists the historical uses of 1,2-DCA in varnish and finish removers, soaps and scouring compounds, organic synthesis for extraction and cleaning, metal degreasers, ore floatation, and paints, coatings, and adhesives. Its commercial production was first reported in 1922. Currently, 1,2-DCA is primarily used in the manufacturing of vinyl chloride.

F.2 Toxicity

The current EPA maximum contaminant level (MCL) in drinking water for EDB and 1,2-DCA are 0.05 and 5 µg/L, respectively. The maximum contaminant level goal (MCLG) for both chemicals is zero, based on increased risk of cancer for 1,2-DCA and increased risk of cancer and "problems with liver, stomach, reproductive system, or kidneys; increased risk of cancer"[17] for EDB. The MCLs for EDB and 1,2-DCA are "set as close to the health goals as possible, considering cost, benefits and the ability of public water systems to detect and remove contaminants using suitable treatment technologies."[18] As a result, the incremental lifetime cancer risk (ILCR) associated with these MCLs is higher than the generally acceptable 10^{-5} value and some states (e.g. California, Florida, and Massachusetts) have lower MCLs for drinking water (Falta, 2004). EPA's cancer risk-based regional screening levels (RSLs) set the tapwater screening levels for 1,2-DCA and ethylene dibromide at 0.15 and 0.0065 µg/L, respectively.

The contaminant source listed in the drinking water regulations is discharge from petroleum refineries for EDB and discharge from industrial chemical factories for 1,2-DCA. According to U.S. EPA (2006), the exposure pathways for EDB and 1,2-DCA include dermal absorption, inhalation, and ingestion, and both chemicals are classified as probable human carcinogens. The International Agency for Research on Cancer (IARC) has a classification of 2A (probably carcinogenic to humans) for EDB and 2B (possibly carcinogenic to humans) for 1,2-DCA.

The Agency for Toxic Substances and Disease Registry (ATSDR) has a toxicity profile for 1,2-DCA, which specifies minimal risk levels (MRLs) for inhalation and oral exposure. The inhalation MRL for 1,2-DCA is 0.6 ppm for chronic exposure (>365 days, but also protective for intermediate exposure of 15-364 days), and an oral MRL of 0.2 mg/kg/day for intermediate-duration (15–364 days) (ATSDR, 2001). Toxicity reference values for both EDB and 1,2-DCA are available from EPA's Integrated Risk Information System (IRIS), with cancer driving the risk for both the inhalation and ingestion exposure routes. **Table F-1** summarizes IRIS noncancer and cancer toxicity reference values along with the corresponding EPA RSLs for residential indoor air and tapwater. Values are provided for EDB and 1,2-DCA, along with benzene for comparison, because benzene usually drives the risk at petroleum contamination sites. As can be seen in **Table F-1**, EDB and 1,2-DCA have higher toxicity values and lower RSLs than benzene and thus may be expected to contribute to risks at petroleum sites where they occur in high enough concentrations.

Table F-1. Summary of US EPA Toxicity Reference Values and Regional Screening Levels for EDB, 1,2-DCA, and Benzene

	Toxicity Reference Values[a]		Regional Screening Levels[b]	
Chemical	SFO (mg/kg-day)$^{-1}$	IUR (µg/m^3)$^{-1}$	Residential Tapwater (µg/L)	Residential Air (µg/m^3)
EDB	2	6.4E-04	0.0065	0.0041
1,2-DCA	0.091	2.6E-05	0.15	0.094
Benzene	0.055	7.8E-06	0.39	0.31

SFO = oral cancer slope factor; IUR = Inhalation Unit Risk; EDB = ethylene dibromide or 1,2-dibromoethane; 1,2-DCA = 1,2-dichoroethane.

[a] Source: IRIS (2012). http://www.epa.gov/IRIS/ Accessed December 2012.

