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# Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites

U.S. Environmental Protection Agency
Office of Underground Storage Tanks
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## Tables

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## Acronyms

| | |
|---|---|
| 1,2-DCA | 1,2-Dichloroethane (also known as ethylene dichloride or EDC) |
| ATSDR | Agency for Toxic Substances and Disease Registry |
| BTEX | Benzene, Toluene, Ethylbenzene, Xylenes (there are three isomers of xylene) |
| CFR | Code of Federal Regulations |
| CSM | Conceptual Site Model |
| EDB | Ethylene Dibromide (also known as 1,2-dibromoethane) |
| IUR | Inhalation Unit Risk |
| ILCR | Incremental Lifetime Cancer Risk |
| IRIS | Integrated Risk Information System |
| ITRC | Interstate Technology & Regulatory Council |
| JEM | Johnson-Ettinger Model |
| LNAPL | Light Non-Aqueous Phase Liquid |
| MTBE | Methyl Tertiary-Butyl Ether |
| NAPL | Non-Aqueous Phase Liquid |
| OIG | Office of Inspector General |
| OSWER | Office of Solid Waste and Emergency Response |
| OUST | Office of Underground Storage Tanks |
| PHC | Petroleum Hydrocarbon |
| PPRTV | Provisional Peer Reviewed Toxicity Value |
| PVI | Petroleum Vapor Intrusion |
| $RBC_v$ | Risk-based Concentration, Soil Vapor |
| RfC | Reference Concentration (inhalation) |
| RSL | Regional Screening Level (for Chemical Contaminants at Superfund Sites) |
| SIM | Selective Ion Monitoring |
| TAME | Tertiary-Amyl Methyl Ether |
| TBA | Tertiary-Butyl Alcohol |
| TEL | Tetraethyl Lead |
| TMB | Trimethylbenzene |
| TML | Tetramethyl Lead |
| TPH | Total Petroleum Hydrocarbons |
| UST | Underground Storage Tank |
| VI | Vapor Intrusion |
| VISL | Vapor Intrusion Screening Level |
| VOC | Volatile Organic Compound |

## Disclaimer

This document presents current technical recommendations of the U.S. Environmental Protection Agency (EPA) based on our current understanding of petroleum vapor intrusion (PVI) into indoor air from subsurface sources. This document provides technical information to EPA, state, tribal, and local agencies. It also informs the public and the regulated community on how EPA intends to implement its regulations. This guidance document does not impose any requirements or obligations on the EPA, the states, or local or tribal governments, or the regulated community. Rather, the sources of authority and requirements for addressing subsurface vapor intrusion are the relevant statutes and regulations. Decisions regarding a particular situation should be made based upon statutory and regulatory authority. Decision-makers retain the discretion to adopt or approve approaches on a case-by-case basis that differ from this document. Contact information for your state's UST-implementing agency may be found at *http://www.epa.gov/oust/states/statcon1.htm*. EPA may revise this document in the future, as appropriate.

# Recommendations

This document provides technical information to regulatory personnel from the U.S. Environmental Protection Agency (EPA) and state[1], tribal, and local agencies for investigating and assessing petroleum vapor intrusion (PVI) at sites where petroleum hydrocarbons (PHCs) have been released from underground storage tanks (USTs). This document is comprised of two parts: *Recommendations*, which provides a description of EPA's recommended approach for addressing PVI, and *Supporting Technical Information*, which provides detailed technical information supporting the recommendations.

## Background

In 2002, EPA's Office of Solid Waste and Emergency Response (OSWER) issued draft vapor intrusion guidance, *OSWER Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Draft Vapor Intrusion Guidance)* (EPA, 2002).[2] This draft guidance explicitly states that it is not recommended for addressing petroleum vapor intrusion (PVI) at UST sites regulated under Subtitle I of the Solid Waste Disposal Act through the Hazardous and Solid Waste Amendments of 1984.

In 2009, EPA's Office of Underground Storage Tanks (OUST), at the request of partners and stakeholders, initiated a collaborative effort to develop a technical guide for petroleum vapor intrusion. Further highlighting the need for information on PVI, EPA's Office of Inspector General later that year released an evaluation report, *Lack of Final Guidance on Vapor Intrusion Impedes Efforts to Address Indoor Air Risks* (Report No. 10-P-0042).[3] The report included recommendations, one of which was for EPA to issue final vapor intrusion guidance that incorporates information on how risks from petroleum hydrocarbon vapors should be addressed. In response to stakeholder requests, EPA's Office of Underground Storage Tanks developed this technical guide, which is a companion to OSWER's more general vapor intrusion guide.[4] Together, these two documents replace the 2002 Draft Vapor Intrusion Guide.

EPA developed the two guides to address different scenarios and meet the needs of different audiences. The UST program regulates a very large universe of sites, typically gas stations, which share many similar characteristics, including small release volumes (compared to pipelines and tank farms, for example) and the potential for aerobic biodegradation of petroleum vapors. Based on these facts, and to meet the request of UST regulators and practitioners, EPA developed a guide specifically focused on petroleum UST releases. This PVI guide provides screening criteria based on physical separation distances between vapor sources and potential receptors. EPA OUST derived the screening criteria from an analysis of a large

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[1] The term *state* refers to regulatory agencies of states, territories, and the District of Columbia.

[2] The OSWER draft guidance is accessible at http://www.epa.gov/osw/hazard/correctiveaction/eis/vapor/complete.pdf

[3] The OIG report is accessible at http://www.epa.gov/oig/reports/2010/20091214-10-P-0042.pdf

[4] *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway From Subsurface Sources To Indoor Air* (OSWER Publication 9200.2-154), accessible at http://www.epa.gov/oswer/vaporintrusion/.

data set of samples from leaking UST sites.[5] In contrast, the OSWER Vapor Intrusion Guide addresses a wide variety of sites and a broader range of contaminants.

**Overview Of Petroleum Vapor Intrusion**

Vapor intrusion is the general term given to migration of volatile organic chemicals (VOCs) from any subsurface contaminant source, such as contaminated soil or groundwater, through the soil and into an overlying building. There are two general classes of VOCs that account for a large number of soil and groundwater contamination sites in the United States:

- Petroleum hydrocarbons (PHCs) and non-PHC fuel additives
- Chlorinated solvents (e.g., the dry cleaning chemical tetrachloroethylene, also known as perchloroethylene, (PCE), and the degreasing solvents trichloroethylene (TCE), 1,1,1-trichloroethane (TCA)).

In this guide, petroleum vapor intrusion (PVI) is defined as the intrusion of vapors from subsurface PHCs and non-PHC fuel additives into overlying or nearby buildings or structures.

Vapors emanating from petroleum-contaminated soil or groundwater that enter buildings may result in indoor air concentrations that pose a risk to building occupants. PVI may pose both immediate threats to safety (e.g., fire or explosion potential from petroleum vapors or methane) and possible adverse health effects from inhalation of toxic chemicals (e.g., exposure to benzene from gasoline). PVI may be associated with three groups of volatile chemicals:

- PHCs found in gasoline, diesel, and jet fuel (e.g., benzene, trimethylbenzenes (TMBs), naphthalene)
- Volatile chemicals other than PHCs that may be found in petroleum fuels, such as ethers, alcohols, and other fuel additives (e.g., methyl tertiary-butyl ether (MTBE), tertiary-butyl alcohol (TBA), ethylene dibromide (EDB), and 1,2-dichloroethane (1,2-DCA))
- Methane, which is generated from anaerobic biodegradation of PHCs and other constituents of petroleum fuels (especially ethanol), and organic matter in soil

In contrast to chlorinated solvents, PHCs generally biodegrade rapidly under aerobic conditions and if biodegradation is complete, produce only water and carbon dioxide. If biodegradation is incomplete a variety of intermediate degradation products may be formed, but these are usually less toxic than the parent PHCs.[6] If chlorinated solvents biodegrade it is usually under

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[5] *Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds* (EPA 510-R-13-001), accessible at *http://www.epa.gov/oust/cat/pvi/PVI_Database_Report.pdf*

[6] Some petroleum hydrocarbons may also degrade anaerobically and may produce methane, particularly if the source is from an ethanol-blended gasoline. A recent modeling study cautions that for releases of high ethanol fuel blends (i.e., greater than E-20) advective methane transport may result in methane buildup inside buildings and pose a risk of explosion (Ma, et al., 2014, Numerical Model Investigation for Potential Methane Explosion and Benzene Vapor Intrusion Associated with High-Ethanol Blend Releases, *Environmental Science and Technology* 48(1):474-481).

anaerobic conditions, which is slower and may produce intermediate degradation products that are more toxic than the parent compounds.

The aerobic biodegradability of PHCs typically reduces the potential for PVI and justifies a different approach for addressing PVI than for vapor intrusion from chlorinated solvents and other non-aerobically biodegradable VOCs.[7]

## Scope And Applicability

This PVI guide focuses on releases of petroleum-based fuels (e.g., gasoline, diesel), including both PHCs and non-PHC fuel additives, from underground storage tanks (USTs) regulated under Subtitle I of the Solid Waste Disposal Act of 1984, which are typically located at gas stations.[8] This guide applies to new and existing releases of PHCs and non-PHC fuel additives from leaking USTs and to previously closed sites where the implementing agency has reason to suspect that there may be a potential for PVI. Although EPA developed the PVI guide based on data from typical UST sites, this technical guide may also be helpful when addressing petroleum contamination at comparable non-UST sites. Petroleum contamination at sites that are not comparable to UST sites (such as refineries, petrochemical plants, terminals, aboveground storage tank farms, pipelines, and large scale fueling and storage operations at federal facilities), or sites with releases of non-petroleum chemicals including comingled plumes of petroleum and chlorinated solvents regardless of the source, should be addressed under OSWER's more general vapor intrusion guide.

This PVI guide does not impose legally binding requirements on implementing agencies or the regulated community. Decision-makers retain the discretion to adopt or approve approaches on a case-by-case basis that differ from this technical guide.

## Recommended Actions For Addressing PVI

Addressing the potential for PVI is an integral part of the normal response to a suspected or confirmed release from any Subtitle I regulated UST system. At any leaking UST site, it is important to have a thorough understanding of the release (i.e., source, composition, and magnitude) and other factors that may influence the distribution and transport of contaminants that impact human safety and health. Until it is clear that human health and the environment are adequately protected from adverse impacts caused by the release, appropriate site characterization, risk assessment, and corrective action activities should continue.

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[7] For more information on the differences between PHCs and chlorinated solvents, see *Petroleum Hydrocarbons And Chlorinated Solvents Differ In Their Potential For Vapor Intrusion* (*http://www.epa.gov/oust/cat/pvi/pvicvi.pdf*)

[8] EPA's UST regulations are contained in 40 CFR Parts 280, 281, and 282.50-282.105 (see *http://www.epa.gov/oust/fedlaws/cfr.htm*). Definitions of key terms such as UST and petroleum are found in 40 CFR 280. These definitions may change if the regulations are revised in the future.

EPA recommends the following actions for situations in which EPA, state, tribal, and local agencies are investigating releases of petroleum-based fuels (including addressing potential risks due to PVI) at leaking UST sites or where 40 CFR 280 requires[9] UST owners and operators to undertake release investigation and corrective action activities:

- ✓ **Assess and mitigate immediate threats to safety – see Section 1** (p.11)
  Identify whether there is a potential threat of explosion or fire due to the presence of flammable PHCs and non-PHC fuel additive vapors or methane[10]. A threat could be indicated by reports of the presence of odors, disagreeable taste of water, or visible signs of PHC contamination by building occupants. If so, alert first responders so they can, if necessary, evacuate these buildings until the potential threat to human safety from fire or explosion due to PVI has been assessed and mitigated as needed.

- ✓ **Conduct a site characterization and develop a conceptual site model (CSM) – see Section 3** (p.39)
  Site characterization data should be integrated into a conceptual site model (CSM). This includes characterization of the physical, biological, and chemical systems at the site, with emphasis on determining the spatial and temporal relationships between receptors and sources of contamination. The CSM should be used as the basis for planning the PVI investigation and making informed risk management decisions about the site and the threat posed by PVI to nearby receptors. EPA recommends that the site characterization include:

    - Determining the full extent and location of contamination and its nature
    - Assessing the potential for biodegradation of PHCs (and non-PHC fuel additives)
    - Defining the hydrologic and geologic characteristics of the site
    - Identifying potential receptors in the vicinity
    - Determining whether preferential transport pathways are present and connect PHC vapor sources with potential receptors[11]
    - Considering whether there are any other factors that may preclude the use of screening criteria

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[9] In the case of a suspected or confirmed release from a regulated UST system, Subparts E and F of 40 CFR 280 require owners and operators to investigate, report, and perform corrective action (including recovery of light non-aqueous phase liquid (LNAPL) to the maximum extent practicable) if contamination is present, and submit timely reports of activities and findings to the implementing agency.

[10] Note that methane cannot be detected based on odor, taste or visible signs. Methane-detecting devices must be used. For additional information on evaluating the presence of methane and potential hazards, see ASTM's "New Practice for Evaluating Potential Hazard Due to Methane in the Vadose Zone", which is accessible at *http://www.astm.org/DATABASE.CART/WORKITEMS/WK32621.htm*.

[11] Preferential transport pathways can short-circuit the protectiveness provided by the extent of the lateral inclusion zone and the vertical separation distances described in this guide. If preferential transport pathways connect a vapor source directly to a building, indoor air sampling paired with sub-slab vapor sampling is recommended.

- ✓ **Delineate a lateral inclusion zone – see Section 4** (p.44)
  Delineate a lateral inclusion zone to focus the investigation on buildings located within these boundaries. The lateral inclusion zone is based on the spacing between clean monitoring points; the closer the spacing of the clean monitoring points, the less extensive the lateral inclusion zone.

- ✓ **Determine vertical separation distances for each building within the lateral inclusion zone – see Section 5** (p.48)
  Further narrow the investigation to potential receptors (e.g., buildings) within the lateral inclusion zone and directly overlie contamination. For such buildings, determine the vertical distance between the contamination and the building basement, foundation, or slab. This distance is determined by collecting soil gas, soil, and groundwater samples as necessary. The thickness of clean soil separating contamination from the deepest point of the building basement, foundation, or slab is the vertical separation distance.

  Additional investigation is generally unnecessary if the vertical separation distance is greater than 6 feet for dissolved contamination beneath buildings of any size, or 15 feet for light non-aqueous phase liquid (LNAPL) if the overlying building has at least one side shorter than 66 feet in length. If the distance to contamination is less than the appropriate vertical separation distance (i.e., 6 feet or 15 feet; see **Section 5**), then additional investigation is recommended.

- ✓ **Evaluate vapor source and attenuation of PHC vapors – see Section 5** (p.48), **Section 8** (p.66), **Section 9** (p.75), **Section 10** (p.81), **Section 12** (p.100), **and Section 13** (p.106)
  If contamination (either dissolved, or LNAPL whether mobile or residual) is in direct contact with a building EPA recommends indoor air sampling. In the case of direct contact, sub-slab samples cannot be collected because there is no subsurface soil between the contamination and the building. Where contamination is not in direct contact with an overlying building, then choose one of two options: (1) collect near-slab (exterior) shallow soil gas samples paired with deep (source) soil gas samples, or (2) collect indoor air samples paired with sub-slab soil gas samples. If the potential for PVI cannot be ruled out based on near-slab and deep soil gas sampling, then EPA recommends indoor air sampling paired with sub-slab vapor sampling. If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends gathering additional information and data to determine whether mitigation is appropriate.

- ✓ **Mitigate PVI, as appropriate – see Section 1** (p.11)
  Mitigation involves interruption of the transport pathway for vapors between the source of contamination and potential receptors. Select a remedial design that is appropriate for the building and site. As necessary, establish institutional controls to limit or prohibit access to affected areas. Remediate the source of the contamination, including recovery of LNAPL (if present) to the maximum extent practicable.

**Community Engagement**

When conducting PVI assessments and follow-up actions, it is important to consider proactive community engagement. EPA acknowledges there is no single correct approach to engage the potentially impacted community in cleanup decisions. Community engagement can occur at any step in the process and may occur more than once. It is generally recognized that earlier and more frequent communication yields positive results, particularly for sites that pose a threat to human health or the environment, or when the public expresses an elevated level of concern or interest in the site. Depending on site circumstances, obtaining meaningful community input is a sound approach that may result in better-informed decisions. EPA developed several community engagement resources, which are available on the Office of Underground Storage Tanks website: Community Engagement And The Underground Storage Tank Program.[12] Some of the resources include:

- Guidelines For Tailoring Community Engagement Activities To Circumstances At Leaking Underground Storage Tank Sites.
- Community Engagement Resources (Toolbox) For Underground Storage Tank Programs.

**Table 1** and **Figure 1** briefly outline the **Recommended Actions for Addressing PVI**. Note that this process is not necessarily linear and some of these activities may occur in a different order or recur throughout the PVI investigation; this is especially true for community engagement. Additional technical information is presented in the second part of this guide, *Supporting Technical Information.*

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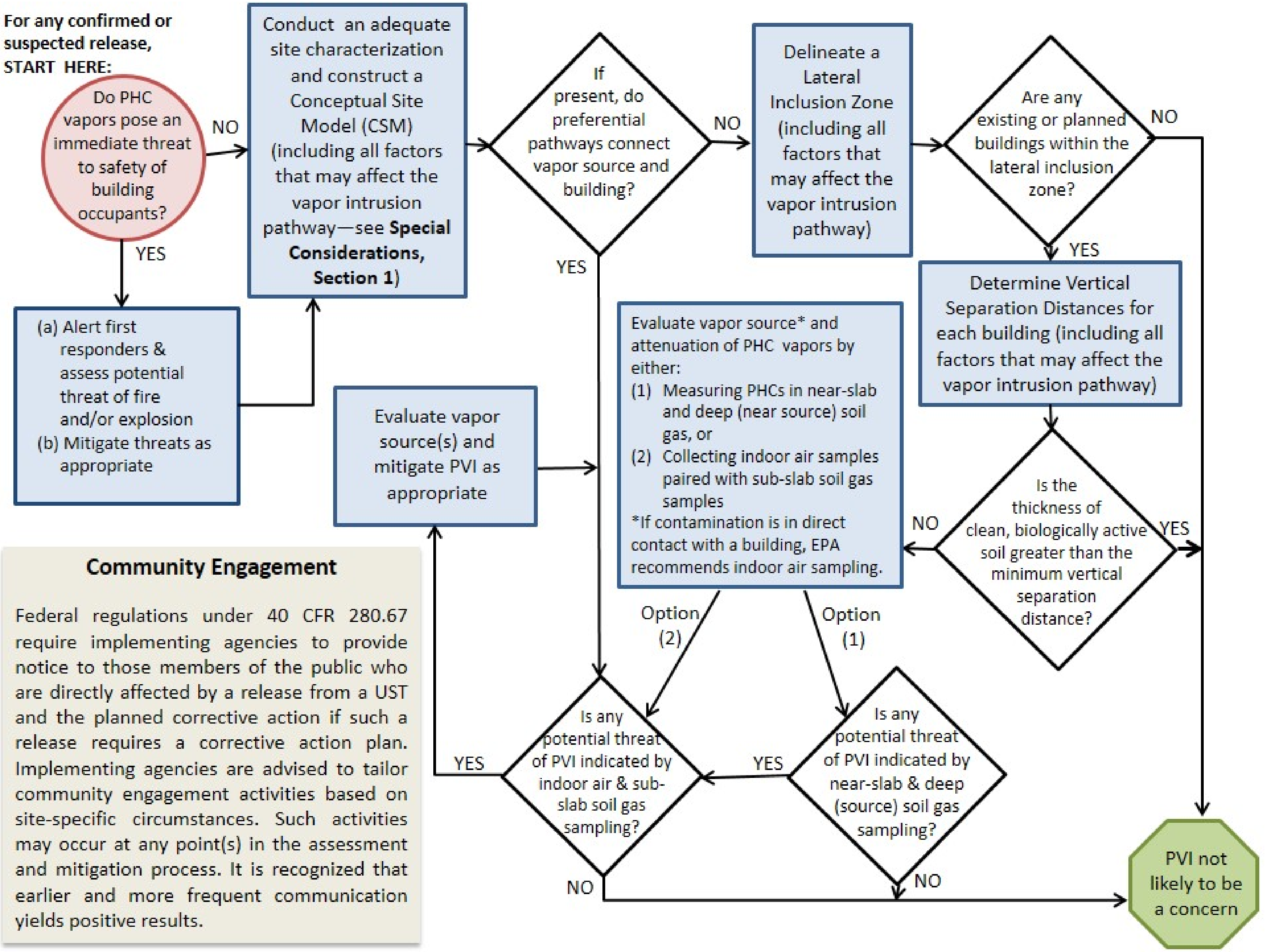
[12] The URL for this web site is *http://www.epa.gov/oust/communityengagement/index.htm*.

## Table 1. Recommended Actions For Addressing PVI At Leaking Underground Storage Tank Sites

| Recommended Actions | Purpose And Objectives | Procedures |
|---|---|---|
| **Assess and mitigate immediate threats to safety** (see Section 1, p.11) | Identify potential threat of explosion or fire due to petroleum vapors or methane. Threat may be indicated by:<br>• LNAPL visible in building, possibly as sheen in sump<br>• Noticeable petroleum odor; headache, dizziness, or nausea<br>• Atypical, unusual, or disagreeable taste or smell in the water supply<br>NOTE: Methane cannot be detected on the basis of odor, taste, or visible signs | • Investigate all reports of petroleum odors and other indicators within buildings<br>• Detection of the presence of methane; requires specialized devices<br>• Alert first responders so that they can, if necessary, evacuate building occupants as necessary until the potential for fire or explosion has been assessed and mitigated as needed |
| **Conduct a site characterization and develop a conceptual site model (CSM)** (see Section 3, p.39) | Characterize the physical, biological and chemical systems at the site, with emphasis on determining the spatial and temporal relationship between receptors and sources of contamination by:<br>• Determining the full extent and location of contamination and its nature<br>• Assessing the potential for biodegradation of PHCs<br>• Defining the hydrologic and geologic characteristics of the site<br>• Identifying potential receptors in the vicinity<br>• Identifying whether preferential transport pathways are present and connect PHC vapor sources with potential receptors. Preferential transport pathways Include both natural (i.e., geologic) and man-made (i.e., underground utilities, excavations) features. | • Collect sufficient site data and information to construct CSM<br>• Identify data gaps<br>• Update CSM as new data become available<br>• Where preferential transport pathways connect PHC vapor sources to receptors (e.g., buildings), indoor air sampling paired with sub-slab vapor sampling is recommended |
| **Delineate a lateral inclusion zone** (see Section 4, p.44) | Screen out buildings that are not likely to be impacted by PVI to narrow the investigation to only those buildings that have a greater potential for PVI and for which further investigation should be conducted.<br>The lateral inclusion zone is site-specific and:<br>• Based on the extent of contamination and distance between clean monitoring points<br>• Decreases in extent as additional data are collected to reduce uncertainty in the CSM | • Construct lateral inclusion zone based on distance between clean monitoring points (includes consideration of the presence of preferential transport pathways) |
| **Determine vertical separation distances** (see Section 5, p.48) | Further screen out buildings that are not likely to be impacted by PVI to focus the investigation on potential receptors that overlie contamination in the dissolved, vapor, and/or LNAPL phase. The vertical separation distance is:<br>• The thickness of clean, biologically-active soil | • For each building within the lateral inclusion zone, collect additional soil gas, soil, and groundwater samples as necessary to determine the vertical separation distance. Additional investigation is generally unnecessary |

| Recommended Actions | Purpose And Objectives | Procedures |
|---|---|---|
|  | (see **Section 9**, p.75) separating contamination from overlying buildings or other potential receptors<br>- Determined by site-specific sampling to determine the depth at which contamination is present | If the distance to contamination is greater than:<br>- 6 feet for dissolved contamination beneath buildings of any size, or<br>- 15 feet for LNAPL if the overlying building has at least one side shorter than 66 feet in length<br>- If the distance to contamination is less than those indicated above, then additional investigation is recommended. |
| **Evaluate vapor source and attenuation of PHC vapors** (see Section 5, p.48, Section 8, p.66, Section 9, p.75, Section 10, p.81, Section 12, p.100, and Section 13, p.106) | Carefully evaluate the potential for PVI into those buildings identified as being the most likely to be impacted by PVI. This is a building-by-building evaluation based on sampling conducted within close proximity to the building or inside the building as necessary. | If contamination is in direct contact with building basement, foundation, or slab, then collect indoor air samples. Otherwise choose either option (1) or (2) below:<br>1. Collect near-slab soil gas samples coupled with deep (source) soil gas samples. If a potential threat of PVI is indicated, then proceed to option 2. If not, PVI is not likely to be a concern.<br>2. Collect indoor air samples paired with sub-slab soil gas samples. If these results indicate a potential threat of PVI, mitigate PVI as appropriate. |
| **Mitigate PVI as appropriate** (see Section 1, p.11) | Interrupt the pathway between the source of contamination and potential receptors.<br>- Numerous approaches depending on building characteristics | - Select a remedial design that is appropriate for building and site<br>- Remediate source of contamination, including recovery of LNAPL (if present) to the maximum extent practicable<br>- Establish institutional controls to limit or prohibit access to affected areas of building, as necessary |

**Figure 1. Flowchart For Addressing PVI At Leaking Underground Storage Tank Sites**



**Community Engagement**

Federal regulations under 40 CFR 280.67 require implementing agencies to provide notice to those members of the public who are directly affected by a release from a UST and the planned corrective action if such a release requires a corrective action plan. Implementing agencies are advised to tailor community engagement activities based on site-specific circumstances. Such activities may occur at any point(s) in the assessment and mitigation process. It is recognized that earlier and more frequent communication yields positive results.

