Evaluating Vapor Intrusion Pathways

Guidance for ATSDR's Division of Community Health Investigations

October 31, 2016

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Acronym List

ATSDR	Agency for Toxic Substances and Disease Registry
BTEX	benzene, toluene, ethylbenzene, and xylene
CalEPA	California Environmental Protection Agency
CV	comparison value
DNAPL	dense non-aqueous phase layer
EPA	U.S. Environmental Protection Agency
HVAC	heating, ventilation, and air conditioning
ITRC	Interstate Technology and Regulatory Council
LEL	lower explosive limit
LNAPL	light non-aqueous phase layer
NAPL	non-aqueous phase layer
PAH	polycyclic aromatic hydrocarbons
PID	photo-ionization detection
PVI	petroleum vapor intrusion
SVOC	semi-volatile organic compound
TCE	Trichloroethylene
TPH	total petroleum hydrocarbon
VOCs	volatile organic compounds

Introduction

This document focuses on how the Agency for Toxic Substances and Disease Registry (ATSDR) health assessors can evaluate the public health implications of vapor intrusion.^{*} It is a technical supplement to the January 2005 ATSDR *Public Health Assessment Guidance Manual* [ATSDR 2005a].

The migration of vapor-forming[†] chemicals and gases from any subsurface source into indoor air is known as vapor intrusion. Figure 1 summarizes the vapor intrusion pathway. U.S. Environmental Protection Agency (EPA) toxicity data indicate that risks from inhaling some chemicals far outweigh the risks of exposure via ingestion [EPA 1996]. Chemicals contaminating groundwater and soil might also off-gas and migrate into the air of homes and commercial buildings. Volatile organic chemicals (VOCs) and other vapor-forming contaminants are commonly released into the environment from hazardous waste sites.

Since the 1980s, vapor intrusion has been the subject of increasing research and scientific discussion. EPA recently published updated and enhanced guidelines for assessing and mitigating vapor intrusion at contaminated sites subject to a federal statute [EPA 2015]. Many federal [DOD 2009; USN 2011a,b,c] and state health and environmental agencies have also issued guidelines and fact sheets for their respective programs. Most state guidelines appear to be consistent with the approach recommended by EPA. A list of state guidance documents is available from Envirogroup [Envirogroup 2016], and a compilation of information from the states is provided by the Association of State and Territorial Solid Waste Management Officials [ASTSWMO 2009]. Under the auspices of the Interstate Technology and Regulatory Council (ITRC), scientists and engineers from numerous state and federal agencies and environmental companies prepared a comprehensive vapor intrusion guidance document: *Vapor Intrusion: A Practical Guideline* [ITRC 2007]. It includes discussion on approaches to investigate and address vapor intrusion issues. Although written to assist regulatory agencies, ATSDR and its cooperative agreement programs (referred to as just ATSDR here-after) are encouraged to use these references.

Questions to consider

What are the potential health risks from the vapor intrusion pathway?

Vapor intrusion into indoor air can be of public health concern via the inhalation pathway [Burk 2013; Zarus 2015]. Exposure to some chemical vapors that migrate from groundwater through the soils and into a home can pose a greater risk than drinking those chemicals in tap water [Schuver 2007]. Intrusion of vapors from contaminated soil or groundwater into indoor air can cause fires, explosions, and acute, intermediate and chronic health effects. Asphyxiation is possible, but less likely. Many people also report that odors reduce their quality of life [ATSDR 2014a].

^{*} This document does not specifically address landfill gas, which is sometimes associated with contaminated groundwater. For a discussion of landfill gas, see EPA's *Guidance for Evaluating Landfill Gas Emissions from Closed or Abandoned Facilities* [EPA 2005b]. ATSDR's historical document, *Landfill Gas Primer: An Overview for Environmental Health Professionals*, may be consulted for general information [ATSDR 2001].

⁺ Vapor forming chemicals are not limited to volatiles as defined by analytical methods. Some semi-volatile and non-volatile chemicals are volatile and toxic enough to pose a vapor intrusion threat.

When should a vapor intrusion pathway be evaluated?

There are two basic criteria for determining if it is necessary to evaluate vapor intrusion:

- 1) vapor-forming contaminants must be present in the subsurface and
- 2) occupied buildings must be laterally and vertically close enough to the subsurface contaminant source to get into indoor air.

Future use of contaminated areas for occupied buildings should also be considered. The 2011 California Department of Toxic Substances Control Vapor Intrusion Guidance [CalEPA 2011] discusses these criteria in more detail.

Why is it so difficult to assess the public health hazard posed by the vapor intrusion pathway?

Vapor intrusion is a complex problem with multiple variables and often limited sampling measurements. Determining the environmental health hazards from indoor air contamination in homes and commercial buildings is often difficult because of the dynamic nature of air and the need to estimate how much of the contaminants people are inhaling over time [Holton 2013]. Various sampling methods may be used to represent time-averaged exposure concentrations over daily exposure periods or longer periods, such as days or weeks, to capture fluctuations [McAlary 2016]. Traditional sampling methods with which ATSDR has extensive experience include using evacuated stainless canisters during periods thought to best capture the greatest concentrations. ATSDR also considers the use of new sampling methods, such as passive sampling, on a case-by-case basis to complement traditional methods. Multiple lines of evidence are recommended to evaluate exposures on a site-specific basis.

Sample collection within buildings can be intrusive. Health assessors should be sensitive to the disruption and inconvenience vapor intrusion investigations can pose on building occupants and should strive to minimize the stress on occupants and others caused by evaluating and addressing vapor intrusion concerns. Vapor intrusion–specific community involvement techniques are outlined by EPA [EPA 2014a; 2015].

Indoor contaminant concentrations from vapor intrusion depend on site-specific and building-specific factors such as the soil type and moisture beneath and near the building, building construction, number and spacing of cracks and holes in the foundation, time of year, and the effect of heating and air conditioning systems on increasing or decreasing air flow from the subsurface. Changes to existing heating, ventilation, and air conditioning (HVAC) systems and building characteristics can significantly alter indoor radon levels [Steck 2009]. For buildings near surface water, rising water levels can affect vapor migration to indoor air. Demands of local industry, commercial, and municipal water suppliers also can affect groundwater trends that influence vapor intrusion. Only indoor air sampling incorporates all of the factors influencing vapor intrusion in a given building at any specific time.

Figure 1. Simplified schematic of vapor intrusion



Health assessors often need to distinguish between the contributions of vapor intrusion contaminants and those of indoor sources. Common indoor sources include household cleaning products, stored fuels, furniture, flooring, and dry-cleaned clothing. Outdoor air might also be a source of contaminants from motor vehicles, outdoor chemical use (e.g., pesticides), and nearby industry.

Indoor air is a dynamic medium. Contaminant concentrations can change significantly over the course of a single day as a result of indoor air exchange rates or the introduction of a temporary source of contaminants, such as furniture polish or paint.

What is the best approach for a public health evaluation of the vapor intrusion pathway?

Many experienced investigators believe that an approach using multiple lines of evidence is the best means of evaluating the vapor intrusion pathway [DOD 2009; EPA 2015; ITRC 2007]. Such an approach is used in the public evaluation steps described in this document. Many state and other technical guidance documents also describe various aspects of the multiple lines of evidence approach [Envirogroup 2016; Levy 2015].

ATSDR assessors should keep in mind that making timely recommendations to protect public health and empowering communities with information about their health are our primary goals. Relatively few lines of evidence might be needed to show significant potential for vapor intrusion to occur at levels of concern, prompting timely health protective recommendations and education. Conversely, more lines of evidence often are needed to confirm with reasonable certainty that there are no health concerns.

Chapter 7 of the EPA technical guide [EPA 2015] notes appropriate lines of evidence for evaluating the vapor intrusion pathway. These include, but are not limited to, the following:

- Subsurface sampling
- Vadose zone conditions (above the water table) and preferential pathways
- Building conditions
- Exposure concentrations
- Indoor and outdoor sources of vapor-forming chemicals
- Remediation and mitigation activities
- Maps and figures showing spatial and temporal characteristics

ATSDR developed a checklist of factors that may be considered in performing health assessments (Appendix A). The checklist's detailed topics fall under the broader lines of evidence listed above, but are covered in more detail in other guidance, such as EPA's *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air* [EPA 2015]. Factors covered on the checklist include the type of site; concentrations, nature, and extent of the contaminated media; factors affecting contaminant migration; data quality; and factors to consider in long-term stewardship of vapor intrusion sites. Use of this checklist is recommended to track information needed to complete the health assessment process outlined in this document.

Public health evaluation

The EPA technical guide for assessing and mitigating vapor intrusion [EPA 2015], the U.S. Department of Defense's *DoD Vapor Intrusion Handbook* [DOD 2009], the ITRC *Vapor Intrusion Pathway: A Practical Guideline* document [ITRC 2007], and most state guidance documents establish a multiple lines of evidence approach for environmental characterization of vapor intrusion. ATSDR developed a 12-step approach for public health evaluation of these types of sites. The major parts of this approach are pathway analysis, exposure evaluation, health evaluation, and conclusions and recommendations.

The multiple lines of evidence approach is recommended for the pathway analysis and exposure evaluation. Just as one soil sample from a contaminated site is not sufficient to fully evaluate the soil pathway, one round of vapor intrusion sampling is not sufficient to evaluate indoor air exposures.