[b] Source: Regional Screening Level summary table. http://www.epa.gov/region9/superfund/prg/. RSLs reflect default residential exposure assumptions and a 1×10^{-6} excess cancer risk.

---

[17] http://water.epa.gov/drink/contaminants/index.cfm#Organic

[18] http://water.epa.gov/drink/contaminants/basicinformation/ethylene-dibromide.cfm

F.3 Physical and Chemical Properties

Select physical and chemical properties of the lead scavengers EDB and 1,2-DCA are summarized in **Table F-2**. Due their moderately high aqueous solubility, both contaminants readily partition into pore water and move downward to the water table with infiltration. This results in greater potential for EDB and 1,2-DCA to move towards the water table as opposed to being present as residual NAPL in the vadose zone, compared to PHCs, which can make them harder to detect through soil gas surveys (Falta, 2004). Sorption to soil particles and organic matter is not a significant process as evidenced by their relatively low octanol-water and soil organic carbon-water partition coefficients (K_{ow} and K_{oc}). Retardation factors less than 2 are generally used for typical aquifer conditions. Both compounds are considered to be more mobile in groundwater than benzene.

Table F-2. Physical and Chemical Properties of EDB and 1,2-DCA

Property	Units	EDB	1,2-DCA	Reference
Solubility (K_s)	mg/L	4,300	8,700	Falta (2004)
Molar weight (M_w)	g/mol	187.88	98.96	Falta (2004)
Gasoline-water partition coefficient (K_p)	—	152*	84	Falta (2004)
Vapor Pressure (V_p)	kPa	1.47	8.10	Falta (2004)
Henry's constant (K_H)	—	0.029	0.050	Falta (2004)
Octonal water partition (K_{ow})	—	58	30	Falta (2004)
Organic carbon partition coefficient (K_{oc})	L/kg	44	14	Falta (2004)
Specific gravity	—	2.17	1.24	US EPA (2006)

*Based on measurements, which differ from the value derived using Raoult's law by about a factor of 0.5.

F.4 Fate and Transport

F.4.1 Degradation Reactions

Table F-3 lists the abiotic and biotic degradation and transformation reactions for EDB and 1,2-DCA.

Table F-3. Degradation Reactions of EDB and 1,2-DCA

Chemical	Abiotic	Biotic
EDB	Hydrolysis, reactions with sulfur nucleophiles, reactions with FeS, photochemical reactions with hydroxyl radicals (in air)	Aerobic cometabolism, anaerobic dehalogenation
1,2-DCA	Reactions with sulfides, reactions with FeS	Aerobic cometabolism, anaerobic reductive dechlorination

Estimated half-lives for abiotic hydrolysis reaction rates reported for EDB range from 1.5 to 15 years (Falta, 2004).

Both chemicals biodegrade aerobically in surface soils more readily than in deeper soils. EDB degrades faster anaerobically in groundwater (15–50 days half-life) as compared to aerobically (35–360 days half-life). On the other hand, 1,2-DCA degrades much more rapidly aerobically (Falta, 2004):

- 1,2-DCA aerobic degradation in soil: 52 days half-life;
- 1,2-DCA aerobic degradation in groundwater: 100 days half-life; and
- 1,2-DCA anaerobic degradation in groundwater: 400 days half-life.

U.S. EPA (2008) summarizes laboratory and field anaerobic biodegradation reaction rates for EDB and 1,2-DCA and compares them to benzene (**Table F-4**).