## Supporting Technical Information

The following sections provide technical information in support of EPA's recommended actions as outlined in **Table 1** (p.7) and depicted in **Figure 1** (p.9). Each section presents information in a standardized format, which is easy to follow and allows for future revisions, as necessary.

Additional sources of information may be found in the Petroleum Vapor Intrusion Compendium (*http://www.epa.gov/oust/cat/pvi/*), located on the Office of Underground Storage Tanks (OUST) website (*http://www.epa.gov/oust/*).

Page

# 1. Petroleum Vapor Intrusion (PVI)

## Description

Petroleum vapor intrusion (PVI) occurs when vapors from petroleum hydrocarbons (PHCs) migrate through the subsurface into overlying or nearby buildings. Fuels such as gasoline, diesel, aviation gasoline, and jet fuel are comprised primarily of PHCs with some non-petroleum based additives. Under certain circumstances, PVI may result in indoor air concentrations that pose a risk to building occupants. PVI may pose immediate threats to safety (e.g., fire or explosion potential from petroleum vapors or methane) or possible adverse health effects from inhalation of toxic chemicals (e.g., exposure to benzene from gasoline). Vapor concentrations generally decrease with increasing distance from a subsurface vapor source due to aerobic biodegradation, and eventually at some distance the concentrations become negligible.

### Composition Of Petroleum Fuels

Petroleum fuels are comprised of hundreds of individual compounds. PHCs present in petroleum fuels generally belong to one of two major groups: aromatics and aliphatics. The aromatic PHCs are characterized as having one or more benzene rings. Benzene, toluene, ethylbenzene, and the three isomers of xylene are collectively referred to as BTEX. The aliphatics are non-aromatic PHCs consisting of straight-chains, branched chains, or non-aromatic rings. Although BTEX represent the group of PHCs that receive the most attention at typical leaking underground storage tank (UST) sites, they are not the only compounds that may pose a risk to human health.[13] Petroleum fuels may also contain a variety of non-PHC volatile organic chemicals (VOCs) as additives to enhance performance. Fuel oxygenates such as methyl

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[13] The federal UST program does not prescribe human health values for contaminants; implementing authorities should use exposure values and attenuation factors appropriate for the contaminants present and the characteristics of exposure (e.g., residential vs industrial). Although there is a lack of toxicological data for many PHCs, EPA provides some information that may be applicable. For example, EPA provides vapor intrusion screening levels (VISLs) for a variety of volatile chemicals known to pose a potential cancer risk or noncancer hazard through the inhalation pathway. These VISLs, which are calculated by the VISL Calculator (EPA, 2014b), are generally recommended, medium-specific, risk-based screening-level concentrations intended for use in identifying areas or buildings that may warrant further investigation and mitigation of vapor intrusion, as appropriate. VISLs are calculated for concentrations of volatile chemicals in groundwater, soil gas (exterior to buildings and sub-slab), and indoor air for default target risk levels and exposure scenarios. The VISL Calculator does not account for biodegradation so attenuation factors may need to be adjusted for biodegradable chemicals. The VISL Calculator draws on toxicity values from Regional Screening Levels (RSLs) for Chemical Contaminants at Superfund Sites, accessible at *http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm*. Both the *VISL Calculator User's Guide* (EPA, 2014a) and *VISL Calculator* (EPA, 2014b) may be downloaded from EPA's web site: *http://www.epa.gov/oswer/vaporintrusion/guidance.html*. RSLs are drawn from a variety of sources according to EPA's three-tiered hierarchy of toxicity data (see "Human Health Toxicity Values in Superfund Risk Assessments" OSWER Directive 9285.7-53, 2003). Tier 1 (highest quality data) is EPA's Integrated Risk Information System (IRIS), accessible at *http://www.epa.gov/iris/*. Tier 2 are Provisional Peer Reviewed Toxicity Values (PPRTVs), accessible at *http://hhpprtv.ornl.gov/* (also see EPA, 2009). Tier 3 include toxicity values from other sources such as the Agency for Toxic Substances and Disease Registry (ATSDR). Several states have also developed toxicity values, including California (CA DTSC, 2009), Hawai'i (HI DOH, 2008, 2012), Massachusetts (MA DEP, 2003), New Jersey (NJ DEP, 2013), and Washington (WA DEC, 2006). Links to these sources are provided under *References Cited* at the end of this section.

tertiary-butyl ether (MTBE) and tertiary-butyl alcohol (TBA), and the lead scavengers[14] ethylene dibromide (EDB), and 1,2-dichloroethane (1,2-DCA), plus other PHCs (e.g., naphthalene), may also pose a risk to human health. If present, their vapor intrusion potential should be assessed (see **Section 10**, p.81). The presence of biodegradable VOCs other than benzene may result in depletion of oxygen that is necessary for aerobic biodegradation of benzene, potentially resulting in farther migration of benzene vapors.

### Phase Partitioning

When petroleum fuels are released into the subsurface from a leaking UST, PHCs may partition into several phases:

- Globules of light non-aqueous phase liquid (LNAPL) trapped within soil pore spaces (i.e., residual LNAPL)
- Dissolved in soil moisture
- Adhered onto the surface of, or absorbed into, soil solids
- Vapors in soil gas
- Accumulations of mobile LNAPL on and in the capillary fringe[15]
- Dissolved in groundwater

Low volume releases may result in contamination of only soil (including soil gas and soil moisture) and remain in the vadose zone. If the volume of a fuel release is sufficient, the fuel may accumulate on and in the capillary fringe and become mobile LNAPL. The mobile LNAPL generally spreads in the direction of groundwater flow, and may accumulate in monitoring wells. Temporal fluctuations in the elevation of the water table typically create a vertical smear zone of residual LNAPL contamination both above and below the average water table elevation. The more soluble components of the LNAPL mass dissolve into groundwater and are transported down gradient by the flowing groundwater as an aqueous phase. The remaining LNAPL mass will contain a sizeable fraction of aliphatic and relatively insoluble PHCs (e.g., naphthalene), especially if the source is large or unweathered (Lahvis, et al., 2013; EPA, 2013a). PHCs in the residual phase (both above and below the water table), the mobile phase (i.e., free product, LNAPL plume), and the dissolved phase (i.e., contaminant plume) all can serve as sources of PHC vapors. **Figure 2** illustrates the typical distribution of petroleum fuels in the subsurface resulting from a leaking UST. See **Section 2** (p.33) for a more detailed discussion of typical PVI scenarios.

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[14] Older sites, where leaded gasoline was released to the subsurface, should be assessed for EDB and 1,2-DCA as they may represent a potential source of vapors (see **Section 10**). For more information about lead scavengers, see Appendix F in *Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds* (EPA, 2013) and EPA's Lead Scavengers web site at *http://www.epa.gov/oust/cat/leadscav.htm*.

[15] Mobile LNAPL is often referred to as free product, especially in older documents and 40 CFR 280.

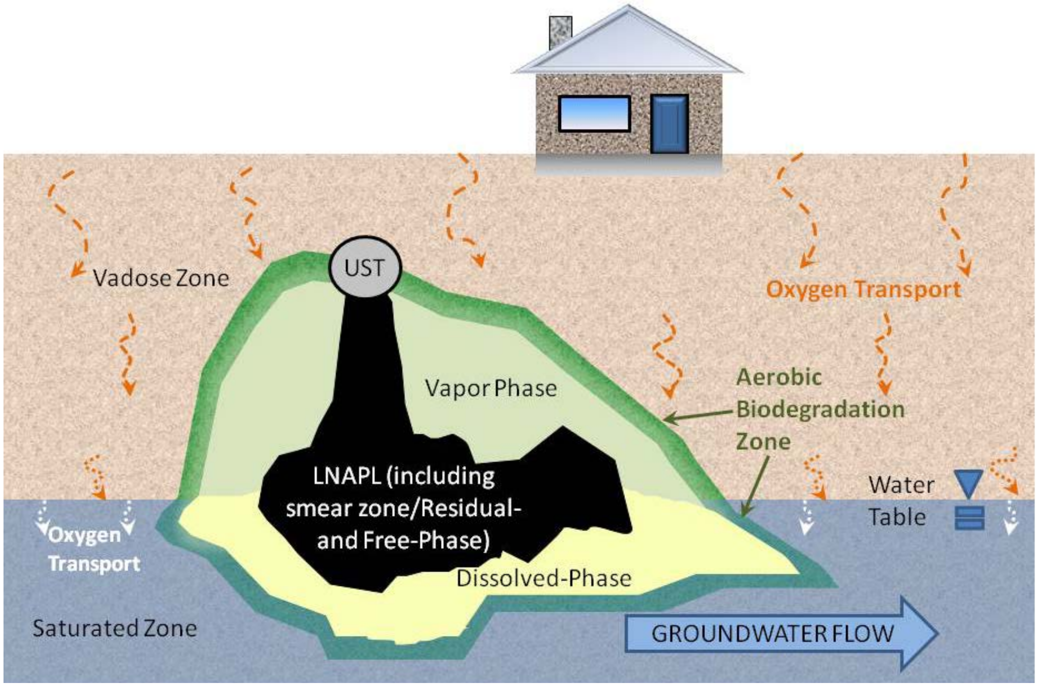

**Figure 2. Conceptual Model Of Typical Petroleum Hydrocarbon Release**

Aerobic biodegradation of PHCs along the perimeter of the vapor and dissolved plumes may limit the spread of subsurface contamination. Effective oxygen transport (dashed arrows) maintains aerobic conditions in the biodegradation zone. Petroleum LNAPL collects at the capillary fringe between the saturated and unsaturated zones (EPA, 2012).

### Vapor Migration

Vapor migration results from two processes: diffusion and advection. Diffusion is the process whereby net transport of vapors from a source area of higher concentration (e.g., LNAPL, residual LNAPL, or dissolved plume) to an area of lower concentration occurs as a result of random molecular motion. Diffusion can also lead to chemical migration into buildings directly through a dirt floor or crawlspace, or through openings in the building slab and foundation such as passages for utility lines, sumps, and elevator pits. Also, intact concrete has appreciable permeability to diffusive gas movement (Kobayashi and Shuttoh, 1991; Sanjuan and Munoz-Martialay, 1996; and Tittarelli, 2009) and the permeability increases substantially when cracks are present (Daoud and Renken, 1999; EPA, 1995).

Advection refers to the movement of soil gas in response to pressure gradients. Advection can be an important mechanism for drawing soil gas and contaminant vapors through cracks in the basement floor or foundation into the building or back into the soil beneath the building. Heating and cooling systems can create differential pressures inside the building. When the pressure inside the building is lower than the pressure in the subsurface, vapors are drawn into the building. Conversely, when the pressure inside the building is greater than the pressure in the subsurface, air within the building may be forced into the subsurface causing some degree of reoxygenation (Lundegard, Johnson, and Dahlen, 2008). Wind or changes in barometric pressure may also drive advective transport of oxygen into the subsurface beneath the building (Lundegard, Johnson, and Dahlen, 2008; Patterson and Davis, 2009; McHugh, DeBlanc, and Pokluda, 2006; Luo and Johnson, 2011; Robinson, Sextro, and Riley, 1997; Luo, et al., 2009; and Hong, Holton, and Johnson, 2012) (see **Section 11**).

### Biodegradation Of PHCs

Biodegradation of PHCs is recognized as one of the primary mechanisms by which petroleum and other hydrocarbon pollutants are removed from the environment (Baedecker, Cozzarelli, and Hoppel, 1987; Leahy and Colwell, 1990). The biodegradability of PHCs often reduces the potential for human exposure from PVI (McHugh, et al., 2010; EPA, 2012; Interstate Technology & Regulatory Council [ITRC], 2014). Microorganisms are widely distributed in the environment and most are recognized as having some ability to metabolize PHCs (Gale, 1951; Ward, Singh, and Van Hamme, 2003; Prince, 2010). Although most microbes degrade a narrow range of organic compounds, they typically exist as a mixed consortium that collectively can biodegrade a wide range of organic compounds. Biodegradation progresses through stages with certain microbes being predominant until environmental conditions (e.g., availability of specific hydrocarbons, micronutrients, electron acceptors) become unfavorable for them at which time different microbes then become dominant (Wang and Deshusses, 2006; Suflita and Mormile, 1993; Corseuil, et al., 1998; Moyer, et al., 1996; Boopathy, 2004; Alexander, 1980; Prince, Parkerton, and Lee, 2007; Prince, 2010; and Bekins, et al., 2001). Thus, aerobic and anaerobic microbes may coexist with one class essentially dormant while the other is active.

Gasoline and diesel fuel (including biodiesel) may be completely biodegraded under aerobic conditions (Hult, 1987; Prince and Douglas, 2010; Prince, Parkerton, and Lee, 2007; Marchal, et al., 2003), though diesel fuel is more difficult and slower to biodegrade (Marchal, et al., 2003).[16] The end products of complete biodegradation (mineralization) of PHCs are water and carbon dioxide. Mineralization of PHCs is almost always the consequence of microbial activity (Alexander, 1981). If aerobic biodegradation of PHCs is incomplete, a variety of intermediate degradation products may be formed, but none of these are more toxic than the parent PHCs.

Aerobic biodegradation is well documented for many individual PHCs and classes of PHCs including:

- N-alkanes (Bouchard, et al., 2005; Prince, Parkerton, and Lee, 2007; Bailey, Jobson, and Rogers, 1973; Hult, 1989; Baedecker, et al., 2011)
- Branched alkanes (Prince and Douglas, 2010; Prince, Parkerton, and Lee, 2007); cycloalkanes (Bouchard, et al., 2005)

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[16] The rate of aerobic biodegradation slows down with decreasing concentration of oxygen. Many aerobic microorganisms continue to function at concentrations as low as 0.1 mg/L of available oxygen, which is equivalent to an air concentration of 0.2%. For more information see research by Alagappan and Cowan (2004), Miralles-Wilhelm, Gelhar, and Kapoor (1997), and Mohamed, Saleh, and Sherif (2010).

- Aromatics (Wang and Deshusses, 2007; Phelps and Young, 1999; Landmeyer and Bradley, 2003; Lahvis, Baker, and Baehr, 2004; Lahvis, Baehr, and Baker, 1999; Bailey, Jobson, and Rogers, 1973; ZoBell, 1946; Corseuil, et al., 1998; Richnow et al., 2003)
- Naphthenes (Prince, Parketon, and Lee, 2007; Bailey, Jobson, and Rogers, 1973; Anderson, et al., 1999; ZoBell, 1946)
- Phenols (ZoBell, 1946; Basha, Rajendran, and Thangavelu, 2010)
- Trimethylbenzenes (Chen, et al., 2009)

Though aerobic biodegradation has been studied for over a century, anaerobic biodegradation of PHCs has been recognized only within the past three decades (Widdel, Boetius, and Rabus, 2006; Spormann and Widdel, 2000; and Townsend, et al., 2003). Anaerobic microorganisms degrade PHCs by using an electron acceptor other than oxygen (e.g., sulfate, nitrate, ferrous iron, or carbon dioxide). Anaerobic biodegradation is a slower process than aerobic biodegradation (Widdel, Boetius, and Rabus, 2006; Bailey, Jobson, and Rogers, 1973; and Lanham et al., 2013) and anaerobes grow slower than their aerobic counterparts (Widdel, Knittel, and Galushko, 2010). Instead of water and carbon dioxide, complete anaerobic biodegradation of PHCs (and naturally-occurring organic matter in soil, such as peat) can produce methane (Zengler, et al., 1999), especially with a release of an ethanol-blended gasoline (Jewell and Wilson, 2011; Ma, et al., 2012; Ma, et al., 2014). Incomplete anaerobic biodegradation of PHCs can produce compounds of higher toxicity, but these vapors are readily biodegraded in the vadose zone under aerobic conditions, and thus should not present a threat of vapor intrusion. Anaerobic biodegradation is typically the predominant mechanism of biodegradation in the source zone (Anderson and Lovley, 1997). Additional references documenting anaerobic biodegradation of PHCs are listed under *Additional Information* at the end of this section.

### Importance

Important factors cited by Lahvis and Baehr (1996) and Suarez and Rifai (1999) as being influential for aerobic biodegradation of PHC vapors include:

- Vapor source hydrocarbon concentration, flux, and composition (including methane)
- Oxygen demand (i.e., the oxygen required to biodegrade the available hydrocarbons and any other organic matter present) and oxygen availability
- Soil type and properties (including texture and moisture content)
- Availability of essential micronutrients
- Ambient temperature in the subsurface
- The pH of the soil and groundwater

Additional factors cited by EPA (2012) as influencing the potential for PVI include:

- Size and characteristics of the building and adjacent land surface
- Distance between the vapor source and the building

### Assessment

An assessment of the potential for PVI is not an isolated activity, but rather an integral part of the normal response to a suspected or confirmed release of PHCs from a leaking UST. At any leaking UST site (including abandoned sites or those that will be redeveloped for other uses), it is important to have a thorough understanding of the nature and magnitude of the release; the physical, biological, and chemical characteristics of the subsurface environment; an understanding of the preferential pathways for contaminant transport; and locations of receptors in the vicinity of the release. This is determined through collection and analysis of samples of soil, soil gas, groundwater, and sometimes LNAPL. Any other conditions (e.g., seasonal, weather-related; see **Section 11**, p.96) that may influence the transport of contaminants and potentially impact the safety and health of nearby building occupants should also be investigated.

Vapors emanating from dissolved-phase sources are primarily water soluble compounds, the more soluble aromatic hydrocarbons (e.g., BTEX) and other volatile and semi-volatile hydrocarbons and fuel additives (Lahvis, et al, 2013; EPA, 2013a). Vapors emanating from LNAPL sources contain a significantly larger fraction of aliphatic compounds and relatively insoluble hydrocarbons, especially if the source is large or unweathered (Lahvis, et al., 2013; EPA, 2012). Analyses of samples of soil, soil gas, groundwater, and LNAPL collected during site characterization (see **Section 3**, p.39) will provide information on specific contaminants that may warrant assessment for potential vapor intrusion.

### Special Considerations

Several factors may preclude the effectiveness of aerobic biodegradation to mitigate the threat of vapor intrusion. They include:

- Source volume and composition (including PHCs and non-PHC fuel additives)
- Soil properties (moisture content, permeability, high organic carbon content, especially peat)
- Large building size
- Extensive impermeable surface covering (e.g., asphalt, concrete)
- Preferential transport pathways (including both natural and man-made)

If present, these factors may reduce the potential for biodegradation of PHC vapors and warrant additional investigative steps (e.g., collection of soil gas samples—see **Section 8**, p.66) to determine if the use of screening criteria (e.g., vertical separation distance) is appropriate.

The age and volume of release should be determined or estimated. When the release is relatively recent or if the volume of the release is relatively large[17], there is greater potential for PVI than for smaller or older releases, which may be more weathered. Large volume PHC

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[17] The adjective *large* refers to either the total volume of the release or the areal extent (footprint) of the LNAPL mass in the subsurface.

releases may require a greater separation distance for biodegradation to be effective due to increased oxygen demand (EPA, 2013a).

Biodegradation of recent releases of high ethanol blended gasoline (i.e., E-20 or greater) may consume oxygen that would otherwise be available for biodegradation of PHCs resulting in an increased potential for PVI (Ma et al., 2014). In addition, the biodegradation of ethanol may result in the advective transport of methane and a potential risk of explosion. Thus, larger separation distances may be necessary to mitigate the threat of explosion or PVI at sites where high ethanol blended fuel has been released into the subsurface (Ma et al., 2014).

Preferential transport pathways may be either natural (e.g., fractures in rock, solution channels in karst terrain, bedding planes, joints, high permeability layers) or man-made (e.g., utility corridors including sewer lines themselves, trenches, excavations). Because they increase the speed at which the contaminants move through the subsurface, preferential transport pathways can potentially short circuit protectiveness that would otherwise be provided by biodegradation of PHCs and other fuel additives in homogeneous soils. Typically, it is difficult to detect and map natural preferential transport pathways, and contamination may present itself in unexpected locations. Local government offices have maps of utility corridors that can provide information on the presence and location of man-made preferential transport pathways.[18]

### Recommended Steps For Addressing The Potential Risk From PVI

EPA recommends the following actions for situations in which EPA, state, tribal, and local agencies are investigating releases of petroleum-based fuels (including addressing potential risks due to PVI) at leaking UST sites or where 40 CFR 280 requires[19] UST owners and operators to undertake release investigation and corrective action activities:

- ✓ ***Assess and mitigate immediate threats to safety***

Some releases from UST systems are discovered through noticeable sensory indicators on neighboring properties. Indicators may include sight, smell, taste, or physiological effects (e.g., dizziness, headache, nausea, vomiting, and confusion). The presence of odors does not necessarily correspond to adverse health or safety impacts from PVI, as the odors could be the result of indoor vapor sources. However, it is generally prudent to investigate any reports of odors in close proximity to UST systems as the odor threshold for some chemicals exceeds their acceptable health-based concentrations. PHC odors are a nuisance and may trigger the need

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[18] A federally mandated national call center was established to ensure that utility lines are marked before digging or boring. Dial 811 to have the locations of utilities marked before conducting site work that involves digging or boring. For more information, visit *http://www.call811.com/default.aspx*

[19] In the case of a suspected or confirmed release from a regulated UST system, Subparts E and F of 40 CFR 280 require owners and operators to investigate, report, and perform corrective action (including recovery of LNAPL to the maximum extent practicable) if contamination is present, and submit timely reports of activities and findings to the implementing agency.

for abatement or mitigation even if the concentration in indoor air is below acute or chronic health-based levels.

In confined spaces, the presence of flammable PHC vapors and non-PHC fuel additive vapors or methane may pose a threat of fire or explosion and endanger building occupants. Federal regulations (40 CFR 280.61) require that immediate action be taken to prevent any further release of the regulated substance into the environment and that fire, explosion, and vapor hazards be identified and mitigated (*Federal Register*, 1988). Section 280.64 requires that free product (mobile LNAPL) be recovered to the maximum extent practicable and that records be kept of the volumes recovered. First responders, typically fire department personnel, should be notified if there are reports of either odor from petroleum or the presence of an oily sheen on basement floors or in sumps, drains, or elevator pits. It may be necessary to evacuate building occupants until the threat from fire or explosion has been mitigated. Since methane is odorless and colorless, monitoring devices are required if methane is suspected.

✓ ***Conduct a site characterization and develop a conceptual site model (CSM)***

Once the immediate threats to safety have been mitigated (or it is determined that immediate threats do not exist), determine whether there is a long-term threat to human health and the environment from intrusion of petroleum vapors. Site characterization[20] and CSM development provide information about the full extent and location of the contamination; the nature and characteristics of the contamination; the characteristics of the site that influence contaminant migration, including the potential for biodegradation of PHCs; and the locations of receptors. Information derived from the CSM helps ensure that sources, pathways, and receptors throughout the site are considered; this knowledge can lead to selection of the most appropriate sampling locations and techniques. A systematic soil gas sampling program may also aid in defining the full extent and location of contamination, detecting the presence of preferential transport pathways, and locating pockets of PHC vapors. Preferential transport pathways are avenues of least resistance to the migration of contaminants whether in the dissolved phase, LNAPL phase, or vapor phase. They include both natural and man-made features such as:

**Natural**

- gravel lenses and channels
- solution channels in karst terrain
- bedding planes
- fractures, joints, and faults in consolidated rock

**Man-made**

- utility corridors (including sewer lines themselves) and trenches
- elevator pits
- sumps and drainage pits
- other types of excavations

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[20] The term *site characterization* is used throughout this document for consistency. *Site characterization* is often used interchangeably with *site assessment*, *site evaluation*, *site investigation*, and sometimes *site check* as they all mean assembling and collecting information and data about a site.

Preferential transport pathways increase the speed at which contamination moves through the subsurface such that contaminants may not biodegrade by the time they reach receptors. They can also allow atypical movement, which in some cases may be opposite groundwater flow (ITRC, 2014). Because preferential transport pathways can short-circuit the protectiveness provided by lateral and vertical separation distances described in this PVI guide, indoor air sampling is recommended in situations where they connect vapor sources and receptors. See **Section 3** (p.39) for more information about site characterization and CSMs.

✓ ***Delineate a lateral inclusion zone***

Based on the CSM, delineate a lateral inclusion zone. The lateral inclusion zone is the area surrounding a contaminant mass through which petroleum vapors may travel, intrude into buildings, and potentially pose a threat to human health and the environment. Buildings directly above contamination sources, whether as mobile LNAPL, residual LNAPL, or PHCs dissolved in groundwater, are considered within the lateral inclusion zone. Buildings outside this zone generally may be excluded from further assessment for PVI unless:

- Site conditions change (e.g., groundwater flow direction changes, contaminant plume migrates beyond the lateral inclusion zone, development or redevelopment of nearby properties)
- Preferential transport pathways are present

In such instances, additional investigation may be warranted to more fully evaluate the risk from PVI. See **Section 4** (p.44) for more information on delineating a lateral inclusion zone.