Appendix B has information on temporal and spatial variability of vapor-forming contaminants in indoor air and subsurface media. To evaluate temporal variability for chronic exposure concerns, multiple samples should be collected over multiple seasons. For contaminants with potential health effects from short-term exposures (e.g., developmental), more rapid decision making is often appropriate. Location and sampling techniques can greatly affect the representativeness of subsurface sampling. A number of resources are available on sampling protocols and characterization of the vapor intrusion pathway [EPA 2015; Hers 2006; ITRC 2007].

Comparison values (CVs) are substance concentrations (environmental guidelines) set well below levels that are known or likely to result in adverse health effects. ATSDR and other government agencies have developed these values to help health assessors make consistent decisions about which concentrations associated with site exposures need further evaluation [ATSDR 2005a]. ATSDR recommends that public health assessors use air CVs to determine which sites need further evaluation for potential health effects from vapor intrusion. Health assessors should carefully evaluate how data were collected and how well those data might represent actual exposures.

ATSDR's air CVs and EPA's recommended screening attenuation factors [EPA 2015] may be used to derive subsurface screening levels for vapor intrusion. Table 1 shows EPA's recommended screening attenuation factors for external environmental media sample concentrations. The following equations can be used to calculate subsurface screening levels:

 $CVsg = CVair / \alpha_{sg}$

where CVsg = screening level in soil gas,

CVair = ATSDR's air CV, and

 α_{sg} = EPA's recommended screening soil gas attenuation factor from Table 1 (unless shallow soil sources or significant pathways exist [i.e., $\alpha_{sg} = 1$])

 $CVgw = CVair / (H' * \alpha_{gw})$

where CVgw = screening level in groundwater,

CVair = ATSDR's air CV,

H' = unitless Henry's Law constant [EPA 2016a], and

 α_{gw} = EPA's recommended screening groundwater attenuation factor from Table 1 (unless shallow groundwater sources or significant pathways exist [i.e., α_{gw} = 1])

Table 1	. EPA's recommended vapor	attenuation factors for risk-b	based screening of the vapor	[,] intrusion
pathway	y [<u>EPA 2015</u>]*			

Sampling medium	Medium-specific attenuation factor for residential buildings [†]
Groundwater, generic value, does not apply for shallow water tables	1E-03 (0.001)
(less than 5 feet below foundation) or presence of preferential vapor	
migration routes in vadose zone soils [‡]	
Subslab soil gas, generic value [§]	3E-02 (0.03)
"Near-source" exterior soil gas, generic value does not apply for	3E-02 (0.03)
sources in the vadose zone (less than 5 feet below foundation) or	
presence of routes for preferential vapor migration in vadose zone soils [¶]	
Crawl space air, generic value	1E-00 (1.0)

* Health assessors can learn more about vapor intrusion conceptual site models and the use of attenuation factors for screening by reading chapter 6 of EPA's technical guide on vapor intrusion [EPA 2015]. Multiple samples collected over multiple seasons with sufficient characterization of spatial variability is recommended before screening out sites. † If sources are within 5 feet of the foundation and significant openings to the building subsurface (sumps, unlined crawlspaces, earthen floors, or significant preferential pathways) are present, screen assuming no attenuation (i.e., assume soil gas and groundwater attenuation factor = 1) [EPA 2013a].

[‡] Section 6.4.5 of EPA's guide describes appropriate groundwater sampling strategies [EPA 2015].

- [§] Section 6.4.3 of EPA's guide describes appropriate subslab soil gas sampling strategies [EPA 2015].
- [¶] Section 6.4.4 of EPA's guide describes appropriate "near-source" exterior soil gas sampling strategies [EPA 2015].

The subsurface screening levels for vapor intrusion provide screening-level concentrations for groundwater and soil gas to assist with evaluating vapor intrusion. Concentrations greater than screening levels do not necessarily mean that people will become sick from exposures, but that further evaluation is necessary to evaluate the potential for health effects. The representativeness of the measured concentrations that are less than screening levels also needs to be evaluated before screening out sites on the basis of that data.[‡]

Appendix C lists chemicals that EPA considers (as of the date of this publication) to be sufficiently volatile and toxic to pose a health risk via vapor intrusion. Other vapor-forming chemicals may be considered on an individual basis.[§] Alternate subsurface screening levels for vapor intrusion may be sought in the absence of air CVs. EPA and several states have developed generic air and vapor intrusion screening levels for groundwater and soil gas [EPA 2016a; Envirogroup 2016].

The EPA recommends that health risk assessors not use the Occupational Safety and Health Administration workplace standards to evaluate the health risk from vapor intrusion in commercial/industrial settings [EPA 2015]. As ATSDR does not develop health guidelines for occupational exposure scenarios, the process for evaluating non-residential exposures is to compare time-adjusted concentrations of contaminants measured in indoor air samples with ATSDR's inhalation health guidelines (ATDSR MRLs and/or EPA RfCs).

ATSDR's inhalation health guidelines are based on continuous (i.e., 24 hour) exposure, typically used for residential exposure assessment. For the evaluation of less than 24-hour exposure (i.e. non-continuous, occupational exposure), the measured indoor air concentration must be modified to account for less than 24 hour exposure. For example, a concentration of $2 \mu g/m^3$ that is time-adjusted for a 10-hour workplace exposure would be modified by a factor of 0.41 (or 10 hours/24 hours) to calculate an air concentration of $0.82 \mu g/m^3$ to be compared with the health guideline for continuous exposure. The adjusted air can also be compared with study effect levels to further evaluate the potential for health impacts. Characterization of non-residential buildings should consider differences such as air exchange rates, HVAC systems, and building construction [EPA 2015; Lutes 2015a].

The U.S. Surgeon General issued a national health advisory urging Americans to prevent indoor radon [HHS 2005]. Radon that emits more than EPA's action level of 4 picoCuries of ionizing radiation per liter of air (pCi/L) is estimated to occur in one of every 15 homes. EPA's estimated cancer risk at 4 pCi/L is 1% for nonsmokers and 5% for smokers [ATSDR 2010]. Although radon is naturally occurring, ATSDR assessors are encouraged to make recommendations to measure radon and take action to protect public health whenever possible based on this national health advisory. Decreasing radon exposures at any level likely decreases cancer risk [WHO 2009], which can be important when considering the benefits of pre-emptive actions. EPA is generally not authorized to take response actions to prevent naturally occurring radon but encourages owners of susceptible buildings to do so. Vapor intrusion investigators may perform radon testing during some investigations to check for a completed vapor intrusion pathway.

[‡] The ability of the available data to represent spatial and temporal variability of contaminants is key.

[§] Other contaminants found in indoor air from vapor intrusion can include asphyxiating and flammable gases, mercury, tetraethyl lead, carbon dioxide, hydrogen sulfide, sulfur dioxide, semi-volatile organic compounds (SVOCs) such as polycyclic aromatic hydrocarbons (PAHs) and pesticides, and naturally occurring radon.

Vapor intrusion evaluation process outline

ATSDR health assessors should use the evaluation steps described in the following outline. More detailed information for these steps are provided after the outline.

Phase I. Pathway analysis

Consider the following questions.

1. Are there site-related vapor-forming chemicals reported or suspected?

Compare site contaminants of concern to the list in Appendix C. If the contaminant's ability to form vapors is uncertain, check resources such as ATSDR toxicological profiles and EPA's list of chemical specific parameters [EPA 2016b] for Henry's law constants to determine volatility.

2. Are there occupied buildings close enough laterally or vertically to vapor-forming subsurface contaminants to be a vapor intrusion concern? Preferential pathways (such as mining shafts, utility conduits, fractures, or karst features) might allow contaminants to travel unusually long distances to occupied buildings. Guidance varies, but 100 feet is commonly used for screening in the absence of preferential pathways, impermeable surfaces, and pressure-driven flow. The possibility of migration over greater or lesser distances should be considered on a site-specific basis (Figure 2).

Evaluate the distance between subsurface vapor-forming contaminant sources (e.g., contaminated groundwater and soil gas) and buildings. According to EPA [EPA 2015], and ITRC [ITRC 2007] guidance documents, buildings 100 feet or more (horizontally) from the edge of groundwater or soil gas with contaminant concentrations above applicable screening levels are less likely to be affected by vapor intrusion contaminants at levels of concern than closer buildings. A vertical distance of 100 feet between the bottom floor of a building and the top of a contaminated groundwater zone is also often considered an adequate buffer. State guidance on the recommended distance might also vary and should be consulted, when available.

Both distances assume no preferential pathways are present and other factors, such as fluctuations in groundwater levels, are minimal. If the vertical distance is very low or occasionally very low, as with shallow groundwater, and the homes above the plume appear to be affected, expanding the zone to include other buildings beyond 100 feet is appropriate.

In a community with shallow groundwater, for example, levels of subslab gas were found to be elevated at distances more than several hundred feet beyond the defined plume (Figure 2) [ATSDR 2013c]. This was discovered over a period of years after the homes immediately above the plume were being monitored. The concentrations of vapors in the basement air of these homes showed great variability over time and after rain. Subslab vapors also varied greatly, with little reliable relationship between the subslab and indoor measurements. On ATSDR and EPA recommendations, the responsible party took air samples at the neighboring houses beyond the plume footprint and discovered vapors at those locations. They then moved to the next neighboring homes. Because a few indoor air levels of vapors (including trichloroethylene [TCE] and perchloroethylene [PCE]) were occasionally above 200 μ g/m³ and subslab levels occasionally exceeded 90,000 μ g/m³, the decision was made to remediate a larger region beyond the plume and begin monitoring beyond that zone. No new pockets of vapors beyond 800 feet were discovered. Figure 2 depicts a snapshot in time. Earlier and later snapshots do not always include the repeat sampling of some homes. We suspect that the subsurface

included preferential pathways and the shallow groundwater was causing short-term pressure gradient or barrier effects.