Table F-4. Comparison of First-Order Rate Constants for Biodegradation of EDB and 1,2-DCA in Anaerobic Aquifer Sediment to Rate Constants for Overall Removal with Ground Water Flow in Anaerobic Aquifers

Material	First-Order Rate Constant for Attenuation (per year)			Reference
	EDB	DCA	Benzene	
Microcosm studies in laboratory, all conducted with methanogenic material				
Sediment from source zone of a spill of leaded gasoline, South Carolina	1.5±1.0	1.3±0.3	1.4±0.2	Henderson et al., 2008, SI
Sediment from mid gradient zone of a spill of leaded gasoline, South Carolina	5.4±0.3	0.3±0.1	3.5±0.8	Henderson et al., 2008, SI
Sediment impacted by leachate from a solid municipal waste landfill, Norman, Oklahoma	17		2.6	Wilson et al., 1986
Sediment impacted by leachate from a solid municipal waste landfill, Norman, Oklahoma		1.7		Klećka et al., 1998
Sediment from manufacturing site contaminated with DCA in Louisiana		4.4		Klećka et al., 1998
Sediment from manufacturing site contaminated with DCA in Texas		1.2		Klećka et al., 1998
Field studies, flow path in aquifer				
Spill of leaded gasoline, South Carolina	1.3	0.9	1.0	Henderson et al., 2008, Supporting Information
Spill of leaded gasoline, North Carolina (1995 data)	0.63	0.71	0.9	Mayer, 2006
Spill of leaded gasoline, North Carolina (2004 data)	0.22		0.26	Mayer, 2006
Leachate from municipal solid waste landfill, Michigan		0.22±0.19	0.42±0.32	Ravi et al., 1998
Fs-12 spill of aviation gasoline on Cape Cod, Massachusetts	0.03		0.14	Falta, 2004

Source: Table 2.3 from U.S. EPA (2008).

The presence of hydrogen sulfide species (H_2S and HS^-) enhances the hydrolysis breakdown of both EDB and 1,2-DCA. Abiotic reaction rates are also sensitive to temperature, and the rates for EDB are about an order of magnitude greater than for 1,2-DCA (U.S. EPA, 2008). Both EDB and 1,2-DCA can react abiotically with iron(II) sulfide, analogous to the reaction involving trichloroethylene (TCE). U.S. EPA (2008) conducted experiments to determine reaction rates of EDB and 1,2-DCA with FeS, following the procedures described by Shen and Wilson (2007) on TCE removal, but without the organic carbon source (plant mulch). The rates for EDB ranged from 62.6 yr^{-1} to 94.8 yr^{-1}, which are similar to the TCE removal rates from Shen and Wilson

(2007). The rates for 1,2-DCA were lower by about an order of magnitude ranging from 6.7 yr^{-1} to 10.2 yr^{-1}.

Field results show much lower degradation rates and persistence in groundwater than observed in the experiments described above. Falta (2004) presents two explanations for the lower field degradation rates:

- Nonequilibrium sorption processes such as intraparticle diffusion and trapping in micropores; and
- Biodegradation stops at lower threshold concentration.

Henderson et al. (2008) conducted microcosm study for the anaerobic biodegradation of EDB and 1,2-DCA from an underground storage tank (UST) site to evaluate the effect of other fuel hydrocarbons on dehalogenation reactions. They found that biostimulation by lactate can enhance the degradation rates for EDB and that degradation of 1,2-DCA is much lower than that of EDB (in agreement with field studies) and does not respond to the lactate biostimulation. The highest EDB removal was measured in microcosms that produced the highest amounts of methane.

Yu (2011) also conducted an experimental study of anaerobic biodegradation of EDB and 1,2-DCA and found that EDB is preferentially degraded when both compounds are present and that the main process is the dihaloelimination to ethene.

F.4.2 Effect of Methane

Methanogenic bacteria can metabolize EDB and 1,2-DCA to ethylene (US EPA, 2008; McKeever et al., 2012). However, the halogenated compounds can be harmful to the methanogenic bacteria at high concentrations (e.g., 1,300 µg/L for EDB and 11,000 µg/L for 1,2-DCA). Bacteria strains of the dehalococcoides group can also metabolize EDB and 1,2-DCA to ethylene.

McKeever et al. (2012) conducted microcosm studies using soil from an EDB contaminated aquifer under aerobic and anaerobic conditions. They found that biostimulation by methane for the aerobic microcosms increased the degradation rate by a factor of eight. In general, however, they found that anaerobic degradation could lead to natural attenuation, while EDB is persistent under aerobic conditions. They conclude that methane could be considered as an amendment to EDB bioremediation in aerobic groundwater conditions.