✓ ***Determine vertical separation distances***

The vertical separation distance is the thickness of clean, biologically active soil (see **Section 9**, p.75) between a contaminant mass and the lowest point of an overlying receptor (e.g., building basement floor, foundation, or crawl space surface). Consolidated rock is not soil and should not be included in the vertical separation distance. For example, for a situation in which there is 3 feet of soil above fractured rock and the depth to contaminated groundwater is 7 feet, the vertical separation distance is 3 feet, not 7 feet. Some buildings within the lateral inclusion zone will overlie PHC contamination that exists as either a mobile LNAPL mass, residual soil contamination (including the smear zone), or dissolved in a groundwater plume. However, not all of these buildings will be threatened by PVI due to aerobic biodegradation of PHCs provided there is sufficient vertical separation distance between the receptor and the vapor source. The vertical separation distance between contamination and overlying buildings is determined as part of the normal site characterization process. The full extent and location of contaminant sources should have been adequately mapped in the subsurface and the nature and characteristics of the contamination should have been determined during site characterization and conceptual site model development (see **Section 3**, p.39).

EPA (2013a) presents analysis of petroleum vapor source data and soil gas data from a number of leaking UST sites across the United States. The report findings support screening criteria for dissolved and LNAPL PHC releases from leaking USTs. For dissolved PHC sources that are separated from overlying buildings by more than 6 feet of clean, biologically active soil, the potential threat of PVI is negligible and further investigation for PVI is generally unnecessary. For LNAPL sources that are separated from overlying buildings by more than 15 feet of clean, biologically active soil, the potential threat of PVI is negligible and further investigation for PVI is generally unnecessary. These separation distances are believed to be sufficiently protective in most situations because they include a number of built-in safety factors, which are discussed in more detail in **Section 5** (p.48). If the distance separating the source of PHC vapors and overlying buildings is less than 6 feet for dissolved sources and 15 feet for LNAPL sources, additional investigation is recommended.

EPA (2013a) recognizes that there are a number of precluding factors that may justify a greater vertical separation distance in some cases. These factors include:

- Influence of methanogenesis on oxygen demand (especially for higher ethanol blends of gasoline)
- Effect of extensive high organic matter content soils (e.g., peat) with potentially high natural oxygen demand
- Reduced oxygen flux caused by certain geologic conditions (e.g., low permeability surface layer overlying coarse-grained soils, soil moisture from precipitation (Luo et al., 2009))
- Limited knowledge of vapor attenuation behavior in fractured rock
- Limited soil gas data for non-UST (e.g., petroleum refinery, fuel terminal) sites
- Limited data on vapor attenuation behavior of aliphatic compounds
- Lack of soil vapor data for the lead scavengers ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA) (see **Section 10**, p.81, for more information on these contaminants)

Other site characteristics that may warrant additional investigation include exceptionally dry soils (<2 percent soil moisture), areas covered by extensive impervious paving or large buildings, and presence of preferential transport pathways (see **Section 3**, p.39). Also, soil gas movement may vary seasonally in response to differential pressures created by heating and cooling of overlying buildings (see **Section 11**, p.96).

✓ ***Evaluate vapor source and attenuation of PHC vapors***

Where contamination is not in direct contact with an overlying building, EPA recommends one of two options: (1) collection of near-slab (exterior) shallow soil gas samples paired with deep (near source) soil gas samples, or (2) collection of indoor air samples paired with sub-slab soil gas samples to evaluate attenuation of PHC vapors and the potential for PVI.[21] When collecting soil gas samples[22], use option 1 under the following conditions (EPA, 2013b):

- A building, with the shortest side no longer than 66 feet, overlies LNAPL and the vertical separation distance is less than 15 feet, but not in direct contact with the building basement floor, foundation, or crawl space surface.
- A building, of any dimension, overlies dissolved PHC contamination and the vertical separation distance is less than 6 feet, but not in direct contact with the building basement floor, foundation, or crawl space surface.

Use option 2 for buildings larger than 66 feet on a side or if near-slab soil gas samples from around smaller buildings do not clearly demonstrate that biodegradation is sufficient to mitigate the threat of PVI by reducing PHC concentrations to below applicable human health thresholds (see Footnote #13).

The purpose of collecting paired samples is to enable determination of a building-specific vapor intrusion attenuation factor. Generic attenuation factors that do not account for biodegradation of PHCs are conservative and, likely overestimate the transfer of contaminants from soil gas to indoor air in most buildings. Attenuation factors (see **Section 12**, p.100) that account for biodegradation can be derived from models such as *BioVapor* or *PVIScreen* (see **Section 13**, p.106). Additional information may be found in Wilson *et al.* (2014).

If contamination (either dissolved, or LNAPL whether mobile or residual) is in direct contact with a building basement floor, foundation, or crawlspace surface, EPA recommends indoor air sampling (these samples cannot be paired with subsurface soil gas samples because there is no clean, biologically active soil between the contamination and the building). Information on collecting and analyzing sub-slab vapor samples and indoor air samples is beyond the scope of this document, but is provided in other documents, for example ITRC (2014) and EPA (2015).

Indoor air in many buildings will contain detectable levels of a number of vapor-forming compounds whether or not the building overlies a subsurface source of vapors, because indoor air can be impacted by a variety of indoor and outdoor sources. The composition of outdoor air surrounding a building is referred to as ambient air throughout this document. The combined contribution of indoor and outdoor sources of vapors to indoor air concentrations is referred to as background throughout this document. To differentiate and quantify the relative contribution of contaminants from PVI versus background sources, indoor air samples must be collected in conjunction with sub-slab (or near-slab, as appropriate) soil gas samples. ITRC

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[21] Implementing authorities may opt for sub-slab soil gas and indoor air sampling in any situation they deem necessary to protect the safety and health of building occupants.

[22] Soil gas samples should be analyzed for oxygen, carbon dioxide, PHCs (and any other fuel constituents likely to be present including fuel additives), and methane. As a quality assurance/quality control check, nitrogen can be added to the analyte list at a nominal cost. This will enable determination of whether significant concentrations of other gases are unaccounted for as these gases should account for nearly 100 percent of the total present. (See **Section 8**).

(2014) and EPA (2015) provide information on background sources, techniques, and methods to account for background contributions to indoor air concentrations.

Information on historic concentrations of background vapors is presented in *Background Indoor Air Concentrations of Volatile Organic Compounds in North American Residences (1990 – 2005): A Compilation of Statistics for Assessing Vapor Intrusion* (EPA, 2011b). In addition, the Montana Department of Environmental Quality (MT DEQ, 2012) conducted an extensive investigation of the indoor air quality of typical uncontaminated buildings in Montana. The objective of these studies is to illustrate the ranges and variability of VOC concentrations in indoor air resulting from sources other than vapor intrusion. While these studies provide expected ranges of indoor air contaminants, EPA recommends building-specific sampling (rather than using literature values) to characterize actual contaminant levels. If measured indoor air concentrations are found to greatly exceed the historic range of background levels, there is a greater likelihood that the indoor air concentrations are the result of vapor intrusion. Studies such as EPA (2011) and MT DEQ (2012) can be employed to determine whether measured indoor air concentrations exceed the historic range of background concentrations.

If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends additional investigation to determine whether mitigation is appropriate.

✓ ***Mitigate petroleum vapor intrusion, as appropriate***

If contaminant concentrations represent a potential threat of fire or explosion (i.e., vapor concentrations are more than 10% of the lower explosive limit), or indoor air sampling indicates that PVI is occurring, EPA recommends that active mitigation measures be immediately initiated. ITRC (2014) and EPA (2015) provide information on mitigation and remediation of vapor intrusion. In addition, the source of contamination should be remediated per Subpart F of the Federal Regulations (40 CFR 280.60 through 280.67) (Federal Register, 1988). In particular, 40 CFR 280.64 requires the recovery of LNAPL to the "maximum extent practicable".

See the following sections for more information on the factors discussed in the paragraphs above:

- **Section 3** (p.39) Site Characterization and Conceptual Site Model (CSM)
- **Section 4** (p.44) Lateral Inclusion Zone
- **Section 5** (p.48) Vertical Separation Distance
- **Section 6** (p.57) Mobile and Residual Light Non-Aqueous Phase Liquid (LNAPL)
- **Section 7** (p.61) Groundwater Flow and Dissolved Contaminant Plumes.
- **Section 8** (p.66) Soil Gas Profile
- **Section 9** (p.75) Clean, Biologically Active Soil

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## 2. Typical PVI Scenarios

### Description

The potential for PVI is primarily a function of the location of the contamination source relative to a potential receptor, source volume and strength, and the source mass distribution in the subsurface. Source concentrations are typically much higher for LNAPL sources than for dissolved-phase sources. Higher source concentrations will generate higher rates of mass diffusion (flux). The higher mass flux will also be more sustained over time because LNAPL sources will contain significantly more mass compared to dissolved-phase sources. Oxygen demand and the potential for encountering anaerobic conditions are also uniquely different between LNAPL and dissolved-phase sources. For both dissolved and LNAPL sources, the biodegradation reaction front is relatively narrow, but it occurs higher in the unsaturated zone (closer to land surface) over an LNAPL source than it does over a dissolved-phase source (**Figure 3**).

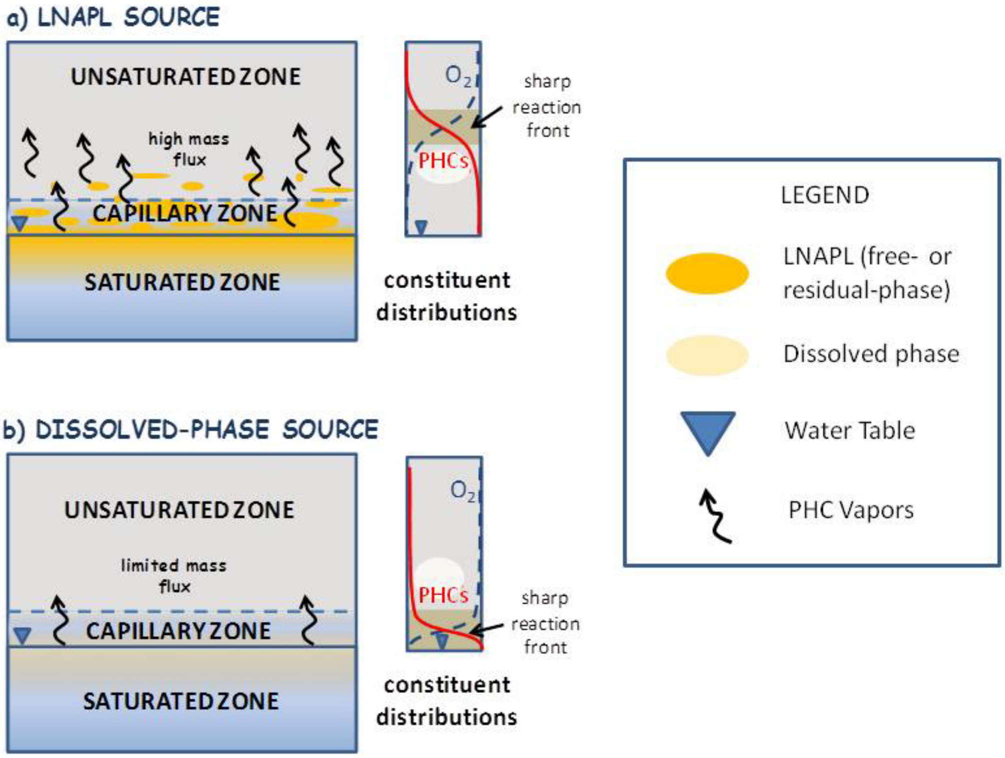

**Figure 3. Difference In Potential For PVI Based On Type Of Source: a) LNAPL, b) Dissolved Phase** (Source: Lahvis, et al., 2013. Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2013.)

LNAPL sources may be distributed both above and below the capillary fringe as a result of smearing from water-table fluctuations. This phenomenon will tend to enhance mass flux to the unsaturated zone because of direct partitioning between LNAPL (residual) and vapor phases. Conversely, the mass flux will be more limited for dissolved-phase sources because vapor transport through water is reduced relative to diffusion in soil gas (Golder Associates, 2006; Lahvis and Baehr, 1996). Vapor diffusion is limited by low effective air-phase porosity (i.e., high moisture saturation) and biodegradation in the capillary zone.

### Importance

Relatively few confirmed occurrences of PVI at petroleum sites are reported in the literature (EPA, 2013, Section 2.6, p.9). The most likely scenarios for PVI to occur are shallow PHC sources directly beneath buildings and mobile LNAPL or groundwater plumes with high concentrations of PHCs that are in direct contact with buildings (Davis, 2009; and McHugh, et al., 2010). A study by Peargin and Kolhatkar (2011) suggests that a dissolved source with benzene greater than 1 mg/L may behave like a LNAPL source in terms of vapor-generating capability.

### Assessment

Recommended steps for investigating PVI are discussed in **Section 1** (p.11). Application of the screening criteria allow for the determination of which buildings are threatened by PVI. Using this approach, resources can be appropriately focused on those buildings potentially impacted by PVI.

**Figure 4** presents typical scenarios of the spatial relationship between PHC sources and potential receptors. However, it is not intended to be a comprehensive depiction of all possible configurations of such a relationship.

**Table 2** summarizes the characteristics of these six scenarios relative to lateral and vertical distances from contamination and necessary investigation activities.

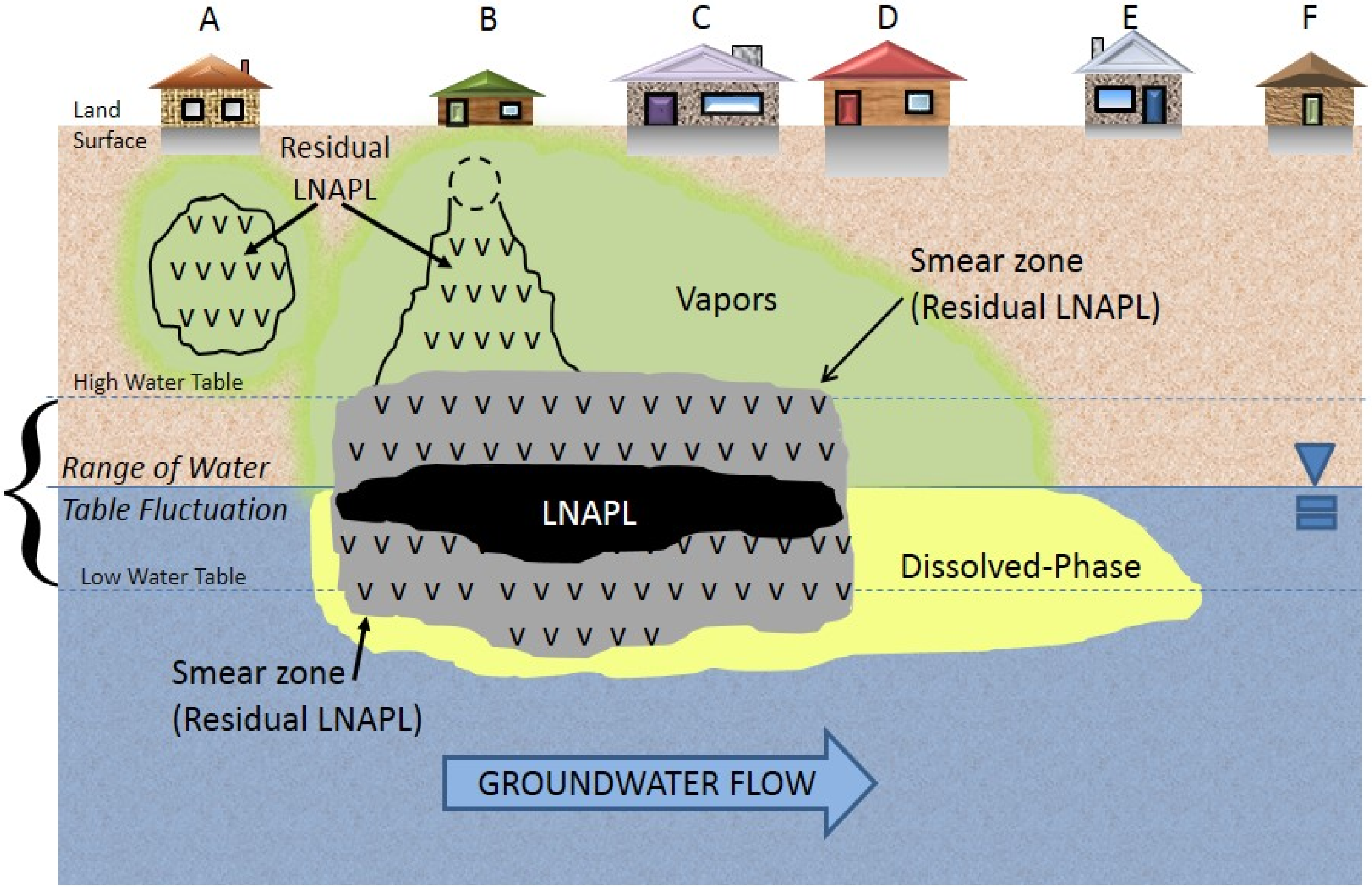

**Figure 4. Typical Scenarios Of Potential PVI Sources And Potential Receptors**

### Table 2. Summary Of Characteristics Of Typical Scenarios Of Petroleum Vapor Sources And Potential Receptors.

| Scenario (as illustrated in Figure 4) | Contamination Beneath Building? (building is within lateral inclusion zone) | Potential For PVI | Near-Slab* Soil Gas Sampling Recommended? |
|---|---|---|---|
| A | Yes; shallow residual LNAPL in the vadose zone | High | Yes, if vertical separation distance is less than 15 feet from the top of residual LNAPL, otherwise No |
| B | Yes; residual including smear zone, LNAPL, dissolved in groundwater | High | Yes, if vertical separation distance is less than 15 feet from the top of the smear zone, otherwise No |
| C | Yes; smear zone, LNAPL, dissolved in groundwater | Medium | Yes, if vertical separation distance is less than 15 feet from the top of the smear zone, otherwise No |
| D | Yes; dissolved in groundwater | Low | Yes, if vertical separation distance is less than 6 feet from the historical high water table elevation, otherwise No |
| E | Maybe; plume may be diving beneath water table | Low – None | Yes, if vertical separation distance is less than 6 feet from the historical high water table elevation, otherwise No |
| F | No | None | No |

*Near-slab soil gas samples should be collected from each side of the potentially impacted building and as close to the building as possible. These samples should be paired with deep (near source) soil gas samples. If these samples do not clearly demonstrate that biodegradation is sufficient to mitigate the threat of PVI into the building, EPA recommends collection of indoor air samples paired with sub-slab soil gas samples.

### Special Considerations

While biodegradation may reduce the potential for human exposure to petroleum vapors, its effectiveness in mitigating PVI may be limited by precluding factors such as:

- Migration of contaminants, especially plumes in flowing groundwater
- Presence of non-PHC chemicals that biodegrade too slowly (or the rate is not known with certainty)
- Presence of preferential transport pathways
- Extensive impermeable surface cover, or very large buildings
- Presence of higher blends of ethanol in gasoline that consumes oxygen that would otherwise be available for aerobic biodegradation of PHCs
- Generation of methane from higher blends of ethanol in gasoline that exerts high oxygen demand and presents a vapor intrusion threat itself
- Soils with high organic content (e.g., peat) that exert a high oxygen demand
- Soil conditions that are inhospitable to microorganisms such as insufficient soil moisture
- Insufficient thickness of clean, biologically active soil
- LNAPL source is relatively unweathered and rich in volatile PHCs

### Recommendation

EPA recommends conducting an adequate PVI investigation and following the steps described in **Section 1** (p.11) to determine which buildings may be at risk for PVI.

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# 3. Site Characterization And Conceptual Site Model (CSM)

## Description

Site characterization is the process by which site-specific information and data are gathered from a variety of sources to characterize the physical, biological, and chemical systems at a contaminated site. A conceptual site model (CSM) integrates all data and information into a three-dimensional picture of site conditions that illustrates contaminant distributions, release mechanisms, migration routes, exposure pathways, and potential receptors (EPA, 2012; ITRC, 2014). The CSM uses a combination of text and graphics to portray both known and hypothetical information (EPA, 2011). The CSM documents current conditions at the site and is supported by maps, cross-sections, and site diagrams. The CSM illustrates potential human and environmental exposure through contaminant release and migration toward receptors (EPA, 1995, 1996a). The CSM should be refined as new data are collected.

## Importance

At any leaking UST site, it is important to have a thorough understanding of the full extent and location of contamination (including both PHCs and non-PHC fuel additives), the characteristics of the site that influence contaminant migration (especially the presence of preferential transport pathways), and the locations of potential receptors. A CSM helps ensure that sources, pathways, and receptors throughout the site have been considered; this knowledge can lead to selection of the most appropriate sampling locations and techniques. The CSM assists the site manager in evaluating the interaction of different site features. Risk assessors use conceptual models to help plan for risk assessment activities (EPA, 1995). The CSM is the basis for making informed risk management decisions about the site and the threat posed by PVI to nearby buildings and their occupants. In addition, remedial action costs are influenced by the quality of the CSM (EPA, 1996b).

## Assessment

An investigation for PVI potential is not separate from the normal response to a confirmed UST release; an adequate site characterization is essential in order to construct an accurate CSM. A primary objective of site characterization is delineation of the aerial and vertical extent of contamination in the subsurface (per 40 CFR 280.65(a)) so that lateral and vertical separation distances can be accurately determined.[23] It is also important to determine whether preferential transport pathways are present and, if so, delineate them to determine if they connect vapor sources directly to potential receptors. Site characterization generally proceeds in a systematic manner, often beginning in or near the source area and working outward and in the downgradient direction in which groundwater flows.

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[23] The separation distances described in this document (**Section 5**, Table 3, p.52) and the protectiveness provided by clean, biologically active soil against vapor intrusion by PHCs may be insufficient to protect against vapor intrusion by non-PHC fuel additives. Additional investigation should be conducted where certain additives are present (see **Section 10**, p.81).

All information and data about the site should be integrated into a CSM, which is continually updated and refined to account for changing conditions and new information. Basic activities associated with developing a CSM include:

- Identification of potential contaminants[24]
- Identification and characterization of the source of contaminants
- Characterization of the geochemical parameters that affect biodegradation
- Characterization of the geologic and hydrogeologic characteristics of the subsurface
- Delineation of potential migration pathways, including preferential transport pathways, through environmental media
- Establishment of background levels of contaminants and areas of contamination for each contaminated medium
- Identification and characterization of potential receptors
- Determination of the limits of the study area or system boundaries

Tracking contaminant migration from sources to receptors is one of the most important uses of the CSM (ASTM, 2008). Uncertainties associated with the CSM should also be identified as well as the efforts taken to reduce uncertainties to acceptable levels (ASTM, 2008). As new information and data become available, the CSM should continually be refined (EPA, 1993; ITRC, 2007). ITRC (2014), EPA (2013, 2015), and Wilson et al., (2014) provide additional information about developing CSMs.

**Special Considerations**

The separation distances described in this document (**Section 5**, Table 3, p.52) and the protectiveness provided by clean, biologically active soil against vapor intrusion by PHCs may be insufficient to protect against vapor intrusion by non-PHC fuel additives. Additional investigation should be conducted where certain additives are present (see **Section 10**, p.81).

The presence and locations of preferential transport pathways should be identified and incorporated into the CSM. All new information and data about a site, including potential future land uses, should also be identified to refine the CSM.

**Recommendation**

Per Subparts E and F in 40 CFR 280.50 through 280.67 (see *http://www.epa.gov/oust/fedlaws/cfr.htm*), EPA recommends that an adequate site characterization considers the following:

- §280.52(b) Release Investigation and Confirmation Steps:

  "Owners and operators must measure for the presence of a release where contamination is most likely to be present at the UST site. In selecting sample types, sample locations, and measurement methods, owners and operators must consider the nature of the stored

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[24] The list of potential contaminants should include BTEX and other PHCs as well as non-PHC fuel additives likely to have been present in the fuel stored at the site. See **Section1** (p.11) and **Section 10** (p.81) for more information.

substance, the type of initial alarm or cause for suspicion, the type of backfill, the depth of ground water, and other factors appropriate for identifying the presence and source of the release."

- §280.62(a)(5) Initial Abatement Measures and Site Checks

"Measure for the presence of a release where contamination is most likely to be present at the UST site, unless the presence and source of the release have been confirmed in accordance with the site check required by §280.52(b) or the closure site assessment of §280.72(a). In selecting sample types, sample locations, and measurement methods, the owner and operator must consider the nature of the stored substance, the type of backfill, depth to ground water and other factors as appropriate for identifying the presence and source of the release. . ."

- §280.63(a)(1-4) Initial Site Characterization

". . .owners and operators must assemble information about the site and nature of the release, including information gained while confirming the release or completing the initial abatement measures. . . This information must include, but is not necessarily limited to the following: (1) Data on the nature and estimated quantity of release; (2) Data from available sources or site investigations concerning the following factors: surrounding populations, water quality, use and approximate locations of wells potentially affected by the release, subsurface soil conditions, locations of subsurface sewers, climatological conditions, and land use; (3) Results of the site check required under §280.62(a)(5); and (4) Results of the free product investigations. . ."