* Trichloroethylene (TCE) indoor and subslab data in $\mu g/m^3$.

The distance that vapors migrate depends largely on site-specific factors, such as an impermeable surface cover and pressure-driven flow [CalEPA 2011]. Petroleum products can attenuate within shorter distances when aerobic conditions support biodegradation [EPA 2013b; NHDES 2006] (see Appendix E). Further discussion of

distance between source and buildings is available in the ITRC guidance [ITRC 2007] (see section 2.6, "Step 4: Are Buildings Located in Close Proximity to Volatile Chemicals in Soil, Soil Gas, or Groundwater?").

3. Are any of the following true?

- Reported concentrations of subsurface vapor-forming contaminants near the buildings are documented to be, or plausibly are, greater than ATSDR's medium-specific vapor intrusion subsurface screening levels.**
- Reported concentrations of vapor-forming indoor air contaminants within buildings are documented to be, or plausibly are, greater than ATSDR's indoor air CVs.
- Data are missing from lines of evidence needed to confidently evaluate the pathway.

Appendix D provides a sample template table for comparing data to ATSDR CVs.

If the answer to any of the first three questions is yes, continue the evaluation process with steps 4 through 12.

4. Search for evidence of any urgent public health hazards, such as fire and explosion hazards, potential exposures to free product (a petroleum hydrocarbon in the liquid free or non-aqueous phase), or acute health risks. Provide timely recommendations and health education as appropriate.

When reviewing information on the site, first check for any urgent public health hazards such as fire, explosive gases, oxygen depletion, or the presence of free product. Investigate short-term meteorological or other triggers for urgent events. For example, ATSDR declared an urgent public health hazard in Hartford, Illinois, when petroleum levels above the lower explosive limit (LEL) were detected in the subslab gas after a heavy rain [IDPH 2010]. If residents or building occupants report unexplainable (i.e., no known indoor sources such as fuel tanks or leaking fuel lines), persistent, or pervasive fuel odor within the home or building, local fire officials should be contacted to check for possible flammable or explosive conditions. Local fire officials also should be contacted to check oxygen levels in homes or buildings if occupants report having headaches or dizziness or problems such as pilot lights going out. These complaints might indicate that seeping carbon dioxide or other gases are replacing the oxygen in some portion of the building.

TCE is a frequently occurring chemical in indoor air as a result of vapor intrusion that can cause health concerns from low level exposures lasting several weeks to months at relatively low levels [ATSDR 2014b]. A fetus is most sensitive to exposure, especially during the first trimester of development [ATSDR 2014b]. For people in general, low-level exposures over a few months can cause immune system effects. Short-term exposures might need to be addressed quickly at sites that have TCE vapor intrusion because of its low effect level and the uncertainties in characterizing indoor air concentrations from vapor intrusion [Schuver 2014a]. Note that some states require immediate notification and action if threshold TCE levels are detected in indoor air [MADEP 2014]. The number of women of child-bearing age should be noted in demographics statistics for sites with TCE contamination.

ATSDR has acute air CVs for many vapor-forming chemicals. If acute environmental guidelines are not available from ATSDR, consider using guidelines from other sources [ATSDR 2005a]. This topic is also

^{**} Medium-specific vapor intrusion subsurface screening levels are calculated using attenuation factors from Table 1. Consider whether subsurface levels might **plausibly** exceed screening values due to inherent spatial and temporal variability (Appendix D).

discussed as "Step 1: Does the Site Represent an Acute Exposure Concern?" in section 2.3 of the ITRC guidance [ITRC 2007].

Urgent public health hazards might need to be addressed by working with regulatory/enforcement agencies to support actions such as the following to reducing exposures:

- Relocating all or sensitive persons [EPA 2002]
- Limiting time in basements or lower floors as much as possible
- Minimizing indoor cardiovascular activities

Other actions, such as the following, might be needed to reduce indoor concentrations from vapor intrusion:

- Adjusting outdoor air intake to increase air exchange rates or create positive pressure indoors [<u>ASHRAE</u> <u>2009</u>]; some HVAC systems have adjustable outdoor air intake dampers or injection fans [<u>ASHRAE 2009</u>; Wozniak and Lawless 2010]
- Creating cross ventilation on lower floors using fans and open windows; intermittent cross ventilation might decrease vapor accumulation indoors when climate control is needed during extremely hot or cold weather
- Sealing entry points around utility and foundation openings [ATSDR 2014c]
- Treating indoor air (e.g., activated carbon adsorption)
- Avoiding use of indoor exhaust fans, clothes dryers, fireplaces, or other pressure-lowering appliances
- Remediating basements wet from contaminated groundwater intrusion
- Installing and verifying effectiveness of mitigation systems, such as active depressurization [EPA 2015]
- Using alarms, such as radon or combustible gas detectors [<u>Schuver 2015a</u>] or real-time pressure sensors with mitigation systems [<u>Hers 2015a</u>] to trigger maintenance or exposure-prevention actions

The effectiveness of interim remedies should be monitored. They might be less effective than long-term mitigation approaches, such as installing subslab depressurization systems [ASHRAE 2009; ITRC 2007]. However, interim mitigation actions provide alternatives for addressing exposure until permanent cleanup or attenuation of vapor sources occurs. EPA provides detailed information on selecting and implementing short-term remedies in *Indoor Air Vapor Intrusion Mitigation Approaches* [EPA 2008b]. Fact sheets on vapor intrusion mitigation systems and soil vapor extraction and air sparging systems can be used or developed for community members [EPA 2012a, 2014b].

5. Use the vapor intrusion checklist (Appendix A) when conducting site visits or evaluations and begin developing and improving the conceptual site model.

Use the vapor intrusion checklist when conducting visits or evaluating sites that might have a vapor intrusion exposure pathway. The checklist is not an exhaustive list, but can be a helpful aid during site visits and a documentation tool. It organizes many of the potential preferential pathways and includes factors that can be used in assessing the vapor intrusion pathway.

The checklist is organized into unranked categories. Boxes on the left can be marked to show that a characteristic or information is relevant to the vapor intrusion pathway. References and attachments can be included to provide information that more fully characterizes the topics.

Develop and improve a conceptual model of the site and the pathway as you gather, review, and evaluate sitespecific information. A written description of the site conditions accompanied by maps, schematics, or figures showing locations and trends of contamination might be helpful.

Key components of conceptual site models include the following:

- known or suspected contaminant sources,
- contaminant migration pathways,
- potential human receptors, and
- the exposure routes by which these receptors might contact contaminants on a site-specific basis [ATSDR 2005a; NJDEP 2005].

Sometimes the source of the vapor-forming contaminants reported in private and monitoring groundwater wells is not known or multiple sources are suspected rather than a single source. Even without a specific source, a conceptual site model can be made that gives a picture of contaminant movement from groundwater or subsurface soil toward indoor air. EPA's document on conceptual model scenarios [EPA 2012b] illustrates idealized fate and transport conditions of actual vapor intrusion settings and scenarios.

Vertical and horizontal spatial information, such as maps, aerial photography, borehole logs, and regional or local stratigraphy, are very useful for creating a conceptual site model. For sites involving several buildings spread over more than a city block area, geographic information systems (GIS) provide useful analytical and visualization tools for conceptual site models and pathway analyses.

In developing the conceptual site model, pay particular attention to the lateral and vertical distances between sample locations at which contaminants are detected and the locations of occupied buildings and subsurface work areas (e.g., buried utilities with man-hole access). For example, determine the lateral and vertical distance from a monitoring well with reported concentrations of vapor-forming contaminants and the basement of a nearby residence. For additional information on conceptual site models, see sections 5.4 and 7.2 of the EPA technical guide [EPA 2015]. Basements or crawl spaces that occasionally flood and shallow ground water that is very close to the bottom floor of the buildings should be included in the conceptual models.

6. Evaluate environmental information, environmental concentrations, and detection limits of contaminants in nearby soil, groundwater, and soil gas, and potential background sources. Are the measurements sufficient to account for temporal and spatial variability and data trends (see Appendix D)? If yes, continue with the vapor intrusion evaluation. If no, formulate recommendations to further characterize the variability and continue with the next steps.

Evaluate the reported contaminant concentrations in groundwater, soil gas, subslab gas, crawl space air, and indoor air for each floor and the sampling locations. Usually only a few of the buildings overlying a vapor source are sampled for vapor intrusion, even though radon and chemical vapor intrusion is highly building specific. Carefully consider how the buildings sampled for vapor intrusion are likely to be representative of the reasonable maximum exposures among the buildings overlying the vapor source. Because a building's vapor entry and retention characteristics are not often visually obvious, it can be helpful to consider screening-level assessments of many of the buildings to identify those with evidence for being susceptible to soil gas intrusion and retention. (This can be accomplished by comparing indoor to outdoor air levels using low-cost tracers or indicators of soil gas intrusion, such as radon, which has its own health impacts and reasons for measuring).