F.4.3 Groundwater Data and Behavior

Studies of public drinking water systems in the U.S. have found that EDB concentrations are greater than its MCL (0.05 µg/L) for about 12 percent of systems serving the U.S. population (third ranking amongst regulated contaminants). Likewise, the 1,2-DCA concentrations were found to exceed its MCL (5 µg/L) for 8.4 percent of the population (Falta, 2004, citing U.S. EPA, 2003). Falta (2004) summarizes two case studies of fuel release containing lead scavengers:

- EDB plume associated with leaded gasoline at the Massachusetts Military Reservation (MMR) contaminant release likely between 1940 and 1970; detached EDB plume in 1999: 2,400m long, 360m wide and average 30m thickness, beginning 30m below ground surface; and
- Service station in operation from 1953–1987; sampling in 1999 revealed concentrations as high as 189 µg/L and 111 µg/L for EDB and 1,2-DCA, respectively; extent of plume beyond the site not known.

While there is correlation in detection of EDB and 1,2-DCA in drinking water samples, co-occurrence of lead scavengers and BTEX is not reported, which suggests that BTEX plumes can separate from the plume of these gasoline additives. Only a few states have requirements to test for lead scavengers at petroleum hydrocarbon contaminated sites, and therefore, U.S. EPA Office of Underground Storage Tanks (U.S. EPA, 2010) recommended states, tribes, and EPA regions to investigate lead scavengers at leaking UST sites.

U.S. EPA (2006) reports ranges of EDB and 1,2-DCA concentrations for PHC sites in three states (**Table F-5**).

Table F-5. Range of Groundwater Concentrations of EDB and 1,2-DCA at Select Sites as Compiled by U.S. EPA (2006)

State	Number of sites	EDB concentration range (µg/L)	1,2-DCA concentration range (µg/L)
Kansas	7	0.05 – 8,200	11 – 1,310
South Carolina	31	0.013 – 1,140	—
California	8	0.084 – 65	0.4 – 101

F.4.4 Vadose Zone Studies

Fate and transport of EDB and 1,2-DCA in the vadose (unsaturated soil) zone were not the focus of any studies obtained for this review. The focus is rather on groundwater contamination as these compounds have high aqueous solubility and low soil organic carbon-water partitioning coefficients (K_{oc}) and are therefore mobile in soil pore waters and groundwater. However, EDB and 1,2-DCA can volatilize from solution, and their volatilization from moist soil surfaces is considered to be an important subsurface loss process (U.S. EPA, 2006).

F.5 Management Strategy

In a review of treatment technologies, U.S. EPA (2006) lists the most widely used groundwater treatment technologies for EDB as air sparging, soil vapor extraction (SVE), and pump and treat with granular activated carbon. Pump and treat is reported as the most widely used technology for 1,2-DCA. U.S. EPA (2006) also reports that monitored natural attenuation has been used at 31 leaking UST sites in South Carolina, while seven leaking UST sites in Kansas use air sparging and SVE or free product recovery for EDB remediation.

McGuire and Wilson (2010) present the results of SVE and air sparging treatment of a plume containing BTEX, EDB, and 1,2-DCA in northwest Kansas. The results show that:

- EDB and 1,2-DCA are degradable when oxygen is available, and they can be remediated along with BTEX;
- Knowledge of hydraulic flow is needed to maximize the effectiveness of the remediation;
- 1,2-DCA is more persistent than EDB and BTEX and slowest to clean up;
- In initial results, EDB and 1,2-DCA levels decreased by greater than 90 percent; and
- Reevaluation of the remedial strategy followed by replacement of deeper sparge wells with shallower ones and installation of new SVE wells resulted in concentrations of benzene, 1,2-DCA, and EDB falling below 0.15, 0.15, and 0.0013 µg/L, respectively.