- §280.64 Free product removal

"At sites where investigations under §280.62(a)(6) indicate the presence of free product, owners and operators must remove free product to the maximum extent practicable as determined by the implementing agency while continuing, as necessary, any actions initiated under §§280.61 through 280.63, or preparing for actions required under §§280.65 through 280.66. In meeting the requirements of this section, owners and operators must: . . . (d) Unless directed to do otherwise by the implementing agency, prepare and submit to the implementing agency, within 45 days after confirming a release, a free product removal report that provides at least the following information: . . . (2) The estimated quantity, type, and thickness of free product observed or measured in wells, boreholes, and excavations;"

- §280.65(a) Investigation for soil and ground water cleanup

"In order to determine the full extent and location of soils contaminated by the release and the presence and concentrations of dissolved product contamination in the groundwater, owners and operators must conduct investigations of the release, the release site, and the surrounding area possibly affected by the release. . ."

- §280.66(b)(1-6) Corrective Action Plan

"In making this determination, the implementing agency should consider the following factors as appropriate: (1) The physical and chemical characteristics of the regulated

> substance, including its toxicity, persistence, and potential for migration; (2) The hydrogeologic characteristics of the facility and the surrounding area; (3) The proximity, quality and current and future uses of nearby surface water and ground water; (4) The potential effects of residual contamination on nearby surface water and ground water; (5) An exposure assessment; and (6) Any information assembled in compliance with this subpart."

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# 4. Lateral Inclusion Zone

## Description

The lateral inclusion zone is the area surrounding a contaminant source through which vapor-phase contamination may travel and intrude into buildings. Determination of the lateral distance within which buildings and other structures may be threatened by PVI is site-specific. In general, with increasing confidence in the site characterization and the CSM, there can be a corresponding decrease in the distance the lateral inclusion zone extends from clean monitoring points.[25] All buildings within the lateral inclusion zone should be further assessed to determine if they are separated from vapor sources by an adequate vertical separation distance (see **Section 5**, p.48). Further assessment may be unnecessary for those buildings outside the lateral inclusion zone unless preferential transport pathways are present. If contaminated groundwater is the source of vapors, migration of the contaminant plume (in the longitudinal, transverse, and vertical directions) should be assessed when evaluating the potential for future risks.

## Importance

The lateral inclusion zone is a screening criterion to help determine which sites should definitely be assessed further for PVI; which sites might need additional site characterization and assessment for PVI; and which sites can reliably be excluded from consideration for further evaluation of PVI. All buildings that overlie, or are reasonably expected to overlie, contamination, whether LNAPL or the dissolved phase, are considered to be within the lateral inclusion zone.

## Assessment

Lateral separation distance is schematically depicted in **Figure 5**. Though in theory the length of the lateral separation distance may be on the same scale as the vertical separation distance (EPA, 2013a; ITRC, 2014), a greater lateral distance is generally warranted in the down gradient direction (Lahvis, et al, 2013; EPA, 2013a). This is because the lateral boundaries of a migrating plume are more difficult to accurately delineate, as they are not stationary. Groundwater elevations fluctuate which may result in changes in the direction and velocity of groundwater flow. The lateral and down gradient investigation should continue until the full extent and location of contamination is determined. This is typically achieved by surrounding the dissolved-phase plume with clean monitoring points.

Both mobile LNAPL and dissolved contaminant plumes are dynamic and may move from one monitoring event to the next. As discussed in **Section 7** (p.61), periodic monitoring of groundwater flow directions and plume migration should be conducted, possibly over more than one annual cycle.

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[25] A *monitoring point* is defined as a sampling point at which soil and groundwater samples are collected (typically from monitoring wells, though not exclusively) and which define the full extent and location of contamination. A *clean monitoring point* is defined by dissolved benzene concentration less than 5 µg/L and soil TPH concentration less than 20 mg/Kg.

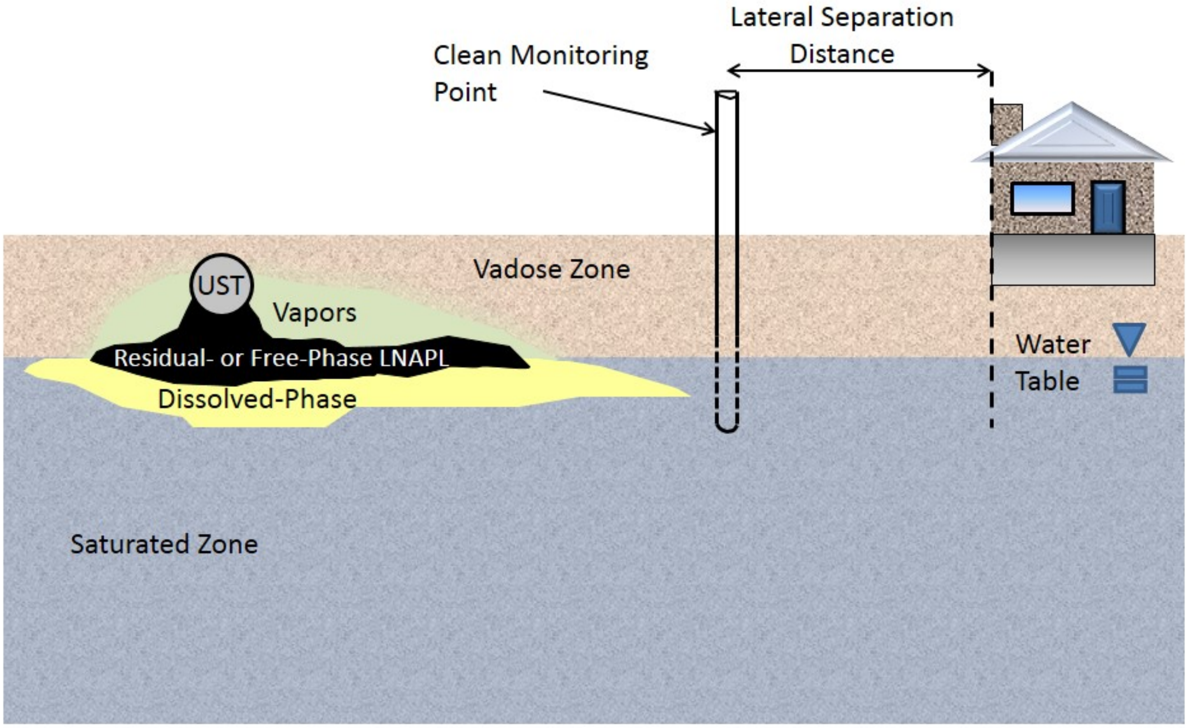

**Figure 5. Lateral Separation Distance Between Source Of PHC Contamination And Hypothetical Receptor**

**Special Considerations**

It can be difficult to accurately determine the exact location of contamination relative to potential receptors. This is in part due to the dynamic nature of contaminant plumes (both LNAPL and dissolved PHCs); the presence of heterogeneities and preferential transport pathways in geologic material; and the distance between monitoring points, such as soil borings and monitoring wells. It may be necessary to assess some nearby buildings for PVI before all site characterization activities have been completed.

It is important to consider whether, and what type of preferential transport pathways are present and could facilitate the migration of petroleum vapors. The presence of preferential transport pathways may circumvent the protectiveness that a sufficiently thick layer of clean, biologically active soil would otherwise provide. Preferential transport pathways such as utility conduits typically enter buildings through holes in the foundation or slab and can facilitate the entry of PHC vapors into the building. For example, if the transport of vapors from the source area to the building could occur along utility conduits, then vapor sampling inside those utility conduits (e.g., sewers) should be considered. Field instrument screening at utility access points may help determine if the utility is acting as a conduit for vapors. Although specific guidance for utility sampling is beyond the scope of this document, EPA recommends that any utility sampling program include safety precautions to protect personnel (e.g., oxygen and combustible gas monitoring, confined-space entry requirements) and to avoid damage to utilities. For guidance on utility sampling, see *A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites* (API, 2005).

Lateral separation distances that are usually protective against PVI may not be sufficiently protective in situations where methane is produced in large quantity, such as sites where high-ethanol blends of gasoline (i.e., E-20 or greater) have been released (Ma et al., 2014), and at sites where non-PHC fuel additives are present (see **Section 10**, p.81). In both of these cases, additional investigation should be conducted to assess the potential for vapor intrusion.

Another consideration is changing site conditions. Factors to consider in deciding whether to include sites for further evaluation of PVI may include future land use—that is, whether: future new buildings will be constructed within the lateral inclusion zone, utility trenches will be excavated through or near previous contamination, groundwater usage will potentially be increased, and additional releases of contaminants may occur.

**Recommendation**

Delineation of a lateral inclusion zone is site-specific. EPA recently published *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, 2013b)*. This Issue Paper describes a procedure for constructing a lateral inclusion zone that decision makers may find useful. EPA recommends that all buildings within the lateral inclusion zone be further assessed to determine if they are separated from vapor sources by an adequate vertical separation distance. Further assessment may be unnecessary for those buildings outside the lateral inclusion zone unless:

- Preferential transport pathways are present that connect PHC vapor sources to receptors
- Impermeable surface cover (e.g., concrete, asphalt, ice, very large buildings) is so extensive that there is concern whether there is sufficient oxygen in the subsurface to support biodegradation
- Soil conditions are inhospitable to microorganisms (e.g., dry soils with less than 2 percent soil moisture by dry weight) such that biodegradation is insufficient to mitigate the threat of PVI

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## 5. Vertical Separation Distance

### Description

The vertical separation distance is the thickness of clean, biologically active soil (see **Section 9**, p.75) between the highest vertical extent of a contaminant source and the lowest point of an overlying building. This lowest point could be a building basement floor, foundation, or crawlspace surface.

### Importance

If the thickness of clean, biologically active soil is sufficient and oxygen and soil moisture are present, aerobic biodegradation will usually degrade vapor-phase PHCs before they can intrude into buildings. EPA (2013a) presents a compilation and analysis of soil gas data from a large number of sites that represent many different hydrogeologic settings where gasoline was released from USTs.[26] This analysis builds on the work of Davis (2009, 2010, 2011a, and 2011b). In addition, EPA (2013a) summarizes the results of a number of parallel efforts (Lahvis, et al., 2013; Peargin and Kolhatkar, 2011; Wright, 2011, 2012). Although these studies used somewhat different data sets, there is a high degree of consistency among them. This consistency supports the establishment of vertical screening distances based on whether PHC contamination is present as LNAPL or dissolved PHCs; that is, the thickness required to aerobically biodegrade PHCs is directly related to the strength of the source. Because LNAPL sources are capable of producing higher concentrations of vapors compared to dissolved sources, the necessary separation distance between receptors and LNAPL is greater than the necessary separation distance between dissolved sources and receptors. At sites where non-PHC fuel additives are present (see **Section 10**, p.81), the vertical separation distance may not be sufficient to protect against vapor intrusion. In this case, additional investigation should be conducted to assess the potential for vapor intrusion.

### Assessment

The vertical separation distance is measured from the lowest point of the overlying building basement floor, foundation, slab, or crawlspace surface and the highest vertical extent of contamination. For dissolved sources this is the historic high water table elevation; for LNAPL sources this is the top of the smear zone or residual LNAPL in the source area. Vertical separation distances for dissolved plumes and LNAPL sources are schematically depicted in **Figure 6a and 6b**, respectively. Both mobile LNAPL and dissolved contaminant plumes are dynamic and may move from one monitoring event to the next. As discussed in **Section 7** (p.61), periodic monitoring of groundwater flow directions and plume migration are recommended, possibly over more than one annual cycle.

The presence of LNAPL may be determined from direct or indirect evidence. Direct evidence includes measureable accumulations of free product in monitoring wells, an oily sheen or floating globules on the water table, and petroleum hydrocarbon-saturated bulk soil samples.

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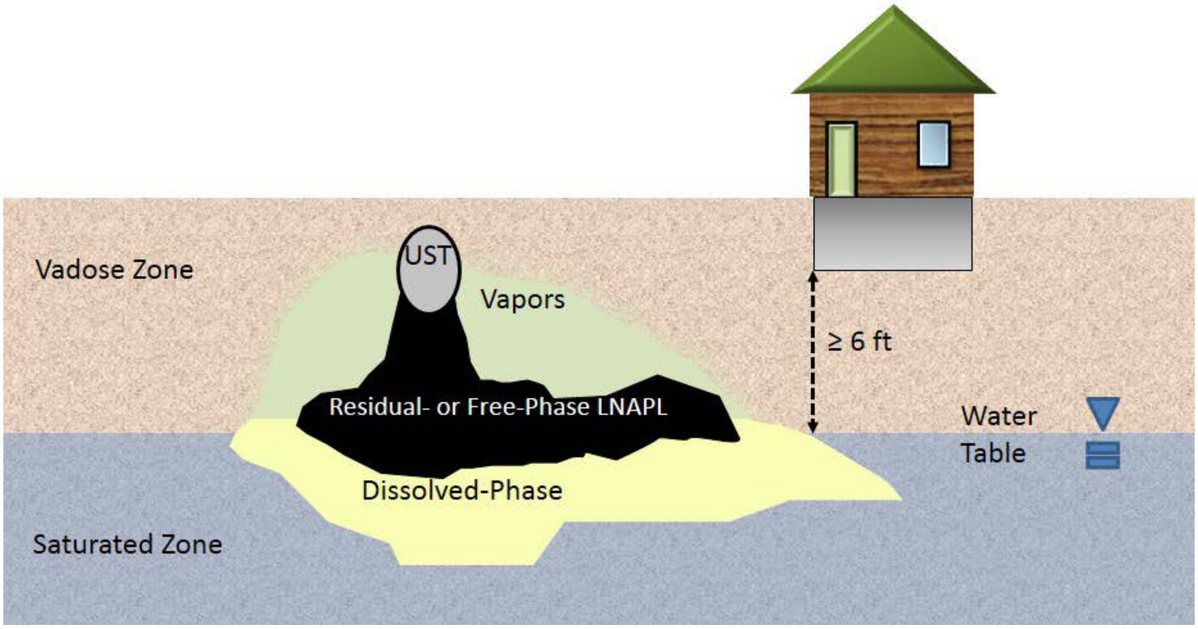
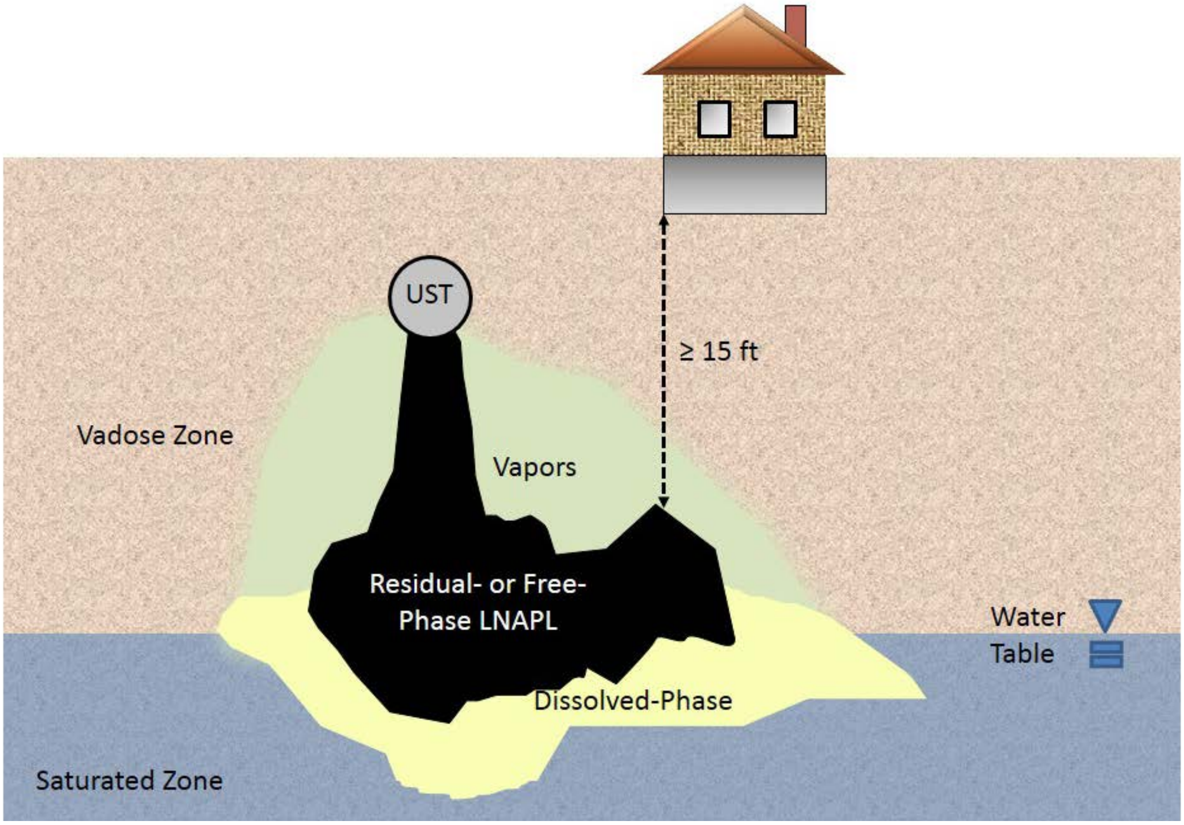
[26] The final report (EPA, 2013a) addresses the peer review comments received. The report, database, and peer review record are accessible on EPA's PVI Compendium Web page: *http://www.epa.gov/oust/cat/pvi/index.htm*.



(a) Vertical separation distance for dissolved-phase source of PHCs.



(b) Vertical separation distance for LNAPL (residual or mobile phase) source of PHCs.

**Figure 6. Vertical Separation Distances Between Source Of PHC Contaminants And Hypothetical Receptor: (a) Dissolved Source, (b) LNAPL Source.**

Lahvis et al. (2013) caution that the presence or absence of free-phase LNAPL in monitoring wells may not be a reliable indicator of the presence of residual-phase LNAPL. The absence of LNAPL can only be determined through analysis of core samples. This is important to recognize because free-phase and residual LNAPL have a greater vapor-generating capability than dissolved sources. Indirect evidence includes high concentrations of benzene and other PHCs, often measured as TPH.[27] There is considerable variation and uncertainty in LNAPL thresholds determined from indirect evidence and Lahvis et al. (2013) suggest that multiple indicators of the presence of LNAPL be evaluated. EPA (2013a) selected a benzene concentration of 5 mg/L to differentiate between dissolved and LNAPL sources. A study by Peargin and Kolhatkar (2011) suggests that a dissolved source with benzene greater than 1 mg/L may behave like a LNAPL source in terms of vapor-generating capability. For more information on indicators of LNAPL, see **Section 6** (p.57).

### Special Considerations

Preferential transport pathways such as utility conduits typically enter buildings through holes in the foundation or slab and can facilitate the entry of PHC vapors into the building. Consideration should be given to field instrument screening at utility access point(s) as an initial step to determine if the utility is acting as a conduit for vapors. If the transport of vapors from the source area to the building could occur along utility conduits, then vapor sampling inside the utility conduits, manholes, or sumps should be considered in addition to vadose zone and sub-slab soil gas sampling. Any utility sampling program should include safety precautions to protect personnel (e.g., oxygen and combustible gas monitoring, confined-space entry requirements) and to avoid damage to utilities. Specific guidance for utility sampling is available in *A Practical Strategy for Assessing the Subsurface Vapor-to-Indoor Air Migration Pathway at Petroleum Hydrocarbon Sites* (API, 2005).

Vertical separation distances that are usually protective against PVI may not be sufficiently protective in situations where methane is produced in large quantity, such as sites where high-ethanol blends of gasoline (i.e., E-20 or greater) have been released (Ma et al., 2014), or beneath very large buildings, or where the ground surface is covered by extensive impermeable material (e.g., pavement) (EPA, 2013c).

In addition, consideration should be given to whether future new buildings will be constructed within the lateral inclusion zone and whether they may be impacted by PVI.

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[27] Toxicological data for TPH fractions may be found in EPA (2009, 2013b), ATSDR (1999), Tveit et al. (1999), and HI DOH (2012). More recently, Brewer et al. (2013) have developed a quantitative method for risk-based evaluation of TPH in PVI investigations.

**Recommendation**

EPA recommends using the criteria presented in **Table 3** to determine the necessary vertical separation distance between PHC contamination from leaking USTs and an overlying building foundation, basement, or slab. These distances are 6 feet for dissolved vapor sources (beneath buildings of any size) and 15 feet for LNAPL sources (beneath buildings up to 66 feet on the shortest side).[28] Where the respective vertical separation distance is met or exceeded, generally no further investigation for PVI is necessary if there are no precluding factors present (e.g., preferential transport pathways) and the PCH source is not a high-ethanol blend (i.e., E-20 or greater) of gasoline. If the applicable separation distance is not met and where contamination is not in direct contact with an overlying building, then choose one of two options: (1) collect near-slab (exterior) shallow soil gas samples paired with deep (source) soil gas samples, or (2) collect indoor air samples paired with sub-slab soil gas samples. If the potential for PVI cannot be ruled out based on near-slab and deep soil gas sampling, then EPA recommends indoor air sampling paired with sub-slab vapor sampling. If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends gathering additional information and data to determine whether mitigation is appropriate.

Although biodegradation is known to occur for many individual non-PHC fuel additives and classes of additives, the rate of biodegradation in soil gas has not necessarily been rigorously quantified; this is especially true for the lead scavengers EDB and 1,2-DCA. Therefore, for these two chemicals in particular, vertical separation distances recommended in this guide may not be sufficient for petroleum fuel releases that contain EDB and 1,2-DCA and additional investigation may be necessary to assess their potential for vapor intrusion (See **Section 10**, p.81 for more information).

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[28] See *3-D Modeling of Aerobic Biodegradation of Petroleum Vapors: Effect of Building Area Size on Oxygen Concentration Below the Slab* (EPA 510-R-13-002)(EPA, 2013c).

**Table 3. Recommended Vertical Separation Distance Between Contamination And Building Basement Floor, Foundation, Or Crawlspace Surface.**

| Media | Benzene | TPH | Vertical Separation Distance (feet)* |
|---|---|---|---|
| **Soil (mg/Kg)** | ≤10 | ≤ 100 (unweathered gasoline), or<br>≤ 250 (weathered gasoline, diesel) | 6 |
| | >10 (LNAPL) | > 100 (unweathered gasoline)<br>>250 (weathered gasoline, diesel) | 15 |
| **Groundwater (mg/L)** | ≤5 | ≤30 | 6 |
| | >5 (LNAPL) | >30 (LNAPL) | 15 |

The thresholds for LNAPL indicated in this table are indirect evidence of the presence of LNAPL. These thresholds may vary depending on site-specific conditions (e.g., soil type, LNAPL source). The value of 5 mg/L benzene is from EPA (2013a, p.31). A study by Peargin and Kolhatkar (2011) suggests that a dissolved source with benzene greater than 1 mg/L may behave like a LNAPL source in terms of vapor-generating capability. Decision-makers may have different experiences with LNAPL indicators and may use them as appropriate. For more information, see **Section 6** (p.57) and **Figure 7** in particular.

Bulk soil samples should be analyzed for Total Petroleum Hydrocarbon (TPH) and BTEX (plus any other potential contaminants). The objective of measuring TPH is to quantify the total vapor phase concentration of PHCs. TPH may be analyzed by methods appropriate for the type of fuel released. These methods may be designated as TPH-gasoline (or sometimes gasoline range organics or GRO), TPH-diesel (or sometimes diesel range organics or DRO). Method TO-15 (see *http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf*) by itself only measures a small fraction of PHCs that may be present in the vapor-phase. TO-15 analyses require a correction factor to estimate bulk TPH. An extended TO-15 analysis can provide such an estimate. For more information on TPH in vapor intrusion studies, see Brewer et al. (2013).

*The vertical separation distance represents the thickness of clean, biologically active soil between the source of PHC vapors (LNAPL, residual LNAPL, or dissolved PHCs) and the lowest (deepest) point of a receptor (building basement floor, foundation, or crawlspace surface).

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## 6. Mobile And Residual Light Non-Aqueous Phase Liquid (LNAPL)

### Description

LNAPLs released from petroleum USTs are typically fuel products such as gasoline and diesel fuel. Fuel products are comprised of a large number of volatile and semi-volatile PHCs and synthetic additives. Among these compounds are some that are volatile and some that are semi-volatile. Newer, unweathered releases typically contain a higher proportion of more volatile PHCs than do older releases that may be more weathered and depleted in the more volatile PHCs. Similarly, gasoline contains a higher proportion of more volatile PHCs than does diesel fuel and other middle distillates such as heating oil and kerosene. Vapors emanating from dissolved-phase sources are primarily BTEX and other aromatic hydrocarbons, and relatively water-soluble PHCs. Vapors emanating from LNAPL sources contain the same constituents in addition to a sizeable fraction of aliphatic and relatively insoluble hydrocarbons (e.g., naphthalene), especially if the source is large or unweathered (Lahvis, et al., 2013; EPA, 2013).