Similarly, even with the increasingly common practice of sampling indoor air for 1 day per season for a year, these sample times only represent approximately 1% of the exposure in the year under study. However, temporal variability in vapor intrusion levels is well documented from radon and chemical vapor intrusion studies over periods of hours, days, weeks, months, years, and even decades [Steck 2014]. It might be helpful to consider more continuous observations, even if only indicators of the periods with higher levels of soil gas intrusion, so that the more expensive chemical sampling could possibly be scheduled during, or least compared with, periods with documented rates of higher soil gas intrusion.

As with all environmental health data, evaluate the applicability of the sampling and analytical methodology before using the results for further public health evaluation [ATSDR 2005a]. Some soil sampling techniques can be used to determine the general presence, composition and location of vapor-forming contaminants but are not recommended to quantify or indicate the absence of vapor-forming contaminants because of the potential for vapor loss [EPA 2015]. The EPA technical guide [EPA 2015], chapter 3 of the ITRC document [ITRC 2007], and chapters 2 (Investigation of the soil vapor intrusion pathway) and 3 (Data evaluation and recommendations for action) from the New York State Department of Health guidance document [NYDOH 2006] address many topics of special concern to sampling during vapor intrusion investigations, including the following:

• Variability — Various media should be sampled at appropriate times and locations to characterize spatial and temporal variability and data trends. The EPA database study of 913 buildings at 41 sites in 15 states shows that subslab gas and groundwater attenuation factors tend to vary by a factor of 10 to 1,000 within individual sites [EPA 2012d]. Significant daily, weekly, and seasonal variability has been documented in detailed studies [Johnston 2013].

Many factors can contribute to short-term (diurnal changes, HVAC operation, weather events) and longterm (seasonal, source migration, degradation) temporal variability in concentration [EPA 2015]. Regional climate is an important factor in HVAC performance; homes in some areas exchange outdoor air more frequently than others [Yamamoto 2010]. Barometric pressure drop and increased humidity can increase vapor intrusion [Johnston 2013; McHugh 2012]. Exposure times may be represented in samples, such as 24 hours for residents or 8 hours for workers, so that short-term variability will be less likely to skew the measurements. Longer collection periods of days, weeks, or months from passive samplers might provide useful concentration estimates for chronic exposures.

Recent studies demonstrate the use of passive samplers to collect time-averaged indoor air samples [McAlary 2015]. Careful design of sampling, analysis, and quality assurance/quality control measures is necessary to achieve high-quality data from passive samplers. Negative bias, which under-predicts exposures, was more common than positive bias in a study of different samplers [SERDP/ESTCP 2014]. Therefore, ATSDR requests inter-method duplicate sampling using more traditional EPA methods, such as stainless canisters and TO-15, when using these new techniques. EPA describes methods for implementing inter-method duplicate (confirmation) sampling and effective quality assurance/quality control measures in a recent Engineering Issue Paper [EPA 2014c]. The Navy and other EPA collaborators present supporting information on sample design, implementation, and research [NAVFAC 2015; Dawson 2016].

Sample collection during multiple seasons is recommended to characterize seasonal variability. Although winter is considered to be the worst season for vapor intrusion in the northern United States, higher vapor intrusion was seen in summer and in homes with air conditioning in the southern states [Hubbard 1996; Johnston 2013; McHugh 2012] and in summer for homes with crawl spaces [Johnston 2013]. Therefore, it is important to have samples from multiple seasons at sites, regardless of location. Year-to-year and decade-to-decade variation in vapor intrusion might occur because of factors such as changing weather patterns and occupant behaviors [Schuver 2015b; WHO 2009; Zhang 2007].

More than one subslab gas sample location might be needed to characterize large floor plans, separately poured slabs, or distinct indoor air zones. State guidances might have more specific requirements for duration, location, and number of samples. Alaska's guidance states that at least three soil gas samples should be collected per building [ADEC 2012]. EPA states that subslab gas samples should be collected near the center of building foundations to avoid areas most likely affected by exterior air infiltration. Nevertheless, soil gas measurements have been shown to be variable despite standardized sampling [EPA 2009b].

• **Background** - The presence of indoor air contaminants does not automatically mean the source is vapor intrusion [Hers 2001]. Background contributions can come from indoor or outdoor air sources [USN 2011a]. Commercial products can contain a range of vapor-forming contaminants [NIH 2016a]. Always evaluate the presence of other potential sources, including the contribution from background concentrations. Additional information about background sources can be found in the EPA's *Background Indoor Air Concentrations of Volatile Organic Compounds in North American Residences (1990–2005): A Compilation of Statistics for Assessing Vapor Intrusion* [EPA 2011].

Some indoor sources of vapor-forming contaminants include commercially dry cleaned clothing, interior buildings components (paint, carpets), consumer products (air fresheners, household cleaning products), and occupant activities (craft hobbies, home and auto repair activities). A building survey guide similar to the one included in appendix G in ITRC's 2007 guidance [ITRC 2007] and appendix C of the New Jersey Department of Environmental Protection's 2005 guidance [NJDEP 2005] can be used to identify potential sources of indoor air contaminants. Generally, building surveys are conducted before vapor intrusion sampling. Surveys provide an opportunity to explain the purpose and rudimentary mechanics of indoor air and subslab air sampling to homeowners and to check buildings for household solvents that could potentially hinder a vapor intrusion investigation. Indoor air results should be compared with ambient air and soil gas (particularly subslab) samples taken at the same building and time to evaluate the potential source(s) of indoor contamination. The following chart shows a variety of scenarios with the estimated levels of concern. The combination of greater concentration (orange) or less concentration (green) in given media or sample types can suggest a potential source and level of health concern (Figure 3). If possible, information should include more than a single point in time sampling.

Theoretically, in the absence of background contributions, the ratio of vapor intrusion contaminant in the subsurface and indoor air would be consistent within each building. If background sources are present, the EPA *Introduction to Indoor Air Quality* [EPA 2013c] and *Indoor Air Pollution: An Introduction for Health Professionals* [EPA 2012e] resources can be consulted for general information about indoor air pollutants and improving indoor air quality. EPA's technical guide [EPA 2015] discusses data evaluation and background concentrations in section 6.3.5. (Note: It is beyond the scope of this ATSDR guidance to comprehensively address the sampling protocols for evaluating background contributions.)

EPA recommends that site-specific values for background levels should be used when available [EPA 2015]. However, typical background values may be used by ATSDR health assessors when site data are limited or site conditions do not allow collection of representative background data.

Media or Sample Type		Relative concentrations within the Various Media								
Indoor Living Space	High	Low	High	Low	Low	Low	Low	Low		
Basement*	High	High	Does Not Matter	Low	Low	Low	Low	Low		
Crawl Space	High	High	Does Not Matter	Low	Low	Does Not Matter	High	High		
Sub-Slab	High	High	Low	Low	Low	High	None	None		
Adjacent Soil Vapor	Does Not Matter	Does Not Matter	Does Not Matter	Low	Does Not Matter	Does Not Matter	High	Low		
Groundwater	Does Not Matter	Does Not Matter	Low	Low	High	High	None	None		
Source Conclusion	Vapor Intrusion	Vapor Intrusion	Indoor or Outdoor Source	No/Low	No/Low	Potential	Potential	Indoor or Outdoor Source		
Health Conclusion	High Concern	Concern	Concern	Clearly OK	OK	Concern	Concern	Concern		

Figure 3. Vapor Intrusion Site Conceptual Model Paradigm (Note: High-quality data required)

* May be occupied or unoccupied

- Weather Local and regional meteorological data can be obtained from the National Oceanic and Atmospheric Administration's website http://www.ncdc.noaa.gov/cdo-web/. Contaminated groundwater that rises into the lower level of a building (i.e., groundwater intrusion) might off-gas directly to indoor air with no attenuation. Heavy sustained rainfall can result in a modest wash-out effect on soil gases, whereas a freshwater lens that forms at the top of groundwater source can lessen volatilization from a groundwater source over longer periods (years) [Shen 2012]. A Minnesota study showed more variation of radon levels indoors in homes exposed to wind [Steck 2009]. A study in Texas found that homes without air conditioners in operation had lower indoor concentrations [Johnston 2013]. Snow cover and frozen ground can form a surface barrier that affects the vapor intrusion pathway [Schumacher 2013].
- Sampling and analysis EPA-approved sampling and analytical methods should be used. Check for respective state guidance for specific requirements such as number and depth of samples. Samples might be needed to determine the direction of groundwater flow or vertical profiling of soil gas concentrations. Check EPA and other guidance specific to sampling equipment installation and use. These might include sample volume and flow rate, soil boring instructions, and equilibration times [EPA 2015]. Commonly used methods for measuring toxic organics are TO-15 (evacuated canisters) and TO-15 SIM (selection ion monitoring, which have lower reporting limits than TO-15 and TO-17 [sorbent tubes]), though other methods are available for different ranges of volatile contaminants [EPA 2015]. Other methods might be needed for targeting semi-volatile contaminants. Sulfur-containing compounds are very reactive and require specific analytical methods, like specially coated canisters that resist reactions and sulfur analysis with very short holding times [OSHA 2003; Restek 2010]. Make sure that the detection limits are sensitive enough to detect down to ATSDR air CVs, subsurface screening levels for vapor intrusion, or surrogate screening levels.
- Non-aqueous phase layers (NAPLs) A release of large volumes of petroleum or chlorinated vaporforming contaminants can form NAPLs. Detected groundwater contaminant concentrations can be compared with chemical-specific solubility limits in the vapor intrusion screening level calculator [EPA 2016a] to see if the proximate presence of NAPLs is indicated. Petroleum forms light NAPLs (LNAPLs), which float on the surface of aquifers, and chlorinated contaminants form dense NAPLs (DNAPLs), which tend to sink. Both forms of NAPL serve as a continuing source of groundwater contamination. Petroleum LNAPLs can off-gas methane and other vapor-forming contaminants in explosive or hazardous concentrations [EPA 2012c].