Davis et al. (2009) conducted a field scale bioremediation experiment for 1,2-DCA on a layered silty and fine-sand anaerobic aquifer. Aerobic conditions were induced by air sparging and estimated aerobic biodegradation rates (0.06 – 0.20 %/day) were greater than laboratory-based studies. Air was injected for 50 days over a 12-month period, and 99 percent of the initial mass was removed.

Henderson et al. (2009) use an analytical model (REMChlor) to evaluate the effectiveness of partial source removal and plume remediation on EDB, 1,2-DCA and hydrocarbon plumes at UST sites. They consider anaerobic biostimulation and two scenarios with long and short plume lengths. First-order degradation rates are assigned for each compound in nine spatio-temporal plume zones (three spatial zones with respect to distance from source and three temporal zones with respect to NAPL release). The model results are assessed based on relative importance, defined as the ratio of predicted concentration to applicable standard (i.e., the MCL). They found that MtBE has the highest relative importance among the four compounds considered (benzene, MtBE, EDB, and 1,2-DCA). The relative importance of 1,2-DCA is low near the source, but it increases downgradient for both EDB and 1,2-DCA because these compounds have much slower aerobic degradation rates than benzene. Henderson and colleagues concluded that if equilibrium concentrations are more than a couple of orders of magnitude greater than the MCLs, a single remediation technique may not be sufficient to treat plumes of lead scavengers, hydrocarbons, and oxygenates.

F.6 Potential for Vapor Intrusion

Due to the relatively high aqueous solubility of EDB and 1,2-DCA, soil gas surveys are complicated to perform (Falta, 2004; and personal communication, August 2012). However, both chemicals are volatile with dimensionless Henry's constants that are about an order of magnitude lower than benzene. Furthermore, EPA considers inhalation to be an exposure pathway for EDB and 1,2-DCA and has developed inhalation toxicity reference values and indoor air RSLs for both EDB and 1,2-DCA (see **Table F-1**).

Table F-6shows the predicted soil gas concentrations for groundwater concentrations at one-half of the lowest detection limits available. The calculations assume that soil gas is in equilibrium with groundwater.

Table F-6. Predicted soil gas concentrations of EDB and 1,2-DCA[a,b]

Chemical	Groundwater Concentration[a] (μg/L)	Predicted Soil Gas Concentration ($\mu g/m^3$)	Predicted Indoor Air Concentration ($\mu g/m^3$)	Regional Indoor Air Screening Level[b] ($\mu g/m^3$)
EDB	0.005	0.1	0.001	0.004
1,2-DCA	0.01	0.5	0.005	0.09

[a] Using a value of one-half of the detection limit from US EPA method 8011 for EDB and US EPA method 8260B for 1,2-DCA.

[b] U.S. EPA Regional Screening Level (RSL), based on a 1×10^{-6} excess cancer risk. See Section F.2.

Assuming a shallow soil vapor-to-indoor air attenuation factor of 0.01 (based on the review and conservative approach described in Section 6.3 of this report), the predicted indoor air concentrations are 0.001 and 0.005 $\mu g/m^3$ for EDB and 1,2-DCA, which are below the RSLs for residential indoor air discussed in Section F.2. The predicted indoor air concentrations for EDB and 1,2-DCA (based on one-half of the detection limits in groundwater) are below the RSL for residential indoor air by a factor of 4 and 20, respectively, with the RSLs based on an excess cancer risk of 1×10^{-6}. Therefore a screening approach is feasible where groundwater concentrations are measured to determine the potential for vapor intrusion risks from EDB and 1,2-DCA.

F.7 References

Davis, G. B., B.M. Patterson, and C.D. Johnston. 2009. Aerobic bioremediation of 1,2 dichloroethane and vinyl chloride at field scale. *Journal of Contaminant Hydrology* 107:91-100.