### Importance

Depending upon the volume of the release and the characteristics of the soil, PHC vapors from LNAPL sources can reach concentrations high enough to deplete oxygen needed by microorganisms to biodegrade them. Compared to a dissolved plume, a LNAPL plume from a leaking UST does not typically migrate far from the site of release (e.g., the leaking UST or connected piping). However, the larger the mass of the release the greater the potential for the LNAPL plume to migrate. When LNAPL underlies a receptor or comes into direct contact with a basement, foundation, or slab, there is increased potential for explosive levels of vapors to accumulate within the building or other structure.

Residual PHCs are non-mobile in the subsurface and occur when the release stops prior to the accumulation of a sufficient amount of LNAPL for flow to occur, or when a fluctuating water table smears the LNAPL across the water table and reduces the LNAPL saturation of the soil. This smearing inhibits the lateral migration of LNAPL. Although residual contamination is not free flowing, residual sources represent a large mass of contaminants that can persist for long periods of time and generate considerable volumes of PHC vapors as well as dissolved-phase contaminants.

Monitoring wells with residual LNAPL may not have a measurable accumulation of LNAPL so they look exactly like monitoring wells with only dissolved contamination (that is, there is no measurable LNAPL in the monitoring well). However, due to the presence of residual LNAPL, the vapor source area acts like a free-phase LNAPL source in terms of vapor-generating character (Lahvis, et al., 2013). A study by Peargin and Kolhatkar (2011) suggests that a dissolved source with benzene concentration greater than 1 mg/L may have the same vapor-generating capacity as a LNAPL source. This situation is depicted in **Figure 7**.

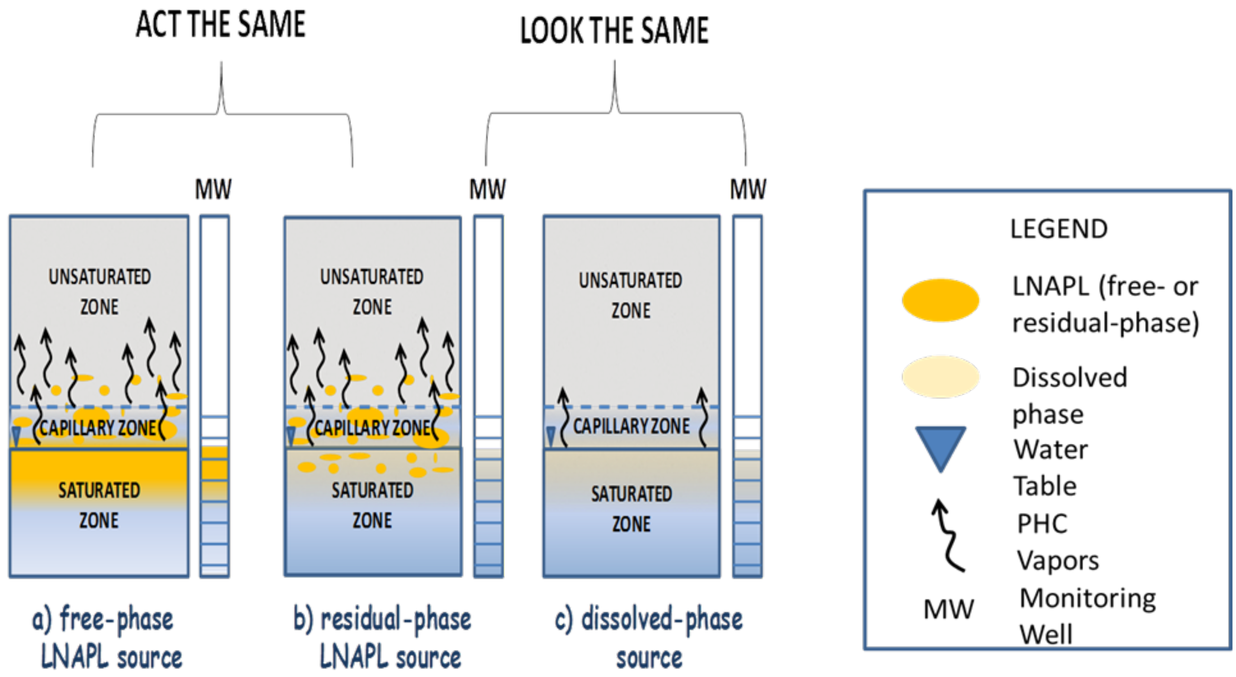

**Figure 7. Conceptual Model Illustrating The Potential For Vapor Intrusion For a) Free-Phase LNAPL Source, b) Residual-Phase LNAPL Source, And c) Dissolved-Phase Source** (Source: Lahvis, et al., 2013. Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2013.)

**Assessment**

The distinction between petroleum contamination present as LNAPL and contamination present purely as a dissolved phase is important. Unfortunately, there is no precise concentration threshold between dissolved phase PHCs and PHCs present in a mixed phase that includes LNAPL.[29] EPA (2013) used a threshold for the benzene groundwater concentration equal to 5 mg/L and a total petroleum hydrocarbon (TPH) threshold groundwater concentration of 30 mg/L for identification of LNAPL sites. The TPH threshold adopted by EPA (2013) is based on the calculated approximate average ratio of the concentration of benzene to TPH in groundwater at UST sites. A site with a LNAPL source was identified on the basis of either the benzene or TPH groundwater concentration exceeding the threshold. The thresholds adopted for identifying LNAPL sites based on soil concentrations are 10 mg/Kg benzene, 100 mg/Kg TPH for unweathered gasoline, and 250 mg/Kg TPH for diesel or weathered gasoline.

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[29] Table 4 in EPA (2013) presents a variety of direct and indirect indicators of LNAPL. For example, Bruce, et al. (1991) suggest groundwater concentrations greater than one-fifth (0.2) of the effective solubility of LNAPL as indirect evidence of the presence of LNAPL. However, because the effective solubility depends on characteristics of the LNAPL mass (e.g., composition, weathering); there is uncertainty in the threshold. Additional discussions of screening concentrations for LNAPL are presented in *Evaluating Hydrocarbon Removal from Source Zones and its Effect on Dissolved Plume Longevity and Concentration* (API, 2002), and ITRC (2014).

### Special Considerations

Direct means for detecting the presence of LNAPL include measurable accumulations of free product in monitoring wells, an oily sheen on the water, and saturation of bulk soil samples.[30] The presence of residual LNAPL may not be recognizable from monitoring well data. This is because the soil is not sufficiently saturated with LNAPL to allow it to flow into wells. Lahvis et al. (2013) suggest that multiple indicators (both direct and indirect) be evaluated to determine whether or not LNAPL is present.

### Recommendation

EPA recommends subsurface sampling to determine the full extent and location of LNAPL (both mobile LNAPL and residual). LNAPL may be present even when there is no measureable accumulation of free product in a monitoring well. In addition, federal regulations (40 CFR 280.64) require that when free product is present, it must be "removed to the maximum extent practicable as determined by the implementing agency." Effective source removal will mitigate a long term source of PHC vapors as well as mitigate dissolved and residual LNAPL contamination.

EPA recommends analyzing bulk soil samples collected in the source area for TPH (e.g., gasoline or diesel depending on which fuels were stored on site) and specific petroleum constituents (e.g., BTEX and other volatile and semi-volatile organic chemicals, and fuel additives). EPA also recommends analysis of LNAPL samples (if present) to determine the degree of weathering and potential for vapor generation.

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[30] Consistent with the findings in EPA (2013) EPA recommends that these same thresholds also be applied for PVI investigations conducted using this guide. These thresholds are presented in **Table 3** in **Section 5** (p.52).

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## 7. Groundwater Flow And Dissolved Contaminant Plumes

### Description

Contaminant plumes are dynamic, three-dimensional distributions of contaminants in groundwater. Contaminants dissolved in groundwater can migrate with flowing groundwater thereby spreading contamination. In some aquifers, where the direction and speed of groundwater flow are stable, the plumes are usually long and narrow. Other plumes appear to spread in both the transverse as well as the longitudinal direction. This apparent transverse dispersion may be the direct result of changes in the direction of groundwater flow. What may appear to be transverse dispersion is actually longitudinal dispersion occurring in different directions as the direction of flow changes (EPA, 2005; Wilson, 2003).

### Importance

The potential for PVI from dissolved PHC contaminant plumes is typically limited to sites where there are high concentrations of dissolved contaminants or the plume is in direct contact with a building foundation, basement, or slab. A study by Peargin and Kolhatkar (2011) suggests that a dissolved source with benzene greater than 1 mg/L may have the same vapor-generating capacity as a LNAPL source.

### Assessment

Contaminant plumes generally necessitate three-dimensional monitoring to assess the transient behavior of groundwater flow and the movement of contaminant plumes (EPA, 2004a, b). Contaminant plumes migrate with flowing groundwater, which can exhibit seasonal variations as well as responses to pumping, tides, or stage of a nearby river.[31] Groundwater flow directions can and often change over time, and may necessitate periodic monitoring over more than one annual cycle to understand the groundwater flow regime at a given site.

(Note: This monitoring need not delay additional investigation activities and measures to mitigate or remediate threats to safety and health.) As the plume migrates, appropriate adjustments to the sampling plan should be made to ensure that potential receptors are

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[31] Groundwater flow directions can change frequently and relatively quickly. Changes in groundwater flow directions may be more prevalent than is realized, because the variation in the direction of groundwater flow is rarely evaluated in any formal way (EPA, 2005). Wilson (2003) studied data from a site in North Carolina where groundwater flow was influenced by the stage of a nearby river. Over the course of one year of monthly monitoring, groundwater flow directions fluctuated by 120 degrees. Wilson et al. (2005) also studied data from a gas station site in New Jersey. Over a six-year period groundwater monitoring data were collected on 23 occasions; the predominant flow direction was 90-degrees from the presumed direction on which the conceptual model was constructed, and the direction of flow fluctuated by nearly 180 degrees. Mace et al. (1997) studied the variation in groundwater flow directions at 132 gas stations in Texas. Fluctuations in flow directions occurred over a range of 120 degrees. Goode and Konikow (1990) characterized a site where PHCs leaked to the water table. Groundwater flow directions changed nearly 90 degrees in less than four months in response to changing flow conditions in a nearby intermittent stream.

protected.  If new PHC releases to groundwater occur, then appropriate mitigation steps can be implemented.

Plume monitoring networks should be able to detect changes in plume boundaries as well as fluctuations in the concentrations of geochemical parameters and contaminant concentrations. Collection of samples from the contaminant plume is needed to determine the extent of contamination and provide information that can be used to estimate the vapor generation capacity of the dissolved contamination.  The contaminant plume should be surrounded by sampling points that are free of contamination (i.e., *clean monitoring points*).

Conventional monitoring wells may provide an incomplete picture of the true distribution of contaminants in groundwater.  If the length of the screen in a monitoring well is long compared to the thickness of the plume of contamination, the sample obtained will be diluted by the inflow of clean(er) groundwater from above or below the plume.  Also, plumes may dive below the screened interval of the wells leading to the false impression that the plume is shorter than it actually is (EPA, 2005).

**Special Considerations**

Dissolved plumes are dynamic and contamination may migrate beneath buildings over time. This is best evaluated by determining the range of fluctuation in groundwater flow direction and water table elevations beneath buildings over at least one annual cycle.  However, in the interim, the remaining PVI-related activities should continue.  Preferential transport pathways, if present, may facilitate the intrusion of petroleum vapors into buildings.[32]  When contaminant plumes intersect preferential transport pathways, the spread of contamination can be very rapid compared to the velocity of groundwater flow through the soil.

Volatilization of contaminants from the plume into soil gas is greatly reduced when a plume dives beneath the water table surface.  Volatile contaminants diffuse more slowly through the water column than through soil gas.

**Recommendation**

EPA recommends groundwater monitoring and sampling to determine the depth to contaminated groundwater and the vertical distribution of contaminants in the water column beneath overlying buildings[33].  Due to the transient nature of groundwater migration, EPA recommends periodic monitoring and sampling over more than one annual cycle to fully

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[32] Dissolved petroleum contaminants may threaten building inhabitant's health through their water supply rather than through vapor intrusion.  Exposure may occur from wells drawing from a contaminated plume, or contamination permeating the water supply piping.  Though fuel constituents generally impart a disagreeable odor and taste, building occupants may still be exposed to potentially harmful levels of contaminants.  Such exposure may occur when PHCs volatilize from the dissolved phase during showering or washing clothes and dishes, or through ingesting contaminated water.  Identifying the mechanism of exposure is important because methods for remediation/mitigation of PVI will be different than treatment or remediation of contaminated groundwater.

[33] If groundwater samples contain greater than 30 mg/L TPH (or greater than 5 mg/L benzene), it is possible that residual LNAPL is present (see **Section 6**, p.57).

understand the groundwater flow regime at a given site. Where the respective vertical separation distance (see **Section 5**) is met or exceeded, generally no further investigation for PVI is necessary if there are no precluding factors present (e.g., preferential transport pathways) and the PCH source is not a high-ethanol blend (i.e., E-20 or greater) of gasoline. If the applicable separation distance is not met and where contamination is not in direct contact with an overlying building, then choose one of two options: (1) collect near-slab (exterior) shallow soil gas samples paired with deep (source) soil gas samples, or (2) collect indoor air samples paired with sub-slab soil gas samples. If the potential for PVI cannot be ruled out based on near-slab and deep soil gas sampling, then EPA recommends indoor air sampling paired with sub-slab vapor sampling. If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends gathering additional information and data to determine whether mitigation is appropriate.

Even in cases where there is no threat of PVI from contaminated groundwater, EPA recommends that the plume be assessed to determine if remediation is necessary to prevent ingestion of contaminated drinking water and protect and restore actual or potential sources of drinking water.

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## 8. Soil Gas Profile

### Description

Aerobic biodegradation of PHC vapors occurs in many subsurface environments (Lahvis, Baker, and Behr, 1998; McHugh, et al., 2010; Roggemans, 1998; Roggemans, Bruce, and Johnson, 2002; ZoBell, 1946; Atlas, 1981; Leahy and Colwell, 1990; DeVaull, 2007). The soil gas profile can provide confirmation that aerobic biodegradation is occurring in the subsurface. Decreasing oxygen concentration and increasing carbon dioxide and methane concentrations indicate biodegradation of PHCs (Hult and Grabbe, 1988). Shallow soil gas typically contains water vapor and fixed gases: nitrogen, oxygen, carbon dioxide, carbon monoxide, and argon. These gases infiltrate into the soil from the atmosphere. Vapor phase PHC contamination may be the result of volatilization from mobile LNAPL released into the subsurface, residual soil contamination (including the smear zone), and dissolved phase contamination. The lower proportion of volatile hydrocarbon compounds in diesel fuel will lead to a comparatively smaller vapor plume in comparison to the release of a similar volume of gasoline (Prince and Douglas, 2010; Marchal, et al., 2003). In addition to PHCs, soil gas may also contain degradation products from the breakdown of PHCs and naturally occurring organic matter. The principal gases resulting from the biodegradation of PHCs are carbon dioxide (under aerobic conditions) or methane (under anaerobic conditions).

**Figure 8** presents a characteristic vertical concentration profile in the unsaturated zone; oxygen concentrations decrease with depth and PHCs (including methane) and carbon dioxide

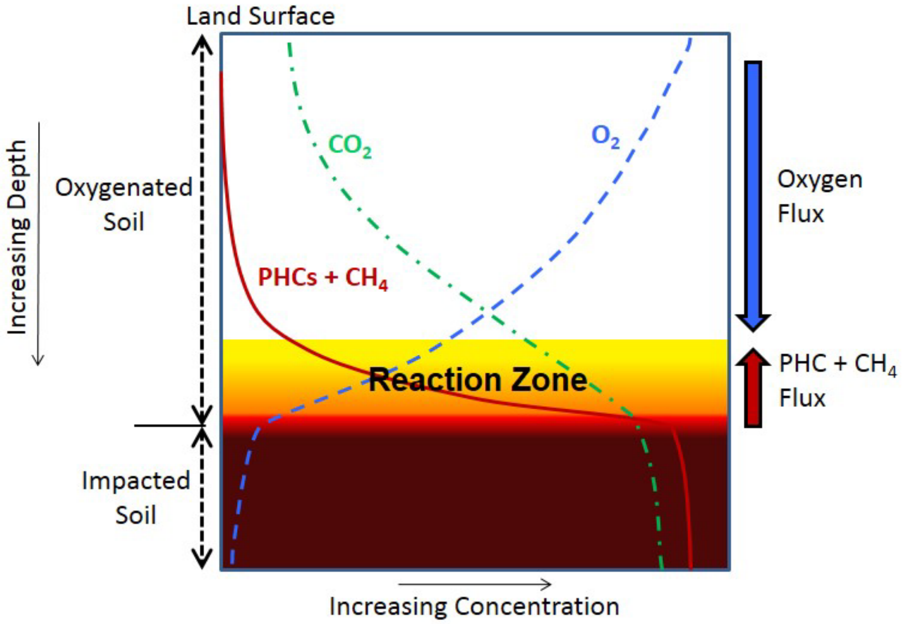

**Figure 8. Typical Vertical Concentration Profile In The Unsaturated Zone For PHCs (Plus Methane), Carbon Dioxide And Oxygen**

concentrations increase with depth toward the source of contamination. This typical vertical profile may vary somewhat in shape depending on site-specific conditions (Roggemans, Bruce, and Johnson, 2002). During aerobic biodegradation in unsaturated soils, PHCs degrade, oxygen is consumed, and carbon dioxide is produced. The aerobic biodegradation zone is within oxygenated soil (generally greater than 1 percent oxygen in soil gas). In the oxygenated soil zone (where aerobic biodegradation occurs between land surface and the depth of impacted soil) the decrease in PHC concentrations is typically quite rapid and occurs over a narrow interval (the reaction zone in **Figure 8**) (Abreu, Ettinger, and McAlary, 2009).

The impacted soil zone, which is anaerobic, is characterized by the maximum PHC concentrations (and often LNAPL) and biodegradation is slow (EPA, 2012a). Generally, PHC vapor concentrations will be much greater adjacent to a LNAPL source than adjacent to a dissolved hydrocarbon plume. If PHC concentrations are high enough, available oxygen may be depleted, which in turn limits aerobic biodegradation. The core of any PHC contaminant mass is typically depleted with respect to oxygen, thus anaerobic biodegradation of LNAPL or other organic sources (e.g., ethanol) can produce significant amounts of methane (Anderson and Lovley, 1997; Wiedemeier, et al., 1999; Koenigsberg and Norris, 1999; Ma et al., 2014). Methane readily biodegrades under aerobic conditions and, when present, will create an additional oxygen demand (Jewell and Wilson, 2011; Ma, et al, 2012). High concentrations of methane, oxygen, and a source of ignition can create a fire or explosion hazard in confined spaces (e.g., utility vaults and passages, basements, or garages) (Ma et al., 2014). For additional information on evaluating the presence of methane and potential hazards, see ASTM's "*New Practice for Evaluating Potential Hazard Due to Methane in the Vadose Zone*".[34]

Differences between near-slab soil gas profiles and sub-slab soil gas profiles are reported in two EPA modeling studies: the conceptual model scenarios report EPA (2012b) and the building size modeling report for PVI (EPA, 2013a). However, EPA (2012b) assumed that building foundations, basements, and slabs were impermeable and, thus, oxygen transport was not simulated through the foundation, basement, or slab into the subsurface beneath the building. Simulations presented in EPA (2013a) allowed for oxygen transport using reasonably expected oxygen permeability values for concrete (Fischer et al., 1996; McHugh, DeBlanc, and Pokluda, 2006; Lundegard, Johnson, and Dahlen, 2008; Patterson and Davis, 2009; Tittarelli, 2009). When oxygen transport is accounted for, the differences in soil gas profiles were less pronounced between near-slab and sub-slab samples very close to the building basement and slab. Thus, near-slab soil gas samples can be substituted for sub-slab samples in situations where dissolved contamination is present within 6 feet of (but not in contact with) a building basement floor, foundation, or crawlspace surface, and where LNAPL is present within 15 feet of (but not in contact with) a building basement floor, foundation, or crawlspace surface. For dissolved sources this holds for buildings of any size, and for LNAPL sources it applies to buildings with the shortest side being no longer than 66 feet (EPA, 2013a). Deep soil gas samples are needed to determine the depth to contaminated soil and the thickness of clean,

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[34] The new ASTM methane guide is accessible at
http://www.astm.org/DATABASE.CART/WORKITEMS/WK32621.htm

biologically active soil necessary to attenuate PHC vapors. Shallow soil gas samples should be paired with deep (near source) soil gas samples to evaluate the strength of the PHC vapor source and the attenuation of PHC vapors.

**Importance**

The potential for PVI is a function of the oxygen demand exerted by all biodegradable vapors, not just the key chemicals of potential concern (Jewell and Wilson, 2011; Ma, et al., 2012). When present, volatile PHCs and methane also exert an oxygen demand that may limit aerobic biodegradation of benzene (Abreu, Ettinger, and McAlary, 2009; Wilson, 2011). An estimate of the biodegradation rate can be determined from the stoichiometric relationship between the flux of oxygen, carbon dioxide, and methane (Lahvis and Baehr, 1996). PHC vapor concentrations generally decrease with increasing distance from a subsurface vapor source. At a relatively short distance from the source, concentrations of PHCs in soil gas will typically fall below potentially significant levels of concern provided that oxygen replenishment is adequate to ensure complete aerobic biodegradation. Lahvis, Baehr, and Baker (1999) observed that PHC vapors from a dissolved plume were almost completely degraded within 1 meter (3.3 feet) above the water table and that significant transport of PHC vapors may only be significant if the vapor source is LNAPL. This is consistent with the findings of EPA’s (2013b) PVI database analysis report and Lahvis et al. (2013).

**Assessment**

Soil gas samples provide information on the distribution of contamination near the source area, whether biodegradation is occurring, and how effective it is in reducing the potential for PVI. When there is an impermeable surface cover adjacent to a building, soil gas probes should be installed beneath the surface in order for the soil gas profile to adequately characterize conditions below the surface. For very large buildings, or where there is extensive impermeable surface cover and the vapor source is relatively shallow, additional investigation is recommended to verify that biodegradation is occurring beneath the building.[35] Vapor samples should be analyzed for PHCs (and non-PHC fuel additives), methane, oxygen, and carbon dioxide (Lahvis, Baehr, and Baker, 1999).

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[35] EPA (2013a) presents modeling results for a variety of soil types, building sizes, vapor source strengths, and vertical separation distances. These results, while not exhaustive, indicate that for dissolved sources and very large buildings, an oxygen shadow does not form, thus the subsurface stays sufficiently oxygenated to support aerobic biodegradation and preclude the potential for PVI. For LNAPL sources, an oxygen shadow was not observed to form beneath buildings up to 66 feet on the shortest side. This length represents the threshold below which oxygen replenishment is sufficient to support aerobic biodegradation; above this length oxygen replenishment may be impeded and there may be insufficient oxygen present to support aerobic biodegradation. For larger buildings underlain by LNAPL within 15 feet of the foundation, basement, or slab, sub-slab soil gas sampling paired with indoor air sampling is necessary to assess whether PVI is occurring. Another potential concern for large buildings and extensive, impermeable surface cover (e.g., asphalt, concrete) is formation of a moisture shadow, which represents soil moisture content too low to support microbial biodegradation (see **Section 9,** p.75, for more information).

An estimate of the total oxygen demand can be determined in two ways: sample for methane and petroleum hydrocarbons (PHCs); or sample and measure the oxygen demand for all the organic compounds in the soil gas at the source.[36] If methane and all the PHCs in soil gas are measured, these concentrations should be converted to an equivalent concentration of benzene and summed. The total oxygen demand of the aggregate of methane and the PHCs (expressed as an equivalent concentration of benzene) can be used to determine an attenuation factor (α) that can be used along with the actual concentration of benzene in soil gas at the source to determine whether aerobic biodegradation is capable of degrading the PHC vapors to acceptable concentrations (see **Section 12,** p.106, **Figure 9**, p.101, and **Figure 10,** p.103).

In some cases, relatively shallow soil gas samples (less than five feet below ground surface) will be needed to characterize active biodegradation zones in the shallow soil (e.g., in the presence of shallow contamination sources). Some state regulatory programs do not allow soil gas sampling at depths less than 5 feet based on the concern that accurate sampling may not be possible at shallow depths because air from the surface may leak into the sample. However, recent research has shown that the collection of accurate shallow-soil gas samples is possible at depths as shallow as 2 feet below ground surface using appropriate field methods (e.g., leak testing), such as those documented in *Temporal Variation of VOCs in Soils from Groundwater to the Surface* (EPA, 2010). It is also possible under certain conditions to collect representative soil gas samples using previously installed groundwater monitoring wells (see Wilson et al., 2014).

**Special Considerations**

There are several factors that can limit replenishment of oxygen to deep soils. These include presence of low permeability layers, concrete or asphalt covering at the surface, high soil moisture from a recent rainfall event or from irrigation, and buildings that are so large that oxygen is depleted beneath the center of the building (Patterson and Davis, 2009). However, a recent study by EPA (2013a) indicates that for an oxygen shadow[37] to form beneath a building, the PHC vapor source must be shallow LNAPL and the building must be greater than 66 feet in length on the shortest side. For simulations with dissolved sources, no oxygen shadow formed even under a square building with sides that were 2,073 feet in length.