• Quality assurance/Quality control — A tracer might be needed to ensure soil gas samples are not being diluted by surface breakthrough. Assess field blanks, duplicate samples and other quality control criteria. The Minnesota Department of Health has useful guidance entitled "Indoor Air Sampling at VOC Contaminated Sites: Introduction, Methods, and Interpretation of Results" [MDH 2009].

7. Document any known building construction characteristics relating to basement floors, walls, sumps, drainage, ventilation systems, relative elevation to average grade, and other critical features.

Evaluate building construction characteristics, such as foundation type (e.g., basement, slab, crawl-space), foundation thickness and condition (e.g., cracks or other openings in basement floors and walls, blocked crawlspace vents), sumps, ventilation systems, drainage, utility lines, and dwelling elevation relative to average grade. Vapor intrusion can occur in any building type. The Wisconsin Department of Health guidance [WDHS 2003] indicates that the condition of the slab or vapor barrier in a building is the more important factor. Older homes can have more entry points and be less tightly sealed, making upkeep a likely determinant in vapor intrusion. Tightly sealed homes commonly found in cold climates can have low air exchange rates [DOE 2011]. Ventilation rates can vary widely in crawl spaces.

Tall buildings in cold climates can have a more pronounced stack effect in the heating season, especially if they have unimpeded vertical air flow, such as through stairwells. Elevator shafts can have a piston-like effect, drawing vapors into the building. Elevators or other preferential pathways could allow vapors to be transported into indoor space from podium foundations, such as buildings with first floor parking garages. Take note of attached garages or storage rooms that might affect indoor air readings. Also look for exhaust vents or adjoining walls to drycleaners or other commercial tenants in multi-tenant buildings. Note poorly ventilated and unventilated rooms. Combustion appliances and exhaust fans can affect pressure differentials.

Nearly all buildings have potential migration routes. Therefore, rather than excluding sites from verification sampling because vapor migration pathways are not known to exist, confirmatory sampling (or some other verification) is recommended. Wet basements might directly off-gas into indoor air with no attenuation. Appendix G of ITRC's guidance [ITRC 2007] contains a building checklist developed by the New York Department of Health.

8. Check for atypical preferential transport pathways from contaminated soil or groundwater toward occupied buildings (i.e., French or stormwater drains, shallow fracture flow zones, solution channels, or old leaky sewer lines).

Some pathways are not identifiable without knowing detailed information about the construction, landscaping, and alterations of buildings. Indoor air sampling and identifying migration pathways are the best ways to determine if preferential pathways might be affecting indoor air during site evaluations, post-mitigation and post-remediation. Indoor air sampling while depressurizing a building is being studied as a method for inducing vapor intrusion to detect completed pathways present at the time of sampling [Guo 2015]. Site records, interviews, or visual inspections might reveal natural or manmade preferential pathways from contaminated soil or groundwater toward occupied buildings. Drains, trenches, and buried utility vaults and corridors such as tunnels and pipelines can act as low resistance conduits for gas or groundwater movement in the unsaturated soil zone. Measuring indoor air is essential to evaluate migration pathways not accounted for by models [Kramer 1998].

A French drain about 6 feet below ground surface was confirmed as a preferential pathway by placing a shut-off valve in the drain adjacent to the home and measuring the difference in vapor intrusion with the valve on and off [Holton 2014]. Sewer lines can contribute substantially to lateral soil gas migration [Lutes 2015b; Riis 2010; WDNR 2013]. In addition to receiving direct discharges, sewers can be indirect receptacles of subsurface contamination via infiltration of NAPL, soil gas, or contaminated groundwater through cracks in piping manholes. For example, Vroblesky et al [2011] found that infiltration of contaminated groundwater into sewers and its transport through and from sewers caused complex and unanticipated patterns of groundwater contamination at a site in South Carolina.

Utility conduit can also serve as a route for vapor intrusion. In one case, sewer gas migration into a building's first floor was identified by sampling basement (low concentration) and first floor (high concentration) air, then sampling air from the sewer line inlet on the first floor [Pennell 2013]. Indoor air samples; vapor samples within utility conduits, such as sewer, plumbing, and drain pipes, manholes, and sumps; and soil gas samples from utility line backfill can help identify active preferential pathways [Wilson 2005]. In one case, a foundation wall was identified as a preferential pathway by depressurizing the wall to lower indoor air levels after failed use of a subslab depressurization system [McDonald 2015a]. Readily unforeseeable circumstances such as these show the importance of measuring indoor air and being cautious in the use of screening and modeling tools that rely on ideal assumptions.

Local geology can have underground pathways, such as fractured rock, desiccation cracks, porous soil, and buried stream channels, through which gases can migrate. Changes such as earthquakes, settling, and burrowing can create or change preferential pathways [Schuver 2014b]. The volume and length of preferential pathways will influence the amount of resistance to vapor flow into buildings. Groundwater level fluctuations from flooding or heavy rain can flush soil gases to the surface. Shallow water tables can rise into basements or crawlspaces where contaminants can freely volatilize into homes. During winter, frozen soils can block vaporforming contaminants from escaping through open ground surfaces, thereby increasing migration through unfrozen soil under buildings.

Phase II. Exposure evaluation

9. Are valid indoor air measurements available to estimate exposures? Modeling may be used as a supporting line of evidence. (Note: ATSDR does not currently use modeling alone to screen out sites or make health hazard conclusions, but strongly encourages the use of modeling in conjunction with measured data to strengthen confidence in conceptual site models.)

Are there an adequate number of valid indoor air measurements available to estimate exposures? Modeling may be used as a supporting line of evidence. (Note: ATSDR does not currently use modeling alone to screen out sites or make health hazard conclusions, but strongly encourages the use of modeling in conjunction with measured data.)

Indoor air sampling provides snap-shots of actual concentrations of chemicals to which an occupant might be exposed. Multiple lines of evidence should be used to support the use of measured indoor air data points as exposure concentrations. For example, if concentrations increase over time as a plume migrates further under a neighborhood, the increases and uncertainties in estimating them should be considered in long-term indoor air estimates. Total indoor air concentrations should be used (i.e., include non-release related chemical contributions). If only indoor air grab samples were obtained, follow-up sampling of a more representative

duration of exposure is advised. One sampling event is generally insufficient for reliable decision making, although single sampling events might be adequate to support health protective decisions such as preemptive mitigation. Indoor air monitoring that reflects seasonal variation usually provides a better basis for an exposure estimate. At a minimum, the California guidance recommends sampling during late summer/early fall and late winter/early spring. Recent studies show that more robust data collection might be appropriate.

Appendix B provides resources and discusses some of the complexities of considering variability in vapor intrusion that must be considered in evaluating data and estimating exposures. Page D-22 of the ITRC guide [ITRC 2007] also discusses indoor air sample locations and frequency. Periodic sampling done appropriately is more likely to accurately detect elevated vapor intrusion at sites where vapor intrusion exposures are continuously or frequently unacceptable; however, periodic sampling is less likely to detect sites with episodic but numerically unacceptable vapor intrusion [Schuver 2015b]. One study on episodic vapor intrusion found that among 723 days measured, 25 days (3.5%) accounted for more exposure than the other 698 days [Johnson 2013].

Indoor air data are often variable and inadequate for developing a reliable average concentration representative of reasonable maximum exposures [MADEP 2011]. The number of data points needed to calculate upper confidence limit exposures is determined using a data quality objective process [EPA 2016c]. This generally requires at least 10 samples [EPA 2013d], which might not be available or practical to obtain. Presenting a range of detected values and maximum detected concentrations collected under generally conservative weather conditions and HVAC operation is often the most practical approach to evaluating exposure concentrations. Vapor intrusion susceptibility is generally worse when

- residential HVACs are operating (causing negative indoor pressure relative to the subsurface) and
- commercial HVACs are not operating (causing less positive indoor pressure relative to the subsurface).

Indoor air samples collected with DOE-recommended thermostat settings of 68°F in winter and 78°F in summer are used to represent average exposure concentrations [DOE 2012]. More conservative settings might need to be used to induce reasonable maximum exposure conditions for vapor intrusion.

Multiple exposure assessments for different receptors, locations, and activity levels might be needed [ATSDR 2012]. Do not average concentrations across different locations of a site that do not represent a person's realistic exposures. Time-weighted averages developed for subdivided exposures in different areas might be warranted. For example, health assessors could assume 12 hours per day is spent in a basement bedroom and the remaining 12 hours per day is spent upstairs in a common living area [MADEP 2011].

Fate and transport modeling of vapor intrusion can be a useful line of evidence when supported by high-quality environmental measurements. However, ATSDR does not use modeling alone to predict indoor air concentrations and screen out sites or make health hazard conclusions. Vapor intrusion modeling with carefully selected inputs can provide useful theoretical information on the potential for vapor intrusion in the absence of robust indoor air measurements. Modeling is also an indicator of indoor air concentrations, independent of background sources and short-term fluctuations. Soil permeability and half-life for contaminant removal from soil were shown to be critical modeling parameters in one study [Ferguson 1995].