Falta, R. W. 2004. The potential for ground water contamination by the gasoline lead scavengers ethylene dibromide and 1,2-dichloroethane. *Ground Water Monitoring & Remediation* 24: 76-87.

Henderson, J.K., D. Freedman, R.W. Falta, T. Kuder, and J.T. Wilson. 2008. Anaerobic biodegradation of ethylene dibromide and 1,2-dichloroethane in the presence of fuel hydrocarbons. *Environmental Science & Technology*, 42: 864-870.

Henderson, J. K., R.W. Falta, and D.L. Freedman. 2009. Simulation of the effect of remediation on EDB and 1,2-DCA plumes at sites contaminated by leaded gasoline. *Journal of Contaminant Hydrology* 108:29-45.

Klećka, G.M., C.L. Carpenter, and S.J. Gonsior. 1998. Biological transformations of 1,2-dichloroethane in subsurface soils and groundwater. *Journal of Contaminant Hydrology* 34:139–154.

Mayer, R. 2006. Analysis of Ground-Water Contamination by Ethylene Dibromide and 1,2-Dichloroethane at Leaded Gasoline Release Sites. M.S. Thesis. Clemson University. 188 pages.

McGuire, E., and J.T. Wilson. 2010. Successful application of air sparging to remediate ethylene dibromide (EDB) in groundwater in Kansas. Presented at the 22nd National Tanks Conference, Boston, MA, September 20–22, 2010.

McKeever, R., D. Sheppard, K. Nüsslein, K-H. Baek, K. Reiber, S.J. Ergas, R. Forbes, M. Hilyard, and C. Park. 2012. Biodegradation of ethylene dibromide (1,2-dibromoethane [EDB]) in microcosms simulating *in situ* and biostimulated conditions. *Journal of Hazardous Materials* 209-210: 92-98.

Ravi, V., J.S. Chen, J. T. Wilson, J. A. Johnson, W. Gierke, and L. Murdie. 1998. Evaluation of natural attenuation of benzene and dichloroethanes at the KL landfill. *Bioremediation Journal* 2:239–258.

Shen, H. and Wilson, J. T. (2007) Trichloroethylene removal from ground water in flow-through columns simulating a permeable reactive barrier constructed with plant mulch. *Environmental Science & Technology* 41:4077-4083.

U.S. EPA (Environmental Protection Agency). 2003. *Occurrence Estimation Methodology and Occurrence Findings Report of the Six-Year Review of Existing National Primary Drinking Water Regulations*. EPA-815/R-03-006, Washington, DC.

U.S. EPA (Environmental Protection Agency). 2006. Lead scavengers compendium: overview of properties, occurrence, and remedial technologies. Available at http://www.epa.gov/swerust1/cat/PBCOMPND.HTM.

U.S. EPA (Environmental Protection Agency). 2008. *Natural Attenuation of the Lead Scavengers 1,2-Dibromoethane (EDB) and 1,2-Dichloroethane (1,2-DCA) at Motor Fuel Release Sites and Implications for Risk Management*. Office of Research and Development, National Risk Management Research Laboratory, Ada, OK, EPA 600/R-08/107, September.

U.S. EPA (Environmental Protection Agency). 2010. Recommendation for states, tribes and EPA regions to investigate and clean up lead scavengers when present at leaking underground storage tank (LUST) sites. Memorandum. Office of Underground Storage Tanks, Office of Solid Waste and Emergency Response, Washington, DC, May.

Wilson, B. H., G. B. Smith and J. F. Rees. 1986. Biotransformation of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: a microcosm study. *Environmental Science & Technology* 20(10):997-1002.

Yu, R. (2011) Biodegradation Kinetics for 1,2-Dichloroethane and Ethylene Dibromide in Anaerobic Enrichment Cultures Grown on Each Compound, Master of Science Thesis, Environmental Engineering and Science, Clemson University, SC, January, 2011.

[This page intentionally left blank.]