At sites with a new release or unweathered LNAPL source, the oxygen demand will be high. It is important to determine whether temporal variations in oxygen flux into the vadose zone will limit the effectiveness of aerobic biodegradation, potentially resulting in intermittent vapor intrusion impacts. For such sites, more than one round of soil gas monitoring may be needed to confirm that aerobic biodegradation consistently prevents PVI impacts at the site.

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[36] EPA recommends using modified Method TO-15 (s*ee* [http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf](http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf)) for organic compounds. The concentration of methane measured as a fixed gas can then be added to the results of TO-15 to give an approximation of TPH.

[37] For the purposes of this modeling study, an oxygen shadow is defined as less than 1 percent oxygen.

## Recommendation

EPA recommends that soil gas samples be analyzed for PHCs, non-PHC fuel additives, methane, oxygen, and carbon dioxide. Sampling for nitrogen (and other fixed gases) in soil gas can provide a check on the quality of the analyses since the sum of these gases should be 100 percent. If they are substantially less than 100 percent, then some constituents are unaccounted for and the analyses should be interpreted with caution.

For buildings of any size within the lateral inclusion zone if the vertical separation distance between the building basement, foundation, or slab and dissolved contamination is less than 6 feet, but not in contact with the building EPA recommends that near-slab soil gas samples paired with deep (near source) soil gas be collected. For buildings up to 66 feet on the shortest side that directly overlie LNAPL masses, and the vertical separation distance is less than 15 feet (but the building is not in direct contact with LNAPL), EPA recommends collection of near-slab soil gas samples paired with deep (near source) soil gas samples. Near-slab soil gas samples should be collected from each side of the building and as close to the building as practicable. If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends gathering additional information and data to determine whether mitigation is appropriate. If contamination is in direct contact with an overlying building (and thus, collection of shallow soil gas samples is not possible), indoor air sampling is recommended.

In addition, for very large buildings or where there is extensive impermeable surface covering, EPA recommends that near-slab or sub-slab soil gas samples be collected if there is concern that these conditions may impede the flux of oxygen to the subsurface and create an oxygen or soil moisture shadow.

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## 9. Clean, Biologically Active Soil

### Description

For a PVI investigation, clean soil does not necessarily mean that it is contaminant-free, but rather that the level of any contamination present is low enough so that the biological activity of the soil is not diminished and the subsurface environment will support sufficient populations of microorganisms to aerobically biodegrade PHC vapors. This means that LNAPL is not present. The oxygen demand of all of the contamination present in the soil should not deplete the available supply of oxygen to such an extent that the rate of biodegradation is reduced.

Effective aerobic biodegradation of PHCs depends on the soil having sufficient oxygen and enough moisture to provide a habitat for adequate populations of active microorganisms. Although most soils contain indigenous microorganisms capable of degrading PHC vapors, typically there is an acclimation period between the time they are exposed to the PHC vapors and the time they begin to biodegrade the vapors. Prior exposure to PHCs has been observed to both increase the number of microbes and the microbial mass available for biodegradation of the PHCs and consequently speed up the degradation rate (ZoBell, 1946; Moyer, et al., 1996; Phelps and Young, 1999; and Siddique, et al., 2007).

The habitat of soil bacteria is the thin film of water held to the surface of soil particles by capillary attraction. EPA (2013a) notes that soil moisture content greater than 2 percent is adequate to support biodegradation activity (Leeson and Hinchee, 1996), although biodegradation is limited when the moisture content is at or below the permanent wilting point (Zwick, et al., 1995; Holden, Halverson, and Firestone, 1997). Adequate soil moisture is also indicated if the landscape supports the growth of non-irrigated vegetation (Riser-Roberts, 1992).

Certain geologic materials do not qualify as biologically active soil and should not be included in the vertical separation distance (see **Section 5**, p.48). These geologic materials include:

- Coarse sand and gravel with a low content of silt, clay, and organic matter, and low moisture content that is less than 2 percent dry weight
- Fractured, faulted, or jointed consolidated rock
- Consolidated rock with solution channels (i.e., karst)

### Importance

Effective aerobic biodegradation of PHCs depends on a thick layer of soil having sufficient oxygen and enough soil water to provide a habitat for adequate populations of active microorganisms. If oxygen is present, these organisms will generally consume available PHCs. Furthermore, aerobic biodegradation of petroleum compounds can occur relatively quickly, with degradation half-lives as short as hours or days under some conditions (DeVaull, 2007).

Some petroleum compounds can also biodegrade under anaerobic conditions; however, above the water table, where oxygen is usually available in the soil zone, this process is less important because it is generally much slower than aerobic biodegradation (Widdel, Boetius, and Rabus, 2006; Bailey, Jobson, and Rogers, 1973; and Bruce, Kolhatkar, Cuthbertson, 2010).

**Assessment**

Scientific research and site characterizations have demonstrated that microorganisms capable of aerobically degrading many PHCs are present in nearly all subsurface soil environments (ZoBell, 1946; Atlas, 1981; Wilson, et al., 1986; Leahy and Colwell, 1990; Bedient, Rifai, and Newell, 1994; EPA, 1999). A number of well-characterized field studies demonstrate extensive aerobic biodegradation of PHC vapors in unsaturated soils (Kampbell, et al., 1987; Ostendorf and Kampbell, 1991; Ririe and Sweeney, 1995; Ririe, et al., 1998; Ostendorf, et al., 2000; Hers, et al., 2000; Roggemans, Bruce, and Johnson, 2002; Sanders and Hers, 2006; Davis, Patterson, and Trefry, 2009; Patterson and Davis, 2009; Lahvis, Baehr, and Baker, 1999; and Lavhis and Baehr, 1996). Several of these studies document vapor concentrations at least two to three orders of magnitude lower than would be predicted to occur merely by simple diffusion in the absence of biodegradation.

EPA (2013a) presents findings of an analysis of a large number of vapor samples from leaking UST sites. These results, which are consistent with several recent analyses of different PVI databases (and which are summarized in the report), indicate that in most settings, PHC vapors are biodegraded over relatively short distances in clean, biologically active soil.

**Special Considerations**

Preferential transport pathways are avenues of least resistance to the migration of contaminants whether in the dissolved phase, LNAPL phase, or vapor phase. The presence of preferential transport pathways can increase the speed at which contamination moves through the subsurface such that contaminants may not biodegrade by the time they reach receptors. Preferential transport pathways include both natural and man-made features (e.g., solution channels, gravel layers, utility corridors and excavations). Natural geologic materials such as coarse sand and gravel with a low content of silt and clay; fractured consolidated rock; or consolidated rock with solution channels, may not have enough soil moisture in contact with soil gas to support adequate densities of biologically active microorganisms. Particularly in cases with shallow contamination, site investigations should evaluate whether a sufficiently thick layer of clean, biologically active soil is present below buildings in the lateral inclusion zone.

In addition, beneath very large buildings or under areas of extensive impermeable surface cover, soil moisture content may be lower than optimal[38] to support an adequate population of biologically active microorganisms necessary to degrade PHC vapors and prevent PVI (see Tillman and Weaver, 2007; EPA, 2013b).

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[38] Such reduced soil moisture beneath large buildings is referred to as a *soil moisture shadow*.

### Recommendation

Based on EPA (2013a), clean, biologically active soil does not contain LNAPL, EPA recommends LNAPL thresholds of 100 mg/Kg TPH (fresh gasoline) and 250 mg/Kg TPH (weathered gasoline and diesel). Except for the geological materials identified in *Special Considerations*, most soils contain indigenous microorganisms, sufficient oxygen, and adequate soil moisture necessary for degrading PHC vapors. Thus, it is typically not necessary to run microcosm studies or plate counts to test for microbial presence. However, if the conditions at the site are uncertain for supporting aerobic biodegradation, EPA recommends that appropriate samples be collected and analyzed to verify conditions at the site.

Due in part to difficulties in measuring this level of accuracy in the field, EPA recommends vertical separation distances of 6 feet for purely dissolved sources of PHCs and 15 feet for LNAPL sources. These distances are believed to be conservative in most environmental settings. The vertical separation distances described in this guidance (see **Table 3** in **Section 5**, p.52) should not be used at sites where the geologic materials may not have enough soil moisture in direct contact with soil gas. EPA recommends collection and analysis of adequate soil samples for soil moisture, which should be greater than 2 percent by dry weight. In situations where densities of biologically active microorganisms may not be adequate to biodegrade PHCs then soil gas samples should be collected following the recommendations in **Section 8**. If the attenuation factor calculated from results of analysis of the chosen pair or vapor samples indicates that there may be a potential for PVI above applicable exposure limits, EPA recommends gathering additional information and data to determine whether mitigation is appropriate.

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## 10. Non-PHC Fuel Additives

### Description

Petroleum fuels are comprised of hundreds of compounds; both natural components of petroleum as well as a number of synthetic (non-PHC) additives intended to improve certain performance properties of the fuel. Contaminants other than PHCs may be present at a site as the result of releases of petroleum fuels that contain additives, including alcohols (e.g., ethanol and tertiary-butyl alcohol [TBA]), ethers (e.g., MTBE), organic lead (e.g., the tetraalkyl lead compounds: tetraethyl lead [TEL], and tetramethyl lead [TML]), and lead scavengers (e.g., ethylene dibromide [EDB] and 1,2-dichloroethane [1,2-DCA]).[39] Non-petroleum contaminants may also be from releases of substances (e.g., chlorinated solvents) other than petroleum fuels. Their presence may be from prior uses of the site or as the result of migration from an off-site source (e.g., dry cleaner, chemical plant, landfill).[40]

### Importance

When assessing the potential threat of vapor intrusion, the presence of non-PHC fuel additives may pose a variety of additional challenges. Depending on the class of additive, the challenges include:

- Uncertainty regarding the aerobic biodegradation rates of some additives as well as some that do not biodegrade aerobically (or do not biodegrade quickly enough) in the shallow subsurface
- Biodegradation of an additive such as ethanol that consumes oxygen that would otherwise be available for biodegradation of other PHCs and produces a VOC (methane), which may migrate into buildings and hasten the spread of PHC vapors
- Toxicity levels of some additives are below the detection limit of conventional analytical methods

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[39] Although leaded gasoline, which also contains the lead scavengers EDB and 1,2-DCA, is no longer used for automotive fuel, it is still used for certain off-road applications such as automobile racing and in aviation fuel (Avgas). At these and older automotive fuel sites where leaded gasoline was released to the subsurface, lead scavengers may be present and could represent a potential source of vapors that should be assessed. For more information about lead scavengers, see Appendix F in *Evaluation Of Empirical Data To Support Soil Vapor Intrusion Screening Criteria For Petroleum Hydrocarbon Compounds* (EPA, 2013).

[40] While these substances are not the primary focus of a petroleum UST release investigation (including site characterization and subsequent cleanup, if necessary), there is the possibility that their presence may be detected through the use of certain analytical methods for identification of contaminants in groundwater, soil, and vapor samples. In particular, both EPA methods 8260B (EPA, 1996a) and 8021B (EPA, 1996b) can detect a number of volatile chlorinated solvents that are not associated with petroleum fuels or typically stored in USTs. The Leaking Underground Storage Tank Trust Fund cannot be used to assess or cleanup contamination from non-UST and non-petroleum sources. Volatile chlorinated solvents (e.g., PCE, TCE, TCA, Carbon tetrachloride, Chloroform) also do not biodegrade under aerobic conditions, therefore their potential for vapor intrusion should instead be assessed using the *OSWER Final Guidance For Assessing and Mitigating the Vapor Intrusion Pathway From Subsurface Sources to Indoor Air* (OSWER Publication 9200.2-154)(EPA, 2015). Should any contaminants from non-UST sources be discovered at a leaking UST site, contact the appropriate state or federal implementing agency.

The separation distances described in this document (**Section 5**, Table 3, p.52) and the protectiveness provided by clean, biologically active soil against vapor intrusion by PHCs may be insufficient to protect against vapor intrusion by non-PHC fuel additives. Additional investigation should be conducted where certain additives are present. The following narrative provides additional information on several additives and introduces the Vapor Intrusion Screening Levels (VISL) Calculator, which may be particularly useful when investigating vapor intrusion from non-PHC fuel additives.

Although biodegradation is known to occur for many individual additives and classes of additives,[41] the rate of biodegradation in soil gas has not necessarily been rigorously quantified; this is especially true for the lead scavengers EDB and 1,2-DCA. Therefore, for these two chemicals in particular, vertical separation distances recommended in this guide may not be sufficient for petroleum fuel releases that contain EDB and 1,2-DCA and additional investigation may be necessary to assess their potential for vapor intrusion. Note: Though the use of ethers and lead scavengers in gasoline has been reduced or eliminated in recent years, these compounds may still be present at some older petroleum release sites (Weaver, et al., 2005, 2008, 2009; EPA, 2008).

Alternative fuels, especially those that contain higher percentages of ethanol present a challenge because ethanol readily biodegrades to create methane (Jewell and Wilson, 2011; Ma, et al., 2012 and 2014; Freitas, et al., 2010). The use of ethanol in motor fuels is increasing. Methane generation may be more significant at sites where large volumes of ethanol-blended gasoline (and higher ethanol content fuels, greater than E-20) have been released into the subsurface (Ma et al., 2014). Methane production can increase soil gas pressures and may result in advective soil gas flow toward receptors. In such situations, intrusion of methane into confined spaces may result in the accumulation of very high concentrations creating a risk of fire and explosion. In addition, methane also biodegrades under aerobic conditions and depletes oxygen that otherwise could be available for the biodegradation of PHCs.
The depletion of oxygen may result in PHC vapors being transported farther than they otherwise would be, possibly increasing the threat of PVI.

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[41] Aerobic biodegradation has been observed for the lead scavengers EDB (Prince and Douglas, 2010; Pignatello, 1986), and 1,2-DCA (Falta, 2004); the ethers MTBE (Prince and Douglas, 2010; Wang and Deshusses, 2007; Phelps and Young, 1999; Landmeyer and Bradley, 2003; Landmeyer, et al., 2010; Bradley and Landmeyer, 2006; Kuder, 2005; Lesser, et al., 2008; Baehr, Charles, and Baker, 2001) and Tertiary-amyl methyl ether (TAME) (Landmeyer, et al., 2010); the alcohols Ethanol (Powers, et al., 2001; Corseuil et. al, 1998), TBA (Wang and Deshusses, 2007; Landmeyer, et al., 2010), and Methanol (Powers, et al., 2001); and some organic lead compounds (Prince and Douglas, 2010; Gallert and Winter, 2004). Although anaerobic biodegradation is slower than aerobic biodegradation, anaerobic biodegradation may be a significant mechanism for destruction of non-PHCs fuel additives (and PHCs, especially in source areas.) Selected references on anaerobic biodegradation of various non-PHC fuel additives are listed under *Additional Information* at the end of this section.

Thus, separation distances that are usually protective against PVI may not be sufficiently protective in situations where methane is produced in large quantity (Ma et al., 2014). For additional information on sampling for the presence of methane, assessing potential risks, and how to manage the risks, see ASTM's "*New Practice for Evaluating Potential Hazard Due to Methane in the Vadose Zone*".[42]

Finally, in addition to the uncertainties regarding the rates of biodegradation of the lead scavengers EDB and 1,2-DCA,existing analytical methods are not able to detect them at very low concentrations representative of a cancer risk level of 1E-06. However, EPA (2013) suggests that although there are no soil gas data for lead scavengers in the PVI database, "a screening approach is feasible where groundwater concentrations are measured to determine the potential for vapor intrusion risks from EDB and 1,2-DCA." (see Section F.6). This approach is illustrated in the *Assessment* subsection through a sequence of equations and detailed discussion of the results for EDB and 1,2-DCA.

**Assessment**

Federal UST regulations (40 CFR 280.52(b)) stipulate that when conducting an investigation of a release from a regulated UST, investigators "must measure for the presence of a release where contamination is most likely to be present. In selecting sample types, sample locations, and measurement methods investigators must consider the nature of the stored substance, the type of initial alarm or cause for suspicion, the type of backfill, the depth of groundwater, and other factors appropriate for identifying the presence and source of release". Results of this sampling should also identify which contaminants should be assessed for potential vapor intrusion.

Once the candidate contaminants have been identified, the next step is to determine the target indoor air screening level for each of them. While the federal UST program does not prescribe human health values for contaminants, implementing authorities should use exposure values appropriate for the contaminants present and the characteristics of exposure (e.g., residential vs industrial). EPA provides a source of such exposure values in the Vapor Intrusion Screening Levels (VISL) Calculator.[43] VISLs for human health protection are generally recommended, medium-specific, risk-based screening-level concentrations intended for use in identifying areas or buildings that may warrant further investigation and mitigation as appropriate.

These VISLs are calculated and documented in the VISL Calculator and are based on:

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[42] The new ASTM methane guide is accessible at http://www.astm.org/DATABASE.CART/WORKITEMS/WK32621.htm

[43] The VISL Calculator provides recommended, but not mandatory, screening levels for use in evaluating the vapor intrusion pathway at Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) and Resource Conservation and Recovery Act (RCRA) sites. The user's guide for the VISL Calculator provides additional information about derivation of the indoor air and subsurface screening levels (EPA, 2014a). Both the VISL Calculator (EPA, 2014b) and user's guide may be downloaded from EPA's website: http://www.epa.gov/oswer/vaporintrusion/guidance.html.

Current toxicity values selected considering OSWER's hierarchy of sources for toxicity values (EPA, 2003)[44]

- Physical-chemical parameters for vapor forming chemicals
- EPA recommended approaches for human health risk assessment

The VISLs include target indoor air screening levels for long-term (i.e., chronic) exposures that consider the potential for cancer and non-cancer effects of vapor-forming chemicals. The VISLs also include subsurface screening levels for comparison to sampling results for sub-slab soil gas, "near-source" soil gas, and groundwater. These subsurface screening levels are back-calculated from the target indoor air screening levels for chronic exposures using medium-specific, generic attenuation factors that reflect generally reasonable worst-case conditions (EPA, 2015, Appendix B). VISLs are not automatically response action levels, although EPA recommends that similar calculation algorithms be employed to derive cleanup levels (see EPA, 2015, Section 7.6 for more information)**.**

The VISL Calculator allows users to specify an exposure scenario, target risk for carcinogens (TCR) and target hazard for non-carcinogens (THQ), and the average groundwater temperature at a site, and calculates screening levels for the target indoor air concentration, sub slab and exterior soil gas concentrations, and ground water concentration.

In the VISL Calculator, target indoor air concentrations are calculated using the equations presented in **Table 4**. For carcinogens, the inhalation unit risk (IUR) is the appropriate toxicity value. For non-carcinogens, the reference concentration (RfC) is the appropriate toxicity value. Each of these toxicity values is weighted by the appropriate exposure factors to determine the target indoor air screening concentrations. The smaller value (between $C_{ia,c}$ and $C_{ia,nc}$) is used as the target indoor air screening value.

Example calculations using the equations in **Table 4** are presented in **Table 5** for EDB and 1,2-DCA in indoor air under a residential exposure scenario. Note that the cancer screening levels ($C_{ia,c}$) are consistently lower than the non-cancer screening levels ($C_{ia,\ nc}$), thus the cancer screening levels would generally be used to assess risk to receptors for a given chemical.

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[44] OSWER's toxicity data hierarchy is three-tiered. Tier 1 are values from EPA's Integrated Risk Information System (IRIS). The IRIS database is web accessible at http://www.epa.gov/iris/. Tier 2 are Provisional Peer Reviewed Toxicity Values (PPRTVs), which are accessible at http://hhpprtv.ornl.gov/. Tier 3 are "Other"sources, such as the Agency for Toxic Substances and Disease Registry (ATSDR), and various states (e.g., California (CA DTSC, 2009), Hawai'i (HI DOH, 2011, 2012), Massachusetts (MA DEP, 2009), New Jersey (NJ DEP, 2013), Washington (WA DEC, 2006). Links to these sources are provided under *References Cited* at the end of this section.) EPA's Regional Screening Levels (RSLs) for Superfund Sites compiles available toxicity information based on this hierarchy. The VISL Calculator draws on these RSL tables for toxicity values that are used to calculate VISLs. RSLs are accessible at http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/index.htm.

**Table 4. Equations For Target Indoor Air Screening Concentrations For Volatile Chemicals**

| | |
|---|---|
| Cancer | $$C_{ia,c} = \frac{TCR \cdot ATc \cdot 365\ (days/year) \cdot 24(hours/day)}{EF \cdot ED \cdot ET \cdot IUR}$$ |
| Non-Cancer | $$C_{ia,nc} = \frac{THQ \cdot RfC \cdot ATnc \cdot 365 \cdot 24 \cdot 1000(ug/mg)}{EF \cdot ED \cdot ET}$$ |

$C_{ia,c}$ is the indoor air concentration for cancer risk, and $C_{ia,nc}$ is the indoor air concentration for non-cancer risk; the smaller value is used as the indoor air screening value. ATc and ATnc are the averaging times for cancer and non-cancer, respectively, and EF, ED and ET are exposure parameters (exposure frequency, duration, and time). The exposure factors should be consistent with those in Human Health Evaluation Manual, Supplemental Guidance: Update of Standard Default Exposure Factors OSWER Directive 9200.1-120 *http://www.epa.gov/oswer/riskassessment/pdf/superfund-hh-exposure/OSWER-Directive-9200-1-120-ExposureFactors.pdf*

**Table 5. Example Target Residential Indoor Air Concentrations For EDB And 1,2-DCA**

| **Chemical** | $C_{ia,c}$ (µg/m$^3$) | $C_{ia,nc}$ (µg/m$^3$) |
|---|---|---|
| 1,2-Dibromoethane (EDB) | 4.7E-03 | 9.4 |
| 1,2-Dichloroethane (1,2-DCA) | 1.1E-1 | 7.3 |

Values (and units) of other variables used in these example residential calculations (equations in **Table 4**) are:

| Variable | Cancer (c) | Non-Cancer (nc) |
|---|---|---|
| IUR(c) or RfC(nc) (EDB) | 6.0E-04 (µg/m$^3$)$^{-1}$ | 9 (mg/m$^3$) |
| IUR(c) or RfC(nc) (1,2-DCA) | 2.6E-05 (µg/m$^3$)$^{-1}$ | 7 (mg/m$^3$) |
| TCR(c) or THQ(nc) (unitless) | $10^{-6}$ | 1.0 |
| ATc or ATnc (years) | 70 | 26 |
| ED (years) | 26 | 26 |
| EF (days/year) | 350 | 350 |
| ET (hours/day) | 24 | 24 |

After target indoor air screening levels ($C_{ia}$) have been established, the next step is to determine vapor source concentrations and assess whether these are high enough to potentially pose a threat of vapor intrusion. The equations in **Table 6** are used by the VISL Calculator to calculate groundwater and soil gas screening levels based on target indoor air screening levels. These groundwater and soil gas screening levels can then be compared to actual field measurements of groundwater and/or soil gas concentrations. If the measured concentrations are greater than the screening levels, then there is a potential for vapor intrusion, otherwise not.[45]

**Table 6. Equations For Groundwater And Soil Gas Screening Levels Based On Target Indoor Air Screening Levels.**

<table>
<tr><td>Ground Water Concentration</td><td>$$C_{gw} = \frac{C_{ia}}{\alpha_{gw} \cdot 1000 \cdot HLC}$$</td></tr>
<tr><td>Soil Gas Concentration</td><td>$$C_{sg} = \frac{C_{ia}}{\alpha_{sg}}$$</td></tr>
<tr><td colspan="2">$C_{ia}$ is the target indoor air screening level concentration (µg/m$^3$).<br>Cgw is the screening concentration in groundwater (µg/L).<br>Csg is the screening concentration in soil gas (µg/m$^3$).<br>HLC is the unitless Henry's Law constant.<br>$\alpha_{gw}$ and $\alpha_{sg}$ are the groundwater and soil gas vapor intrusion attenuation factors, respectively (both unitless).<br>1,000 is the number of liters per m$^3$ (to convert from units of µg/m$^3$ to µg/L).</td></tr>
</table>

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[45] An individual subsurface sampling result that exceeds the respective, chronic screening level does not establish that vapor intrusion will pose an unacceptable human health risk to building occupants. Conversely, these generic, single-chemical VISLs do not account for the cumulative effect of all vapor-forming chemicals that may be present. Thus, if multiple chemicals that have a common, non-cancer toxic effect are present, a significant health threat may exist at a specific building or site even if none of the individual substances exceeds its VISL (see discussion of non-cancer hazard index in EPA (2015) Section 7.4.1).

These equations also may be rearranged to calculate a potential upper-bound indoor air screening concentration based on actual field measurements of groundwater and/or soil gas concentrations. For groundwater, the equation is rearranged like this:

$$(upper\ bound)C_{ia} = C_{gw} \cdot \ \alpha_{gw} \cdot 1000 \cdot HLC$$

Note that in order to calculate a screening level concentration in groundwater, a value for Henry's Law constant (HLC) is necessary.[46]

For soil gas the equation is rearranged like this:

$$(upper\ bound)C_{ia} = C_{sg} \cdot \ \alpha_{sg}$$

Appropriate values for the field measured concentration in groundwater or soil gas, and for the respective attenuation factors are plugged into the equation to yield an upper bound indoor air screening level for $C_{ia}$. The respective upper-bound indoor air screening level (derived from either groundwater or soil gas sampling data) is then compared to the target indoor air screening concentration ($C_{ia}$) from the VISL Calculator. If the upper-bound value is greater than the target value, then there is a potential for vapor intrusion, otherwise not (see Footnote #45).