EPA does not currently endorse its former workbooks for modeling vapor intrusion using the Johnson and Ettinger algorithm [EPA 2013e]. The Johnson and Ettinger model has been found to under-predict vapor

intrusion at some well-characterized sites [Hers 2003]. Therefore, ATSDR only recommends Johnson and Ettinger modeling as a tool to complement robust indoor air and subsurface sampling results. EPA is working on a new version of the model with guidance to improve the reliability and applicability of modeling results.

Modeling parameters generally showing the most uncertainty and sensitivity include soil and capillary zone water-filled porosity, thickness of capillary zone, vapor flowrate into the building, soil vapor permeability, soil to building pressure differential, indoor air exchange rate, enclosed space height, and crack-to-total area ratio [EPA 2004]. Probabilistic and stochastic models are being developed to further investigate model uncertainty and sensitivity and might become more widely used to characterize site-specific variability in the future [Moradi 2015; Provoost 2014; Schreüder 2006; Weaver 2013].

Health conclusions from vapor intrusion exposures cannot be made with high certainty using modeling alone, given the inherently substantial site-specific variability that has been demonstrated to occur [EPA 2012d]. However, finding concurrence between sampling and modeling results strengthens confidence in an evaluation. If the modeling results do not concur with site measurements, the model parameters might need to be modified to the conceptual site model or further site evaluation might be warranted [Sanders 2006].

Modeling of vapor intrusion into future buildings, such as at brownfields sites [EPA 2008a], can be a useful planning tool. Modeling is useful to corroborate the conceptual site model and to study how exposures might shift with different assumptions [Hers 2002, 2003; Johnson 2005]. Three-dimensional models have been used to demonstrate the effect of site features, such as surface barriers, subsurface heterogeneities, and building conditions, on lateral and vertical soil gas migration [EPA 2012b; Pennell 2009]. However, three-dimensional models are not usually readily available to health assessors unless they are partnering with academic or other researchers to perform in-depth study of a site. Another useful approach to modeling is to perform bounding (i.e., estimating a range of predictions based on a range of feasible inputs) [Tillman 2007]. The value of the model results should be discussed and the uncertainties clarified when using the data [ATSDR 2004a; EPA 2005a]. Modeling that lacks robust indoor air measurements might be used to show that sampling is urgently needed.

10. If valid indoor air measurements are not available, explain the limitations of the data and request further site-specific information and measurements. Note that some sites might be candidates for pre-emptive mitigation before site characterization is completed (see section 7.8 of <u>EPA 2015)</u>.

Ask for more information if valid indoor air measurements are not available or there is low confidence in the indoor air measurements. When requesting additional information, consider the type, quantity, and quality of environmental measurements needed to determine an exposure concentration. For example, if only one sampling event occurred, additional sampling should be conducted to adequately characterize seasonal variability. ATSDR prefers concurrently collected indoor air, ambient air, and subsurface air (subslab or crawlspace) data. Consider the feasibility and intrusiveness of sampling. Follow-up sampling is recommended if detection limits are greater than air CVs or subsurface screening levels. Supplemental measurements might also be warranted if previous sampling was performed during or after heavy precipitation or unusual meteorological events [ITRC 2007]. Essentially, any data gaps that reduce confidence in estimating the indoor air exposure concentration beyond what is reasonable for making health-based decisions should be addressed.

Because of the variability of the vapor intrusion pathway and the need for multiple sampling events, sites are sometimes identified as having a reasonable potential for concern from vapor intrusion before the pathway has been completely characterized. EPA's database work indicates that subslab gas concentrations above 1,000 times $(1,000\times)$ target indoor air concentrations will likely lead to indoor air concentrations greater than air comparison values for 75% of sites^{††} and that more work is needed to evaluate exposures. In such cases, actions to address the problem might be warranted before the characterization is complete. Actions might include short-term approaches or pre-emptive mitigation, depending on the nature of the concern.

Phase III. Public health implications

11. If a valid exposure concentration can be estimated from information discussed in Phase II, proceed to evaluate the public health implications as described in the ATSDR Public Health Assessment Guidance Manual [<u>ATSDR 2005a</u>]. If a valid exposure concentration cannot be estimated, state this in the conclusions and recommend following up. If preemptive mitigation is being considered, some discussion of public health implications may be warranted, even if only using preliminary data, while stating the limitations of the analysis.

The potential public health effects from breathing air contaminants are assessed by comparing air concentrations to the ATSDR air CVs or surrogates, if ATSDR CVs are not available. If people are breathing levels greater than the CVs, then a more detailed assessment is performed using ATSDR's toxicological profiles [ATSDR 2016] and other suitable scientific studies, as described in the ATSDR *Public Health Assessment Guidance Manual* [ATSDR 2005a]. As with other media, this assessment requires further review of the key toxicological studies, whether the conditions of those studies apply to the site exposures, and whether sensitive individuals should be evaluated separately. Non-residential exposures might need to be estimated by adjusting for exposure less than 24 hours per day and 7 days a week. For example, the measured air level at a commercial site could be multiplied by 5/7 days per week and 8/24 hours per day:

Exposure concentration = Measured concentration $\times \frac{5}{7} \times \frac{8}{24}$

Excess lifetime cancer risk might need to be calculated using standard risk assessment methods and agedependent adjustment factors for some chemicals [EPA 2009a]. Respiration rate might be elevated in some situations, resulting in greater-than-normal inhalation exposures, and might require help from a toxicologist to evaluate. Combinations of chlorinated vapor-forming contaminants and petroleum hydrocarbons are common at vapor intrusion sites and might require a chemical mixtures assessment [ATSDR 2013a].

Phase IV. Public health conclusions, recommendations, and public health action plan

12. Follow guidance in the ATSDR Public Health Assessment Guidance Manual [<u>ATSDR 2005a</u>] to provide conclusions and recommendations.

Follow instructions in the ATSDR Public Health Assessment Guidance Manual and other appropriate federal, state, and stakeholder guidance to provide public health conclusions, recommendations, and a public health action plan.

⁺⁺ The 25th percentile of subslab gas attenuation factors at residences was 0.0015 for 377 measurements from basement homes and 0.00087 for 20 measurements from slab-on-grade homes (<u>EPA 2012d</u>).

Short-term hazardous inhalation exposures might warrant recommendations to implement engineering controls and monitoring or to relocate sensitive persons, depending on the immediacy of the potential risks (Step 4). Adjusting ventilation, sealing entry points, or treating air are exposure-reducing engineering controls that can be implemented rapidly [ITRC 2007; ATSDR 2014c]. The performance of engineering controls depends on site-specific situations; timely follow-up monitoring is recommended to demonstrate efficacy [McDonald 2015b].

Chronic inhalation exposures of health concern may be addressed by performing source remediation or installing vapor intrusion mitigation systems [EPA 2008b]. Vapor intrusion mitigation fact sheets for current [USN 2011b] and future [USN 2011c] buildings are outlined by the Navy. In one radon study, 81 homes reported 247 changes to the HVAC system, the structure, or occupants over 2 decades of monitoring [Steck 2009]. This shows the need for periodic monitoring of all vapor intrusion sites with a hazardous subsurface vapor source until the source has been remediated or attenuated.

Health assessors might also recommend various other actions to protect public health at vapor intrusion sites, such as the following:

- Conduct additional monitoring to
 - further characterize spatial or temporal variability during different seasonal or meteorological conditions,
 - show the effectiveness of engineering controls [McDonald 2015b], and
 - evaluate potential changes following renovation, landscaping, or natural changes to the site, such as earthquake or water level changes.
- Continue monitoring until the source is determined not to pose a public health hazard.
- Include degradation products or common mixture components in sample analyses.

ATSDR may also work with remedial project managers and building occupants to emphasize health protective messages, such as how to

- observe instructions in vapor intrusion mitigation system operation and maintenance plans (i.e., do not unplug fans or otherwise interfere with equipment operation);
- interpret and respond to warning devices and indicators, such as pressure gauges, carbon monoxide monitors, and combustible gas meters;
- observe exposure controls, such as signs limiting access to non-ventilated areas; and
- evaluate and minimize increased cancer risks from radon in indoor air.

ATSDR may support options being explored for institutional controls by recommending input to zoning committees, regulatory agencies, and commercial or private property owners. Institutional controls can be recorded in EPA (e.g., memorandums of understanding [MOUs] or administrative orders on consent [AOCs]) or government documents (e.g., land zoning or building permits). Examples of institutional controls at vapor intrusion sites include:

- restricting land use (e.g., prohibit housing, schools, or day-care centers)
- requiring vapor intrusion mitigation system operation and maintenance and securing access for future monitoring
- requiring vapor intrusion mitigation systems or specialized HVACs in building permits

Recommendations to implement institutional controls might have a higher chance of success if health assessors engage the responsible entity to evaluate willingness to adopt controls and options for enforcement.

Contact the ATSDR, Division of Community Health Investigations, Office of the Associate Director of Science, and subject matter experts for assistance with and training on vapor intrusion assessments.

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Appendix A. Vapor Intrusion Health Assessment Checklist*

Date: / /

This checklist can help you track and assess the lines of evidence to support or refute a complete vapor intrusion pathway and future considerations in ATSDR assessments. Mark each box for which information is available. Circle specific factors that apply to the site. Include any notes and references by marked items or on attached pages. Health assessors often lack complete information; data limitations increase uncertainty and often necessitate more caution in conclusions and recommendations. Indoor air data and evidence to support the presence or absence of a vapor intrusion pathway are required to confidently characterize people's exposures. Sufficient information also must be included to assess variability over time and space.

1) Historical source type (include approximate release date next to source type)

- □ a. Dry cleaning/fabric laundering
- □ b. Wood processing/pulp and paper/creosote/resins
- □ c. Sanitary/industrial/construction landfill
- □ d. Metal working or degreasing/electronics/electroplating/engine maintenance
- e. Agriculture/fumigation
- f. Chemical manufacturing/transport/bulk storage (list main chemicals of concern)
- □ g. Refining/manufactured gas/oil production/pipelines/other petroleum (list petrochemicals)_____
- h. Other/unknown (list main chemicals of concern)______

2) Contaminated media on the property or nearby

- □ a. Odors reported in indoor air (*expedite assessment*)
- D. ALL SITES: Indoor air concentrations, dates; heating, ventilation, and air conditioning (HVAC) settings; weather
- C. Outdoor air vapors: concentrations, dates, locations ______
- d. Crawl space air/soil gas/soil: concentrations, dates, depths _____
- e. Groundwater: concentrations, dates, depths, and flow direction ______
- □ f. ALL SITES: Note whether groundwater use is potable/non-potable and radon zone[†]______

3) Nature and extent of contamination

- a. Describe source distribution in vadose (unsaturated) and phreatic (saturated) zones and capillary fringe______
- b. Describe aquifers affected, depths and lateral continuity (delineation wells below screening levels Y/N)_____
- c. Remediation complete or underway: soil excavated with clean sidewalls, soil vapor extraction, air sparging, pump and treat, skimming, in-situ chemical oxidation, other method______
- d. Temporal factors: contamination stable or trending, ongoing release, seasonal fluctuation_____
- e. Light non-aqueous phase layer (LNAPL)/dense non-aqueous phase layer (DNAPL): thickness or source volume____
- □ f. Above ground or underground storage tanks with or without product
- □ g. Surface water features (natural or manmade) present: rivers/ponds/drainage/dry wells
- □ h. Preferential pathways possibly connecting contamination to occupied buildings (provide maps with feature depths if possible): underground utilities/sewer/water/pipeline/lateral drains
- i. Vertical and horizontal distance between occupied buildings and concentrations greater than screening levels____
- j. Biodegradation evidence: vertical profiling oxygen, carbon dioxide, methane, degradation products; other factors

4) Pervious/permeable foundation

- a. No foundation or vapor barrier (describe floor characteristics)
- b. Crawl space (note number of open/closed vents, skirting, and condition of vapor barrier)_____
- c. Slab (note cracks or openings and slab thickness, if visible)
- □ d. Basement (note cracks or defects if visible)_____
- □ e. Floor drains/French drain/sump
- f. Wet basement

5) Conveyances to and into building

 $\hfill\square$ a. Public or private sewer; public or private water

[†] http://www.epa.gov/radon/zonemap.html.

^{*} Assumes the user is generally familiar with http://www.atsdr.cdc.gov/hac/PHAManual/, http://www.epa.gov/vaporintrusion, http://www.epa.gov/vaporintrusion</

- □ b. Unsealed electrical conduits or plumbing
- **c**. Infrequently used drains with water trap (example: a rarely used guest bathroom shower or sink drain)
- **d**. Pressure driven flow is enhanced (decomposing material, landfill, buried pressurized containers)
- e. Fractured bedrock/karst/heterogeneous fill (note kind, if known) _
- □ f. Tree roots/earthquakes/erosion/other factors that might compromise foundation
- g. Other preferential pathways observed or studied (such as by injecting tracer gas) _
- h. Nearby emissions (dry cleaners, commercial/industrial operations, heavy traffic, cigarette smoke)_____
- □ i. Evaluate other indoor air sources, such as building materials, commercial products
- j. Mitigation system (describe type and on/off status during visit/sampling)

6) Building and meteorological factors

- a. Number of floors and type of occupants on each _
- □ b. Location and type of HVAC features: central/window unit; fresh air intake; ventilated/unventilated areas
- □ c. Large ventilation features: bay doors/large open windows/large fans (such as in workshops)
- **d**. Diagnostic results: air exchange rate/pressures (indoor vs subsurface and outdoor pressures)
- e. Depressurizing features: elevator shaft/clothes dryer in basement/exhaust fans to outside/other____
- □ f. Climate: hottest month_____,__°F/coldest month_____,__°F/snowiest month ______,__inches/ground ice
- g. Precipitation: rainiest month______, ____ inches/driest month______, ____ inches/flooding potential
- h. Prevailing wind direction and speed (often seasonal)_
- □ i. Building shape, orientation, dimensions, and surrounding surface terrain (provide map, photo, or sketch)

7) Sub-surface influence (consulting a geologist might be helpful)

- a. Site soil descriptors: type/stratification/staining/odor/other_
- b. Measured site soil parameters: porosity/moisture/density/organic content/other_____
- c. Describe or map regional geology, lithology, and topography ____
- **d**. Hydraulic connectivity: groundwater influenced by contaminated surface water/tides/heavy run-off
- e. Note changes in seasonal groundwater depth and flow direction ____
- □ f. Impervious surface between building and source (seasonal ice or snow, concrete, paving, surface water)
- □ g. Large building footprint_

8) Data quality[‡]

- □ a. Indoor air and soil gas/crawl space samples collected appropriately
- b. Sufficient number of samples placed appropriately to assess spatial variability
- □ c. Multiple samples taken in multiple seasons to assess temporal variability. Do the data reflect reasonable maximum exposures (i.e., collected in the more extreme seasons)?
- d. Included hazardous degradation products (e.g., vinyl chloride for TCE, methane for gasoline with ethanol)
- e. Collected appropriate sample durations: 8 hours for worker/24 hours for resident/longer passive samples
- □ f. Assessed contribution from indoor sources: indoor products survey/chemical ratios/handheld data
- **G** g. Groundwater wells screened properly: groundwater surface for vapor intrusion/deep for DNAPL detection
- □ h. Samples were collected appropriately: stainless canisters were not at zero pressure on collection/soil gas assemblies were leak tested/no heavy rainfall occurred 2–3 days before sampling
- □ i. Detection limits were at or less than comparison values and screening levels
- □ j. Analytical methods showed good data quality by use of duplicate, split, repeat, reference, and spiked samples/measurements of percent recovery and bias/data flags used appropriately

9) Future considerations (until all media are below screening levels)

- a. Future periodic monitoring of indoor air to confirm long-term protection of health
- **b**. Monitoring trends and migration of contaminants in groundwater and soil gas
- **C** c. Initiate or continue operation and maintenance of mitigation systems and monitoring devices
- d. Periodic inspections of structural, landscaping, and other factors affecting the conceptual site model
- Le. Follow-up sampling if structural, landscaping, or other changes occur affecting conceptual model
- □ f. Educating occupants on visible gauges, alarms, and equipment and who to notify in case of malfunction
- **G** g. Supporting institutional controls: future use restriction/access for future monitoring/zoning

⁺ These items generally indicate data quality: precision, bias, accuracy, representativeness, comparability, completeness, and sensitivity

Appendix B. Information for Evaluating Variability

Changes in vapor intrusion over time (temporal variability) or differences in vapor intrusion at different locations (spatial variability) must be considered when estimating exposures to chemicals in air from vapor intrusion. Health assessors must take care not to eliminate health hazards based on false negative sample sets. False negatives are possible for the vapor intrusion pathway because there tends to be relatively few data points to characterize the temporal and spatial variability. Therefore, the data might not adequately reflect the range and average of overall exposures to building occupants over time and space. The discussion below summarizes studies attempting to quantify the variability that occurs in vapor intrusion and the factors that qualitatively affect the variability. This information may be used to assist in performing site-specific evaluations and to characterize the limitations of sparse data sets. Health assessors should always acknowledge that variability and uncertainty exist in evaluating the vapor intrusion pathway. A statistician can help in evaluating the level of confidence in a given sample set.

Temporal variability

Indoor air samples are typically collected over a 24-hour period to reflect a daily exposure for residents or an 8-hour period to reflect workday exposure for employees. However, day-to-day vapor intrusion can vary by a factor of 10 (10×), and measurements from season to season might vary by a factor of 100 (100×) [Schumacher 2013]. Another study showed a temporal variation of indoor air by a factor of a 1,000 (1,000×) [Holton 2013]. Radon studies have shown vapor intrusion changes from year to year, ranging from about 3% to 110% [Steck 2009]. Greater vapor intrusion in winter and spiky behavior lasting up to 2 days were observed at the Redfield and Colorado Department of Transportation Materials Testing Laboratory [CDOT-MIL] sites, both in Denver, Colorado [Kurtz 2013]. Time series analysis of radon studies showed that variation was strong on tens of days (i.e., a monthly or seasonal component), which would not be evident from short-term sampling [Steck 2014]. During the 17 years monitored, temperatures were cooler than average by more than a standard deviation in 3 years [Steck 2009]. Post-mitigation variability typically occurs by a factor of 10 (10×) [Kurtz 2013].