In both cases, if there is a potential for vapor intrusion and where contamination is not in direct contact with an overlying building, then paired vapor samples should be collected to assess vapor attenuation. These paired samples should either be (a) near-slab (exterior) shallow soil gas samples paired with deep (source) soil gas samples, or (b) indoor air samples paired with sub-slab soil gas samples.

**Table 7** presents example screening concentrations of EDB and 1,2-DCA in groundwater and soil gas using the equations in **Table 6**. These values represent the upper-bound concentrations according to Henry's Law that could be present in groundwater and soil gas, respectively, and not result in indoor air concentrations in excess of the target screening levels (i.e., VISLs) presented in **Table 5**. If concentrations measured in groundwater ($C_{gw}$) exceed these thresholds, it is possible that the target indoor air concentration will also be exceeded and mitigation may be necessary.

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[46] The VISL Calculator is one source of Henry's Law constants. Because these constants are temperature dependent, the VISL Calculator automatically calculates the correct constant based on a temperature that is selected by the user.

**Table 7. Example Screening Concentrations For EDB And 1,2-DCA In Groundwater And Soil Gas**

| Chemical | $C_{gw}$ (µg/L) | $C_{sg}$ (µg/$m^3$) |
|---|---|---|
| 1,2-Dibromoethane (EDB) | 0.18 | .16 |
| 1,2-Dichloroethane (1,2-DCA) | 2.2 | 3.7 |
| Target residential indoor air concentrations ($C_{ia,c}$) are from **Table 5**.<br>Selected attenuation factors (α) are 0.001 for groundwater and 0.03 for soil gas. These are taken from the VISL Calculator and do not account for biodegradation.<br>Dimensionless Henry's Law constants (HLC) for groundwater at 25°C are 0.0266 for EDB and 0.048 for 1,-DCA. These values are also taken from the current version of the VISL Calculator. | | |

The lead scavengers present an additional challenge in that existing analytical methodology is not able to detect them at very low concentrations representative of a cancer risk level of 1E-06 for either EDB or 1,2-DCA. As shown in **Table 8**, Selective Ion Monitoring (SIM) is able to achieve a detection limit representative of the 1.0E-04 risk level for EDB and 1.0E-05 for 1,2-DCA. Commercial low level is able to achieve a detection limit representative of the 1.0E-05 risk level for 1,2-DCA. However, an analytical detection limit does not impact the risk level for a certain chemical. The chemical may be present at a concentration greater than the appropriate risk level concentration, but below the limit of detection, which may result in undetected risk to potential receptors. Approaches to compensate for such analytical limitations include using available modeling data and professional judgment to evaluate whether the chemical may be present and having samples reanalyzed by special analytical services. For the screening level assessment, the chemical should be carried through assuming that it is present at the concentration equivalent to the quantitation limit. This allows the risk at the quantitation limit to be compared to the risks associated with other chemicals at the site. At minimum, the chemical should be addressed qualitatively. These topics are beyond the scope of this PVI guide; additional information may found in EPA's *Risk Assessment Guidance for Superfund* (RAGS).[47]

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[47] The *Risk Assessment Guidance for Superfund (RAGS)* document is accessible at http://www.epa.gov/oswer/riskassessment/ragsa/index.htm. In particular see Section 5.3 in Part A, and Part F: Supplemental Guidance for Inhalation Risk Assessment.

**Table 8. Comparison Of Risk Levels And Achievable Analytical Detection Limits For The Lead Scavengers EDB And 1,2-DCA In Indoor Air.**

| Compound | Target Indoor Air Concentration | | | Analytical Method | | |
|---|---|---|---|---|---|---|
| | **Risk Level 1.0E-04** | **Risk Level 1.0E-05** | **Risk Level 1.0E-06** | **Commercial conventional** | **Commercial low level** | **Commercial SIM** |
| EDB | 🟩 0.47 | 🟥 0.047 | 🟥 0.0047 | 3.8 | 0.77 | 0.23 |
| 1,2-DCA | 🟩 11 | 🟩 1.1 | 🟥 0.11 | 2.0 | 0.40 | 0.12 |

NOTE: all values in µg/m$^3$
1.0E-04 = increased lifetime cancer risk of 1 per 10,000
1.0E-05 = increased lifetime cancer risk of 1 per 100,000
1.0E-06 = increased lifetime cancer risk of 1 per 1,000,000
Commercial conventional = EPA Method TO-15 (see *http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf*)
Commercial low level = EPA Method TO-15 (modified)
SIM = Selective Ion Monitoring
The achievable detection limits in this table are representative of the general state of the technology as of the present date. Some laboratories may be able to achieve lower detection limits using modified techniques. Future technological improvements may also result in lower detection limits.
🟩 Achievable
🟥 Not Achievable

**Special Considerations**
VISL Calculator screening levels do not include the effects of biodegradation on the concentrations of vapors in soil that could potentially intrude into indoor air. The generic attenuation factors used in calculating VISLs (i.e., 0.001 for groundwater, 0.03 for soil gas) are conservative, and may overestimate the transfer of some contaminants (e.g., those that biodegrade aerobically) from soil gas to indoor air in some buildings. As a result these screening levels will usually overestimate the true indoor air concentrations of aerobically-biodegradable volatile contaminants (e.g., PHCs). Decision-makers may choose to use alternate approaches (e.g., attenuation factors that account for biodegradation) that may be more appropriate for specific sites where circumstances do not match the underlying assumptions used in calculating the VISLs.

When Information is available on the separation distance between the source of contamination and the receptor, on the total concentration of biodegradable compounds in soil gas, and on the rate constant for degradation of contaminant vapors in soil, it is possible to refine the estimate of the attenuation factor (α) between soil gas and indoor air for some VOCs and PHCs. Approaches to refine the estimate of the attenuation factor (α) for PHCs are discussed in **Section 12** (p.100) and by Wilson et al. (2014). Also see **Section 13** (p.106) for information on the use of models to estimate attenuation factors. However, until more is known about the rates of biodegradation of EDB and 1,2-DCA in soil gas, the separation distances for PHCs shown in Section 5 and the approaches described in **Section 12** or **Section 13** for determining attenuation factors are not recommended for these two contaminants.

In addition to concerns discussed earlier, other potential concerns with increasing ethanol content are in relation to (re)mobilization of LNAPL (McDowell, et al., 2003; Yu, et al., 2009) and increased solubility of PHCs (Powers, et al., 2001). The implications of these impacts may extend beyond vapor intrusion; see **Section 7** (p.61) for information about LNAPL and **Section 6** (p.57) for information about dissolved contaminant plumes.

**Recommendation**

EPA recommends that groundwater samples be analyzed for PHCs and non-PHC fuel additives (e.g., alcohols, ethers, organic lead, lead scavengers) typically found in petroleum-based fuels, when appropriate. At the present level of knowledge, the groundwater and soil gas screening levels in **Table 7** are the best values to use to determine whether indoor air target levels will be exceeded for EDB and 1,2-DCA. If measured concentrations of EDB and 1,2-DCA in groundwater exceed the screening levels in **Table 7**, EPA recommends gathering additional information and data to determine whether mitigation is appropriate. The methodology illustrated in the *Assessment* subsection above can be applied to any non-PHC (or any VOC for that matter) for which an appropriate toxicity value and attenuation factor are available.

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# 11. Seasonal And Weather Effects

**Description**

The generation and movement of petroleum vapors are subject to seasonal effects such as temperature trends and fluctuations; and weather effects such as precipitation, barometric pressure changes, and wind (Lundegard, Johnson, and Dahlen, 2008). Cycling of heating and cooling systems inside buildings in response to seasonal and weather effects may also influence vapor intrusion.

**Importance**

Biological processes slow down with decreasing temperatures, though microorganisms continue to biodegrade PHCs at environmentally significant rates even when temperatures are near freezing (Bradley and Chapelle, 1995; Bradley, Richmond, and Chapelle, 2005; Hers, et al., 2011). Bradley and Landmeyer (2006) documented microbial degradation of MTBE in the wintertime when groundwater temperatures were below 5˚C.

There is conflicting evidence as to whether, and under what additional conditions, frozen or ice-covered soil reduces the movement of oxygen into the subsurface. Hers, et al. (2011) studied a residential site in Canada where subsurface oxygen readings taken throughout the winter did not indicate a decrease in oxygen content of soil gas and there was evidence that biodegradation was occurring. However, the residence was above a crawl space and the soil below the house was never covered by ice or snow. It is known that the air permeability of a snow layer is a complex function of pore size, grain size, ice fraction, and density (Armstrong, 2008; Bender, 1957; Conway and Abrahamson, 1984). Rike (2003) observed ongoing biodegradation in frozen arctic soils. In that study, a lengthy period of subfreezing soil temperatures at a petroleum contaminated site did not result in decreasing oxygen concentrations. In contrast, Freyman (1967) and Yanaia (2010) report that oxygen depletion has been observed in other studies of soils under ice sheets and snow cover. More study is needed to resolve this issue.

Precipitation events can impact biodegradation of petroleum vapors. A certain amount of soil moisture is necessary for microorganisms to live; not enough and they are not actively degrading PHC vapors; too much and reoxygenation is impeded, possibly leading to anaerobic conditions at greater depths (Silver, 1999; Ludemann, 2000; Pezeschki, 2001). Wind and barometric pressure changes can produce pressure gradients inside buildings. Negative pressure inside buildings can result in enhanced intrusion of PHC vapors. Positive pressure inside buildings can both prevent intrusion of PHC vapors into buildings and facilitate oxygen transport through cracks in the foundation into the subsurface. This can result in reoxygenation of the soil beneath the building that would otherwise be depleted of oxygen (Lundegard, Johnson, and Dahlen, 2008).

Heating systems in buildings, which operate most frequently during winter months, can create a chimney effect, whereby PHC vapors are pulled into buildings at much higher rates than they would ordinarily. Cooling systems, which operate only during summer months, can have the opposite effect, creating positive pressure gradients in basements that both prevent intrusion of PHC vapors into buildings and allow oxygen to enter the soil (Lundegard, Johnson, and Dahlen, 2008).

**Assessment**

Seasonal and weather conditions can influence the characteristics of PHC vapor migration over time. Data on temporal changes in temperature, barometric pressure, wind speed and direction, relative humidity, and precipitation can aid in correctly identifying trends and result in a more accurate CSM.

In addition, site characteristics that may indicate susceptibility to the effects of seasonal and weather factors should be assessed. These include:

- Poor drainage around the building indicated by flooded soils
- Area subject to permafrost/long lasting snow cover (based on altitude or latitude)
- Shallow and highly variable water table

**Special Considerations**

Seasonal effects may also influence the formation and migration of dissolved plumes and LNAPL. Changes in water table elevation can create a smear zone of residual LNAPL contamination. LNAPL in the smear zone can act as a long-term source of dissolved contamination during periods of high water table elevation and as a source of petroleum vapors during periods of low water table elevation when contaminants reemerge from a previously submerged condition. Groundwater levels in the vicinity of USTs may also be subject to the influence of water within the tank pit. After rainfall events (and potentially snowmelt) water levels within tank pits are typically above the level of ambient groundwater; consequently a groundwater recharge mound may form. This mound disrupts the local groundwater flow field and contaminants can migrate away from the tank excavation, potentially in all directions.

**Recommendation**

During site characterization activities, weather conditions such as temperature, barometric pressure, and wind speed/direction should be recorded to aid in recognizing the cause of trends or anomalies in the PVI data and not merely attributed to unknown factors. This information may be obtained from the National Oceanic and Atmospheric Administration (NOAA) (see *http://www.noaa.gov/wx.html*) or a nearby airport where weather data are recorded hourly.

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## Web Resources

U.S. Geological Survey's Soil Surveys http://websoilsurvey.nrcs.usda.gov/app/HomePage.htm

U.S. Department of Homeland Security Federal Emergency Management Agency's flood plain maps https://msc.fema.gov/portal

2012 U.S. Department of Agriculture Plant Hardiness Zone Map http://planthardiness.ars.usda.gov/PHZMWeb/

## 12. Vapor Intrusion Attenuation Factor (α)

### Description

When Johnson and Ettinger (1991) published their vapor intrusion model they introduced a parameter to relate the vapor concentration of a volatile chemical inside a building to its vapor concentration at the subsurface source. The parameter, designated alpha (α), is also called the vapor intrusion attenuation factor. It is defined mathematically as the concentration in indoor air divided by the concentration in soil gas at the source (with concentrations in the same units). The source is defined as the region of highest vapor concentration in the vadose zone. Large values of α (i.e., values approaching one) indicate that little attenuation is taking place, whereas small values of α (i.e., values much smaller than one) indicate that significant attenuation is taking place.

### Importance

As part of a risk evaluation, the concentrations of a chemical in indoor air can actually be measured, or they can be predicted. The attenuation factor is used as a part of a risk evaluation to predict or estimate the concentration of a chemical in indoor air from the concentration measured in soil gas below or near a building. To predict the indoor air concentration, the measured concentration in soil gas is multiplied by the suitable attenuation factor.

### Assessment

U.S. EPA (2013, Table 6-1) provides recommended vapor attenuation factors for risk-based screening of the vapor intrusion pathway for residential buildings. For example, the generic values of α in EPA (2015) are 1.0E-03 (0.001) for groundwater, 3.0E-02 (0.03) for sub-slab soil gas, and 3.0E-02 (0.03) for deep (near-source) soil gas. These values of α are derived from measurements made during case studies of the vapor intrusion of chlorinated solvents such as trichloroethylene (TCE), which are not biologically degraded in aerobic unsaturated soil or sediment. Likewise, values for concentrations in indoor air that are derived from the model of Johnson and Ettinger (1991) also do not include any consideration of biodegradation. As a result, the generic values of α in U.S. EPA (2015) and values for indoor air that are calculated using the Johnson and Ettinger model (JEM) overestimate the indoor air concentrations of PHCs. Thus, these values of α are not applicable to PVI from leaking USTs.[48] For additional information on estimation of sub-slab attenuation factors, see Brewer et al. (2014).

To provide estimates of α that are more suitable for PHCs, Abreu, Ettinger, and McAlary (2009) developed a three-dimensional computer model to predict the effects of biodegradation in the unsaturated zone below a building on the concentrations of chemicals in the indoor air of the building. They performed a series of model simulations to estimate semi-generic values of α from site-specific information on the vertical separation distance between the receptor building

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[48] Attenuation factors that account for biodegradation can be derived from models such as *BioVapor* or *PVIScreen* (see **Section 13**, p.106 for more information). Additional guidance may be found in Wilson *et al.* (2014).

and the source, and the total concentration of biodegradable compounds in soil gas at the source of the hydrocarbons. **Figure 9** compiles the computer simulations conducted by Abreu, Ettinger, and McAlary (2009) of the attenuation factor during vapor intrusion into a building with a basement. This figure presents the concentration of biologically degradable hydrocarbon in an unconventional unit (mg/L as benzene).

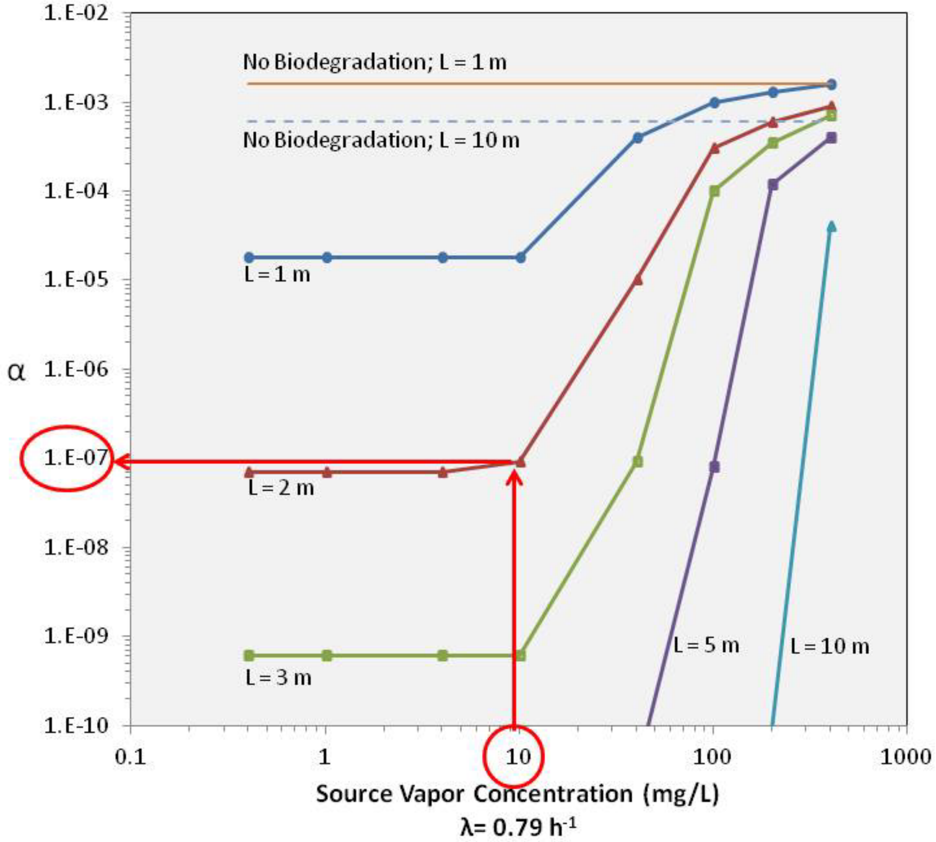

**Figure 9. Relationship Between Source Vapor Concentration And Vapor Intrusion Attenuation Factor (α) As A Function Of Vertical Separation Depth Between Contaminant Source And Base Of Building (Receptor)** (Source: modified from Abreu, Ettinger, and McAlary, 2009, Figure 7, page 114. Reprinted from *Groundwater Monitoring & Remediation* with permission of the National Ground Water Association. Copyright 2009.)

To generate **Figure 9**, Abreu, Ettinger, and McAlary (2009) used conservative assumptions for the rate of biodegradation. In this particular set of simulations, the first order rate constant for biodegradation (λ) was set at 0.79 $h^{-1}$, a reasonable average rate based on the range of rates published in the literature (DeVaull 2007). Model simulations assume the building has a basement and that it is surrounded by homogeneous, uniform sandy soil that is directly exposed to the atmosphere and that preferential pathways for vapor migration into the building or through the vadose zone are not present. As a result, the concentration of oxygen in the soil gas in the topmost layer of exposed soil is the concentration of oxygen in the atmosphere. Compared to silty or clayey soils, sandy soils have more air filled porosity and as a result, vapors diffuse more rapidly through them (and they also allow more oxygen to diffuse from the atmosphere). The simulations assumed that the square building was 10 meters (33 feet) on each side.

**Figure 9** can be used to estimate the value of α for situations where the total concentration of vapors at the source and the vertical separation distance between the contaminant source and the bottom of the building are known and all of the other input parameters match site conditions. For example, for a source vapor concentration of 10 mg/L and a vertical separation distance (L) of 2 meters (6.6 feet), the estimated value of α would be approximately 1.0E-07. To complete the exposure assessment, the measured concentration of benzene in soil gas at the source of contamination is multiplied by the value of α, to predict the indoor air concentration in a building.

**Figure 10** is a redraft of **Figure 9**, where the source concentration of vapors is expressed in more conventional units for vapors in soil gas ($\mu g/m^3$). The oxygen demand of all the hydrocarbons that might be in soil gas is expressed as the concentration of TPH (gasoline) plus the concentration of methane. The concentration of TPH (gasoline) can be determined by modified EPA Method TO-15 (see *http://www.epa.gov/ttn/amtic/files/ambient/airtox/to-15r.pdf*) referenced to heptane. The concentration of methane can be determined as a fixed gas or by EPA Method 3C. The concentration of methane is multiplied by 1.136 to correct for the differences between the theoretical oxygen demand of methane and heptane.

**Special Considerations**

**Figure 9** or **Figure 10** should only be used for UST sites with the same characteristics that were simulated by Abreu, Ettinger, and McAlary (2009). These conditions were relatively conservative. **Figure 9** and **Figure 10** are not appropriate for use at sites where the oxygen flux from the surface is impeded.

Some documents define the vapor intrusion attenuation factor differently than defined by Johnson and Ettinger (1991) and discussed in this section. The JEM (see **Section 13**, p.106) ignores background sources when estimating the indoor air concentration arising from vapor intrusion. When used in this PVI guide, the Greek letter alpha (α) refers strictly to attenuation during vapor intrusion, which might be observable if there were no background (ambient) vapor sources. In contrast, some empirical attenuation factors (sometimes designated *AF*) are based on indoor air concentrations that include both background sources and vapor concentrations that intrude into the building from a subsurface vapor source. Thus, when there is a measurable contribution from an ambient source, an attenuation factor such as *AF* (which includes the contribution of ambient sources) would be somewhat greater than the Johnson & Ettinger alpha (α), which would indicate less attenuation than is actually occurring.

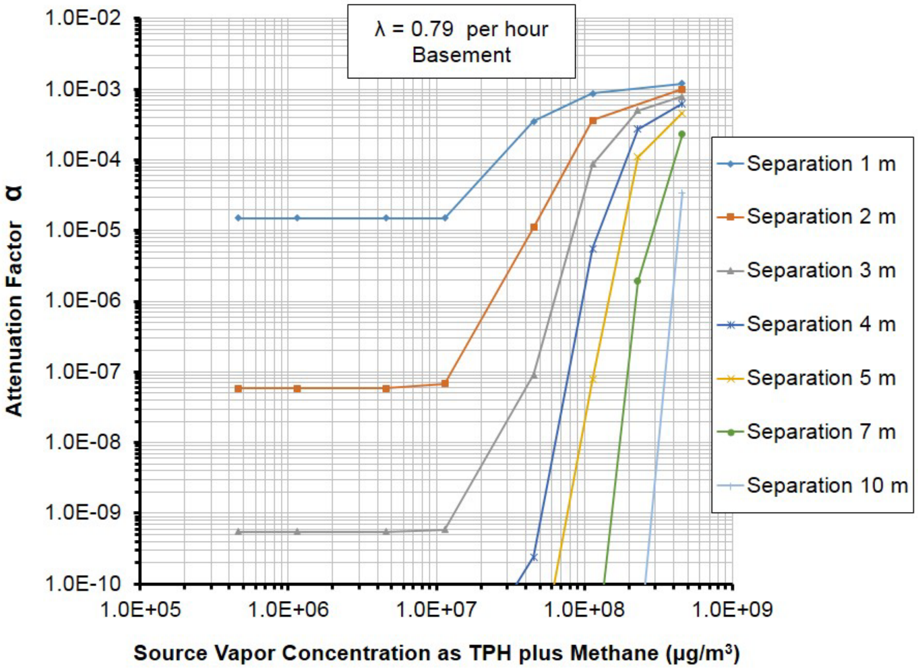

**Figure 10. Rescaled Figure 9 That Expresses The Source Vapor Concentration In Conventional Units.**

### Recommendation

When evaluating the vapor source and attenuation of PHC vapors, paired vapor samples are required to measure the actual attenuation that occurs due to aerobic biodegradation. Where contamination is not in direct contact with an overlying building, choose one of two options: (1) collect near-slab (exterior) shallow soil gas samples paired with deep (source) soil gas samples, or (2) collect indoor air samples paired with sub-slab soil gas samples. Note that for option 2 if the measured concentration of vapor in indoor air is below the applicable allowable indoor concentration there is no need to measure sub-slab vapor concentration. If contamination is in direct contact with a building basement, foundation, or slab, it is necessary to collect indoor air samples as it will not be feasible to collect sub-slab vapor samples. If a generic vapor intrusion attenuation factor and the measured concentration of a PHC in shallow soil gas predict an acceptable concentration in indoor air, that prediction may be adequate to support a screening decision. However, generic attenuation factors may not be appropriately representative of conditions at a particular site.

Models may provide better estimates of α, but only if the actual conditions at a specific site match the assumptions of a particular model. For biodegradable PHCs it would be better to implement a transport and fate model that is designed to simulate the contribution of biodegradation. The three-dimensional models of Abreu, Ettinger, and McAlary (2009) and Verginelli and Baciocchi (2014) are potential options. BioVapor, a model developed by the American Petroleum Institute, is another option. U.S. EPA is developing a model called PVIScreen that is intended for this purpose. See **Section 13** (p.106) for more discussion of the appropriate use of computer models for PVI investigations.

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## 13. Computer Modeling Of Petroleum Vapor Intrusion

### Description

A number of models have been developed and applied in estimating transport of volatile chemicals from subsurface soil and groundwater to indoor air (Bekele, et al. 2013). Lahvis (2011) presents a summary of 35 different analytical screening-level models, including a discussion of features, and assumptions. Models generally used for simulation of PVI are either the Johnson-Ettinger model (JEM) or BioVapor.

#### *Johnson-Ettinger Model (JEM)*

Johnson and Ettinger introduced one of the first vapor intrusion models in 1991. This model is referred to as the Johnson-Ettinger Model or JEM. Features of the JEM include:

- A steady or transient source of subsurface vapors from groundwater or residual chemicals
- Gaseous-phase diffusive vapor flow through a layer of soil
- Vapor transport through a slab-on-grade or basement foundation
- Building air exchange

The JEM presumes that the concrete foundation is impermeable and vapor movement occurs only through cracks and other openings. However, concrete is permeable to vapors and gases. Effective diffusion rates for intact air-dry concrete have been measured for hydrocarbons, oxygen, methane, and radon with an overall measured range from 1.08 to 15.6 $cm^2$/hr (Haghighat, et al., 2002; Patterson and Davis, 2009; Kobayashi and Shuttoh, 1991; Tittarelli, 2009; Yu, et al., 1993). Thus, diffusive vapor flow for typical foundation areas and thicknesses can be significant (McHugh, de Blanc, and Pokluda, 2006; Luo, et al., 2012). Actual measurement of differential pressure across varied building foundations show a significantly variable component over time (Nazaroff, et al., 1985; Hintenlang and Al-Ahmady, 1992; Robinson, et al., 1997a,b; McHugh , de Blanc, and Pokluda, 2006; Lundegard, Johnson, and Dahlen, 2008; Patterson and Davis, 2009; Luo and Johnson, 2011).

For sites where PHCs are present and aerobic biodegradation of PHCs occurs in the vadose zone, comparisons to JEM consistently show the model to over-predict indoor air concentrations by at least several orders of magnitude (Fitzpatrick and Fitzgerald, 2002; Sinke, 2001; Ririe, Sweeny, and Daugherty, 2002; Hers, et al., 2003; Davis, 2006; Golder Associates, 2008; Davis 2009). The potential for over-prediction is greatest for sites with low concentrations of PHCs in soil and groundwater (API, 2009; Davis, 2009; Energy Institute, 2009).

The original model has been revised numerous times to attempt to account for biodegradation, which was not included in the original JEM (see Johnson, Kemblowski, and Johnson, 1998; Ririe, et al., 1998; Johnson, Hermes, and Roggemans, 2000; Spence and Walden, 2010; Parker, 2003; Environmental Systems and Technologies, 2004; DeVaull, 2007a; Mills, et al., 2007; Turczynowicz and Robinson, 2007; API, 2010; Lahvis, 2011). EPA also revised the original JEM.

The most current information on EPA's revised model may be found on EPA's website at *http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm*.

### *BioVapor*

The BioVapor model (DeVaull, 2007a; API, 2010) is a Microsoft Excel© macro that uses a conceptual model similar to the JEM. BioVapor includes the following features:

- A steady subsurface petroleum vapor source.
- Gaseous-phase diffusive vapor flow through a layer of soil.
- Vapor transport through a slab-on-grade or basement foundation.
- Building air exchange.

In contrast to JEM, BioVapor accounts for oxygen-limited, aerobic biodegradation. Aerobic biodegradation is included as a coupled reaction between petroleum vapors and oxygen. Oxygen availability in the subsurface is dictated by transport through and around the building foundation, and by diffusion into the soil. The BioVapor model requires estimates of chemical-specific aerobic degradation rates for vadose zone soils. DeVaull (2007a,b) provides default values based on measured data. DeVaull (2011) provides improved estimates of both median values and observed ranges for an expanded set of specific chemicals.

### *PVIScreen*

PVIScreen (Weaver, 2015) is based on the equations of BioVapor but is coded in Java to improve computational efficiency and allow for implementation of algorithms to automate uncertainty analysis. Most computer models must be run multiple times with varying input parameters in order to conduct a typical sensitivity analysis. PVIScreen automates this function by treating input variables as ranges and then conducting a Monte Carlo analysis. The results, which are provided in a matter of seconds, are presented as the probability that the indoor air concentration is less than a risk-based level. This is in contrast to most models that provide single values for various output parameters. PVIScreen also allows for flexible unit choices and presents results in an automatically-generated report.

## Importance

Vapor intrusion models that include oxygen limited biodegradation support development of petroleum-specific exclusion distance criteria (i.e., lateral inclusion zone—see **Section 4**, p.44; vertical separation distance—see **Section 5**, p.48). Model results are consistent with empirical exclusion distance values derived from several PVI field investigations. These include Lahvis, et al. (2013); Davis (2009); Peargin and Kolhatkar (2011); Wright (2011); McHugh, et al. (2010), and Verginelli and Baciocchi (2014). Site assessment and field data including the depth to contamination, source strength, and type (LNAPL or dissolved) are key parameters for determining these exclusion distance criteria.

Estimates using the BioVapor model indicate that for moderate or weak sources (especially dissolved plumes), biodegradation effectively eliminates the potential for PVI. Conversely, where vapor sources are both high in concentration and in close proximity to the bottom of a foundation, the BioVapor model predicts significant potential for PVI.[49] Notably, in these cases the BioVapor model predicts significantly higher potential for PVI below a foundation, where oxygen availability is more limited, than adjacent to the foundation where the soil surface is open to air and oxygen availability is greater. This prediction is consistent with measured vertical profiles of hydrocarbons and oxygen for high concentration vapor sources taken both below a foundation and beside a foundation (Patterson and Davis, 2009; Laubacher, et al., 1997).

Weaver (2012) presents results of a sensitivity analysis that indicates when biodegradation occurs, it dominates the other processes included in the BioVapor model. In these cases, the parameters representing aerobic biodegradation, source depth, and source strength dominate the model results. In the other cases where biodegradation is insignificant, building parameters become more important, as they are in the JEM (Tillman and Weaver, 2007).

More complex numerical models including oxygen-limited biodegradation have been developed and applied. Abreu and Johnson (2006) present results for a three-dimensional model. With matched model parameters, there is reasonable agreement between the three dimensional results and those predicted with the BioVapor model (DeVaull, 2007b) and PVIScreen (Weaver, 2015). Each of these model results show similar sensitivities to changes in model parameters, and support the use of exclusion distances such as those recommended in this document (see **Section 4**, p.44, lateral inclusion zone, and **Section 5**, p.48, vertical separation distance).

### Assessment

When selecting an appropriate computer model, the mathematical formulation needs to be consistent with conditions at the site and the CSM. If the computer model is not matched to conditions at the site, then error is likely introduced into the computer model results. This means that input parameters for the computer model should be representative of the actual physical, chemical, and biological properties of the site. Typically all factors influencing vapor intrusion are not included in currently available models. Even with more advanced modeling, resource limitations would prevent the detailed characterization necessary to determine representative values for some of the input parameters. Some of these factors include subsurface heterogeneity, variation in building operation, subsurface moisture content, variations in weather and others. For most other types of environmental models, limitations in characterization are mitigated by calibration to known endpoints, typically concentration distributions. Though calibration results may not be unique (that is the same results could potentially be obtained using different values for the same suite of input parameters), when these results match field conditions, a model is deemed to be useful for predictive simulations.

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[49] Moderate or weak sources are associated with dissolved plumes. Strong sources are associated with LNAPL. **Table 3** on page 52 presents concentration thresholds associated with dissolved plumes and LNAPL.

**Special Considerations**

Most of the parameters describing model processes will not be known with certainty. A common limitation is that field measurements of all the input parameters (e.g., biodegradation rates, soil moisture content beneath buildings, air exchange rates) are typically not available, and those that are (e.g., source concentration) may be spatially or temporally variable. Literature values are typically substituted for site-specific data. This leads to uncertainty as to whether parameter values are truly representative of site conditions. Model results will likewise inevitably lack certainty (Bekele, et al, 2013). The importance of these (and other) parameters is determined through an uncertainty analysis. By determining the impact of parameter variability on the model results, the uncertainty analysis adds confidence to the conclusions drawn from the model.

**Recommendation**

An appropriate framework for the use of a mathematical model and understanding of model characteristics is critical when using the results of mathematical models for regulatory purposes (Hers, et al., 2003). The appropriate role for a model in a PVI investigation is as a means to explain observed behavior. EPA recommends the use of a model that considers aerobic biodegradation when assessing the potential for PVI. Regardless of which model is used to simulate PVI, EPA recommends that an uncertainty analysis be conducted to provide error bounds on predictions of the computer model.

Model results obtained by using site-specific inputs can provide results that inform decision-making. In particular, model results can be used to demonstrate that: sufficient oxygen exists to degrade petroleum contaminants, contaminant vapor distributions are plausible given conditions at the site, estimates of the vapor attenuation anticipated in the subsurface due to biodegradation are reasonable. Models may also be used for purposes such as improving a site-specific sampling strategy, validation (or refutation) of the CSM by comparing a model to measured soil gas data, and in estimating the effect of varied or changed site conditions (e.g., including construction of a new building on a brownfields site).

Model results can thus be used as one line of evidence that a building is not likely to be impacted by PHC vapors. At the present time and state of knowledge, EPA cautions that model results should not be used as the sole rationale for determining that a building is not threatened or impacted by PVI.

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# Glossary

Note: Most of these definitions are from EPA's on-line glossaries (see http://iaspub.epa.gov/sor_internet/registry/termreg/searchandretrieve/termsandacronyms/search.do).

**Absorption:** the penetration of atoms, ions, or molecules into the bulk mass of a substance. In contrast, adsorption is the retention of atoms, ions, or molecules onto the surface of another substance

**Advection:** the process of transfer of fluids (vapors or liquid) through a geologic formation in response to a pressure gradient that may be caused by changes in barometric pressure, water table levels, wind fluctuations, or infiltration

**Aerobic:** able to live, grow, or take place only when free oxygen is present

**Anaerobic:** able to live, grow, or take place where free oxygen is not present

**Analyte:** the element, ion, or compound that an analysis seeks to identify; the element of interest

**Attenuation:** the reduction or lessening in amount (*e.g.*, a reduction in the amount of contaminants in a plume as it migrates away from the source)

**Biodegradability (or biodegradation potential):** the relative ease with which organic chemicals will degrade as the result of biological metabolism. With respect to petroleum hydrocarbons, although virtually all petroleum hydrocarbons are biodegradable, biodegradability is highly variable and dependent somewhat on the specific type of hydrocarbon. In general, biodegradability increases with increasing solubility; solubility is inversely proportional to molecular weight.

**Biodegradation:** a process by which microbial organisms transform or alter (through metabolic or enzymatic action) the structure of chemicals introduced into the environment

**Biologically active soil:** in the context of a PVI investigation means that the subsurface soil environment will support populations of microorganisms that are present in sufficient quantities to aerobically degrade PHC vapors before they intrude into a receptor. Effective aerobic biodegradation of petroleum hydrocarbons depends on the soil having sufficient oxygen and enough soil water to provide a habitat for adequate populations of active microorganisms. The presence of sufficient oxygen must be determined by the collection and analysis of soil gas. Soil that is too dry will not support microbial life. The soil generally will not be too dry for bacteria if the depth to the water table is less than 300 feet, or if the soil around the receptor supports the growth of plants characteristic of temperate climates. (NOTE that in hot, arid climates lack of soil moisture may inhibit biodegradation of PHCs) Concentrations of carbon dioxide which are ten-fold higher than concentrations in the atmosphere are an acceptable indication that conditions support microbial respiration. The actual habitat of soil bacteria is the thin film of water held to the surface of soil particles by capillary attraction. Coarse sand and gravel with a low content of silt or clay or organic matter, or fractured consolidated rock, or consolidated rock with solution channels, may not have enough soil water in intimate contact with soil gas to support adequate densities of biologically active microorganisms. These geological materials do not qualify as "biologically active soil."

**BTEX:** acronym for the aromatic hydrocarbons benzene, toluene, ethylbenzene, and xylenes (three isomers)

**Capillary fringe:** the zone of a porous medium above the water table within which the porous medium is saturated by water under pressure that is less than atmospheric pressure. See also *vadose zone* and *unsaturated zone*.

**Clean monitoring point:** Concentration thresholds for "clean" monitoring points are: the BTEX concentration in groundwater is equal to or less than the respective maximum contaminant level (e.g., 5 µg/L for benzene); the TPH concentration in soil is less than 20 mg/Kg; there is no potential presence of liquid or residual phase LNAPL; the oxygen concentration is greater than 0.2 percent; and the combustible gas concentration in soil gas is less than 100 ppm (v/v).

**Clean soil:** In the context of a PVI investigation, clean soil does not necessarily mean that the soil is free from all contamination, but rather that any contamination present is at concentrations low enough that the biological activity of the soil is sufficient to biodegrade PHC vapors before they reach a receptor.

**Computer model:** a mathematical representation of a physical process or system. Computer models are based upon sound conceptual site models to provide meaningful information. As the complexity of computer models increases, so does the amount of data required, and the quality of the output from computer models is directly related to the quality of the input data. Because of the complexity of natural systems, models necessarily rely on simplifying assumptions that may or may not accurately represent the dynamics of the natural system. Calibration and sensitivity analyses are important steps in the appropriate use of models.

**Conceptual site model (CSM):** a three-dimensional representation that conveys what is known or suspected about potential contamination sources, release mechanisms, and the transport and fate of those contaminants. The conceptual model provides the basis for assessing potential remedial technologies at the site. "Conceptual site model" is not synonymous with "computer model"; however, a computer model may be helpful for understanding and visualizing current site conditions or for predictive simulations of potential future conditions.

**Contamination:** in the context of a PVI investigation, contamination means that: the BTEX concentration in groundwater is greater than the respective MCL; or the TPH concentration in soil is greater than 100 mg/Kg; or there is potential presence of liquid or residual phase LNAPL; or the combustible gas concentration in soil gas is greater than 100 ppm (v/v).

**Diffusion:** the process by which molecules in a single phase equilibrate to a zero concentration gradient by random molecular motion (Brownian motion). The flux of molecules is from regions of high concentration to low concentration and is governed by Fick's Second Law.

**Dispersion:** the process by which a substance or chemical spreads and dilutes in flowing groundwater or soil gas

**Downgradient:** in the direction of decreasing potentiometric head; the general direction of groundwater flow

**First responder:** refers to those individuals who in the early stages of an incident are responsible for the protection and preservation of life, property, evidence, and the environment. Typically these are police, firefighters, or emergency medical personnel.

**Fixed gases:** refers to the gases nitrogen, oxygen, argon, carbon dioxide, and carbon monoxide. The volume of these gases together accounts for virtually 100 percent of the composition of the earth's atmosphere. Presence and concentration of these gases are determined using gas chromatography (GC).

**Flux:** the rate of movement of mass through a unit cross-sectional area per unit time in response to a concentration gradient or some advective force

**Free product:** a petroleum hydrocarbon in the liquid ("free" or non-aqueous) phase (see also light non-aqueous phase liquid, LNAPL)

**Gradient:** the rate of change in value of a physical or chemical parameter per unit change in position For example, hydraulic gradient is equal to the difference in head measured at two points (usually wells) divided by the distance separating the two points. The dimensions of head and distance are both lengths, therefore the gradient is expressed as a dimensionless ratio (L/L).

**Groundwater:** the water contained in the pore spaces of saturated geologic media

**Henry's law constant:** the ratio of the concentration of a compound in air (or vapor) to the concentration of the compound in water under equilibrium conditions

**Henry's law:** the relationship between the partial pressure of a compound and the equilibrium concentration in the liquid through a proportionality constant known as the Henry's law constant

**Heterogeneous:** varying in structure or composition at different locations in space

**Homogeneous:** uniform in structure or composition at all locations in space

**Hydraulic gradient:** the change in total potentiometric (or piezometric) head between two points divided by the horizontal distance separating the two points

**Hydrocarbon:** chemical compounds composed only of carbon and hydrogen

**Inclusion zone:** the area surrounding a contaminant mass through which vapor-phase contamination may travel and intrude into buildings and potentially result in adverse health effects to inhabitants

**Indian country:** (1) All land within limits of any Indian reservation under the jurisdiction of the United States government, notwithstanding the issuance of any patent, and, including rights-of-way running through the reservation; (2) All dependent Indian communities within the borders of the United States whether within the original or subsequently acquired territory thereof, and whether within or without the limits of a state; and (3) All Indian allotments, the Indian titles to which have not been extinguished, including rights-of-way running through the same.

**Indigenous:** living or occurring naturally in a specific area or environment; native

**Isotropic:** the condition in which hydraulic properties of an aquifer are equal when measured in any direction

**Lateral inclusion zone:** the area surrounding a contaminant mass and for which all buildings within its boundaries should be assessed for potential PVI. By definition, all buildings that overlie contamination in any phase are within the lateral inclusion zone.

**Light non-aqueous phase liquid (LNAPL):** contaminants that remain as the original bulk liquid with a density less than that of water (see also free product)

**Microorganisms:** microscopic organisms including bacteria, protozoans, yeast, fungi, mold, viruses, and algae

**Permeability:** a qualitative description of the relative ease with which rock, soil, or sediment will transmit a fluid (liquid or gas). Often used as a synonym for hydraulic conductivity or coefficient of permeability.

**Petroleum:** 40CFR280.12 defines the term *petroleum* to include crude oil or any fraction thereof that is liquid at standard conditions of temperature and pressure (60 degrees Fahrenheit and 14.7 pounds per square inch absolute).

**Petroleum hydrocarbons (PHCs):** hydrocarbons (i.e., compounds comprised of combinations of hydrogen and carbon atoms) that are components of petroleum (crude oil), including the various products that result from distillation of crude oil

**Petroleum vapor intrusion (PVI):** intrusion of petroleum hydrocarbon vapors into buildings or other structures

**Porosity:** the volume fraction of a rock or unconsolidated sediment not occupied by solid material but usually occupied by water or air (gas)

**Preferential transport pathways:** pathways through which contaminants may be transported at a higher rate than through surrounding materials. Preferential transport pathways are heterogeneities within geologic media and include features that are natural (such as facies changes, sand or gravel stringers, solution channels in karst, bedding planes and weathered surfaces, fractures, and joints) as well as man-made (such as utility corridors, trenches, other types of excavations).

**Regulated substance:** (a) Any substance defined in section 101(14) of the Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) of 1980 (but not including any substance regulated as a hazardous waste under subtitle C), and (b) Petroleum, including crude oil or any fraction thereof that is liquid at standard conditions of temperature and pressure (60 degrees Fahrenheit and 14.7 pounds per square inch absolute). The term regulated substance includes but is not limited to petroleum and petroleum-based substances comprised of a complex blend of hydrocarbons derived from crude oil through processes of separation, conversion, upgrading, and finishing, such as motor fuels, jet fuels, distillate fuel oils, residual fuel oils, lubricants, petroleum solvents, and used oils.

**RfC (reference concentration, inhalation)**: an estimate (with uncertainty spanning perhaps an order of magnitude) of a continuous inhalation exposure of a chemical to the human population through inhalation (including sensitive subpopulations), that is likely to be without risk of deleterious noncancer effects during a lifetime

**Selective ion monitoring (SIM):** a mass spectrometry scanning mode in which only a limited mass-to-charge ratio range is transmitted or detected by the instrument, as opposed to the full spectrum range

**Semi-volatile organic compound (SVOC):** an organic compound which has a boiling point higher than water and which may vaporize when exposed to temperatures above room temperature. Semi-volatile organic compounds include phenols and polynuclear aromatic hydrocarbons (PAHs).

**Site assessment:** see site characterization

**Site characterization:** (verb) the process by which site-specific information and data are gathered from a variety of sources to characterize the physical, biological, and chemical systems at a contaminated site. A primary objective of site characterization is delineation of the areal (both horizontal—longitudinal and lateral—transverse) and vertical extent of contamination. This includes changes in plume boundaries, changes in geochemical parameters that affect biodegradation, and contaminant mass (or concentration) increases or decreases. (noun) The product (e.g., CSM, report) resulting from the site characterization process. (Note: Site assessment, site investigation, site evaluation, and site check are all synonyms of site characterization.)

**Site check:** see site characterization

**Site evaluation:** see site characterization

**Site investigation:** see site characterization

**Soil moisture:** the water contained in the pore spaces in the unsaturated zone

**Solubility:** the amount of mass of a compound that will dissolve in a unit volume of solution

**Sorption:** a general term used to encompass the processes of absorption, adsorption, ion exchange, and chemisorption

**Source material:** material that includes or contains contaminants that act as a reservoir (either stationary or mobile) for migration of contamination to the ground water, to surface water, to air, (or other environmental media), or acts as a source for direct exposure. Contaminated ground water generally is not considered to be a source material although non-aqueous phase liquids (NAPLS [occurring either as residual- or free-phase]) may be viewed as source materials.

**Source zone:** the impacted area immediately surrounding the source of a release of regulated substances comprising source materials

**Total petroleum hydrocarbons (TPH):** a measure of the concentration or mass of petroleum hydrocarbon constituents present in a given amount of air, soil, or water. (Note: The term total is a misnomer, in that few, if any, of the procedures for quantifying hydrocarbons are capable of measuring all fractions of petroleum hydrocarbons present in the sample. Volatile hydrocarbons are usually lost in the process and not quantified. Additionally, some non-petroleum hydrocarbons may be included in the analysis.)

**Travel time:** the time it takes a contaminant to travel from the source to a particular point downgradient

**Tribe:** Indian tribe or tribe means an Indian or Alaska Native tribe, band, nation, pueblo, village, or community that the Secretary of the Interior acknowledges to exist as an Indian tribe pursuant to the federally Recognized Indian Tribe List Act of 1944, 25 U.S.C. 479a.

**Underground storage tank (UST):** 40CFR280.12 defines an *underground storage tank* as any one or combination of tanks (including underground pipes connected thereto) that is used to contain an accumulation of regulated substances, and the volume of which (including the volume of underground pipes connected thereto) is 10 percent or more beneath the surface of the ground. This term does not include any: (a) Farm or residential tank of 1,100 gallons or less capacity used for storing motor fuel for noncommercial purposes; (b) Tank used for storing heating oil for consumptive use on the premises where stored; (c) Septic tank; (d) Pipeline facility (including gathering lines) regulated under: (1) The Natural Gas Pipeline Safety Act of 1968 (49 U.S.C. App. 1671, *et seq.* ), or (2) The Hazardous Liquid Pipeline Safety Act of 1979 (49 U.S.C. App. 2001, *et seq.*), or (3) Which is an intrastate pipeline facility regulated under state laws comparable to the provisions of the law referred to in paragraph (d)(1) or (d)(2) of this definition; (e) Surface impoundment, pit, pond, or lagoon; (f) Storm-water or wastewater collection system; (g) Flow-through process tank; (h) Liquid trap or associated gathering lines directly related to oil or gas production and gathering operations; or (i) Storage tank situated in an underground area (such as a basement, cellar, mine working, drift, pit, or tunnel) if the storage tank is situated upon or above the surface of the floor. The term underground storage tank or UST does not include any pipes connected to any tank which is described in paragraphs (a) through (i) of this definition.

**Unsaturated zone:** the zone between land surface and the capillary fringe within which the moisture content is less than saturation and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is not included in the unsaturated zone.

**Vadose zone:** the zone between land surface and the water table within which the moisture content is less than saturation (except in the capillary fringe) and pressure is less than atmospheric. Soil pore spaces also typically contain air or other gases. The capillary fringe is included in the vadose zone.

**Vapor intrusion attenuation factor (α):** a parameter defined by Johnson and Ettinger (1991) to relate the vapor concentration of a volatile chemical inside the building to its vapor concentration at the subsurface source. This parameter, designated alpha (α), is defined mathematically as the vapor concentration in indoor air divided by the vapor concentration in soil gas at the source (with concentration being in the same units), and thus it is a ratio. The source is defined as the region of highest vapor concentration. Therefore, α values are always less than one. The vapor intrusion attenuation factor is an inverse measurement of the attenuation: α values *decrease* with *increasing* attenuation and α values *increase* with *decreasing* attenuation. In other words, α values represent the fraction of soil gas contaminant that reaches indoor air. Large α values (i.e., values approaching 1) indicate that a large fraction of the soil gas contaminant has reached the indoor air; therefore, little attenuation is taking place, whereas small α values indicate that a small fraction of the soil gas contaminant has reached the indoor air; therefore, significant attenuation is taking place.

**Vapor pressure:** the force per unit area exerted by a vapor in an equilibrium state with its pure solid, liquid, or solution at a given temperature. Vapor pressure is a measure of a substance's propensity to evaporate. Vapor pressure increases exponentially with an increase in temperature.

**Vertical separation distance:** the thickness of clean, biologically active soil that separates the source of contamination from a building basement, foundation, or slab

**Volatile:** is a tendency of a substance to vaporize or the speed at which it vaporizes. Volatility is indicated by a substance's vapor pressure. Substances with a higher vapor pressure will vaporize more readily at a given temperature than substances with a lower vapor pressure. A volatile organic compound is an organic compound which has a boiling point below that of water and which can easily vaporize or volatilize.

**Volatile organic compound (VOC):** organic compound that at room temperature and normal atmospheric pressure produces vapors that escape easily from volatile liquid chemicals. Volatile organic compounds include a variety of chemicals such as gasoline, benzene, toluene, xylene, formaldehyde, tetrachloroethylene, and perchloroethylene.

**Volatilization:** the process of transfer of a chemical from the aqueous or liquid phase to the gas phase. Solubility, molecular weight, and vapor pressure of the liquid and the nature of the gas-liquid interface affect the rate of volatilization.

**Water table:** the water surface in an unconfined aquifer at which the fluid pressure in the pore spaces is at atmospheric pressure

**Weathering:** the process during which a complex compound is reduced to its simpler component parts, transported via physical processes, or biodegraded over time

**Wilting point:** the minimal point of soil moisture the plant requires not to wilt. Wilting point values under field conditions are not constant for any given soil, but are determined by the integrated effects of plant, soil and atmospheric conditions.