Meteorological factors such as wind, snow, ice, barometric pressure, and temperature difference between indoor and outdoor air can affect vapor intrusion over time [Lutes 2014]. Changes to heating, ventilation, and air conditioning (HVAC) systems and structural renovations, such as the addition of a porch, can dramatically change vapor intrusion rates [Steck 2014]. In one study, increased indoor radon levels in 158 houses in Iowa were associated with the use of central air conditioning, a basement clothes dryer, a sump, and different types of concrete foundation [Barros 2014]. Many of these types of factors are frequently altered in buildings, supporting a need for follow-up sampling every few years in buildings susceptible to subsurface vapor-forming chemicals. Temporal variability is of particular concern for chemicals that have small windows of susceptibility for health effects, such as the 3-week window of development associated with TCE exposure and cardiac malformations. Short-term spikes in vapor intrusion can occur when snow and high wind overwhelm subslab depressurization systems [Lutes 2014].

To gain a better understanding of variability over time, readers are strongly encouraged to review recent studies being conducted by the U.S. Environmental Protection Agency's (EPA's) Office of Research and Development that are exploring temporal variations on a daily basis over several years in residential study homes in Utah and Indiana [Holton 2013; Lutes 2014]. These studies show substantial dynamics of indoor air concentrations from vapor intrusion during different weather conditions, even with subslab depressurization systems [Johnson]

<u>2015</u>]. A lognormal distribution of indoor air concentrations is expected from vapor intrusion, for which limited sampling might underestimate the mean [Schuver 2015b]. Holton et al. [2013] used a statistical method to predict that a summer and winter sample will detect an exceedance of the screening level 54% of the time when the true mean in indoor air is twice the screening level. In contrast, quarterly sampling showed an 80% chance of detecting an exceedance of the screening level. So quarterly sampling decreases the chances of false negatives substantially compared with only collecting a summer and winter sample. The EPA studies are ongoing and will likely lead to improved sampling strategies for evaluating temporal variability, although they represent limited geographical areas and building configurations.

Spatial variability

Vapor-forming contaminant concentrations can vary substantially in different rooms, levels, and locations of buildings; in different areas under the slab or foundation of buildings (subslab gas); and within the subsurface (soil gas, dissolved in groundwater, and free product). EPA, the Agency for Toxic Substances and Disease Registry (ATSDR), and the Louisiana Department of Health and Hospitals found that short-term (less than 1 minute) concentrations of several chemicals varied by a factor of 1,000 depending on the location within a room or home sampled [ATSDR 2000]. Understanding the degree to which this variability occurs and how to evaluate the variability at sites is currently an active field of study and will likely improve and evolve over time.

Subsurface variability: Sites having heterogeneous hydrogeology might require many soil borings to characterize. Building locations near a source area might be more greatly affected than farther away, depending on soil type and groundwater direction (Figure B.1.). The Redfield site plume in Colorado (quarterly sampling of more than 400 homes for 6–12 years) migrated along a narrow alluvial channel that expanded from a dozen residences wide, contracted to one home wide, then expanded again [Kurtz 2013]. Vapor intrusion was detected in most homes over the plume except in one area with a bedrock high area [Kurtz 2013].

An investigation for the Chicago Heights Boulevard site in Missouri [<u>ATSDR 2013c</u>] found homes with vapor intrusion several hundred feet beyond the reported groundwater plume (Figure 2). This highlights the challenge of delineating groundwater plumes relative to the distance between sources and buildings susceptible to vapor intrusion. Identifying which homes are susceptible to vapor intrusion near plumes requires an understanding of complex geologies and the limitations of plume mapping. The use of generic or regional geology data can increase uncertainty and necessitate expanded lateral and vertical screening distances.

Subslab variability: Subslab gas concentrations can vary substantially beneath different areas of a slab. Spills from work performed within a structure can migrate in complex patterns by groundwater, free product, and soil gas flow in the subsurface, making them difficult to evaluate (Figure B.2.). Cracks, openings, or joints between slabs can create a path for convective flow and form a pressure gradient in that area beneath the foundation, increasing concentrations. Rooms in buildings containing gas stoves, fireplaces, oil or gas furnaces, and similar combustion appliances or active venting to the outdoors might draw in vapors from the subsurface increasing subslab concentrations in those areas. Subslab aggregate might be more compact under some portions of a building than others. Subslab footings or support beams can impede vapor connectivity between different subslab locations, whereas pipe chases and other utility conduits can create preferential pathways [ATSDR 2013b]. Subslab vapors might also migrate up through basement sidewalls.



Figure B.1. Example of soil gas variability [EPA 2009b]

Figure B.2. Example of heterogeneous subslab migration [EPA 2009b]



EPA collected three subslab gas samples to assess spatial variability in a number of residences and commercial buildings smaller than 1,500 square feet [EPA 2015]. Different zones of occupant usage, such as a garage versus a nursery room over different areas of the slab might influence subslab sampling strategies. High data density in surrounding buildings with similar construction and homogenous geology can be a useful line of evidence in evaluating exposures.

Indoor air spatial variability

Occupants of basements and the first floor of buildings generally experience the greatest air exposures from vapor intrusion within a given building [EPA 2015]. However, air exchange from room to room can vary considerably, as can air exchange rates with fresh outdoor air. Appliances such as bathroom and kitchen venting fans and dryers can draw vapors into those rooms. Some rooms, such as garages, storage areas, or basements, might have separate or no ventilation. The American Society of Heating, Refrigerating, and Air-Conditioning Engineers (ASHRAE) provides generic assumptions for calculating appropriate air exchange rates for commercial buildings [Trane 2002] and residential buildings [ASHRAE 2004]. Conceptual site models that show elevator shafts, plumbing lines that lack proper vapor traps, and infiltration from outdoor sources might account for upper floors of buildings with elevated indoor air concentrations relative to the lower floors. Portable sampling methods, such as those using the highly sensitive trace atmospheric gas analyzer (TAGA) or hand-held gas chromatography-mass spectrometry devices, can be used to track down vapor entry points and rooms with concentrations at or below background levels. The TAGA monitors down to 50 parts per trillion or lower for TCE, similar to lab-based analytical methods, in real time.

Statistical analysis

EPA-recommended methods for statistical analysis of contaminated groundwater systems [EPA 2009c] include ways to evaluate how well the samples represent the actual contamination. Evaluating whether samples change over time (trends) or not (stationarity) is important. Identifying outliers and the distribution of sample concentrations are key to determine the representativeness of samples. The potential for false positive and false negative conclusions affects the statistical power of the data analysis. Data analysis often depends on whether the analyst is attempting to demonstrate *proof of hazard* or *proof of safety*. One sample showing exposure to hazardous levels is generally enough to show proof of hazard. However, a statistically significant number of samples under all possible conditions is needed to prove safety. This makes describing uncertainties in trying to show proof of safety particularly important, especially in vapor intrusion studies where few data points are usually available.

In comparison with contaminated groundwater systems, the vapor intrusion pathway is more complex, with vadose zone, building, and meteorological factors affecting exposures. Air and soil gas data sets usually provide "snapshots" of contaminant levels, but often are not sufficient to determine all of the spatial distribution, preferential pathways, and changes that occur over time with high certainty. Yet health assessors must still evaluate the data available, evaluate the quality of the data for assessing health, and make conclusions and recommendations to protect public health.

Simple statistics, such as range, mean, and median, are often most helpful to show limited data set characteristics. EPA's ProUCL software is automated to evaluate data sets, perform decision making statistics, and provide useful parameters, such as upper confidence limits, percentiles, and standard deviations [EPA]

<u>2013d</u>]. Calculation of these parameters usually requires several dozen data points, though some distributions with as few as 10 data points can be analyzed. However, many vapor intrusion sites have under 10 data points for per population.

A summary of EPA's database of attenuation factors on residential sites demonstrates the data spread from 431 subslab gas attenuation factors from 12 sites, 106 exterior soil gas attenuation factors from 11 sites, and 774 groundwater attenuation factors from 24 sites (Figure B.3.). The dates of sample collection are always important to note for vapor intrusion samples. Appendix D provides a basic chart to summarize data, but additional information on sample locations, conditions, type, detection limits, and total number of samples are very helpful. Recording as much information as possible with the data, perhaps in footnotes, helps the reader interpret how representative the samples are and how to use the data in a health assessment. Explaining potential uncertainties and variability in evaluating exposures from vapor intrusion are extremely important in health assessments and consultations and should be included in all document summaries evaluating vapor intrusion.

Figure B.3. Summary of the U.S. Environmental Protection Agency's vapor intrusion database of attenuation factors for chlorinated volatile organic chemicals and residences [EPA 2012d]



Appendix C. Chemicals for Vapor Intrusion Assessment

CAS #	Chemical Name	CAS #	Chemical Name
83-32-9	Acenaphthene (SVOC)	120-61-6	Dimethylterephthalate
75-07-0	Acetaldehyde	513-37-1	Dimethylvinylchloride
67-64-1	Acetone (VOC)	505-29-3	Dithiane, 1,4-
75-86-5	Acetone cyanohydrin	106-89-8	Epichlorohydrin
75-05-8	Acetonitrile	106-88-7	Epoxybutane, 1,2-
98-86-2	Acetophenone	759-94-4	EPTC
107-02-8	Acrolein	141-78-6	Ethyl acetate
107-13-1	Acrylonitrile	140-88-5	Ethyl acrylate
107-05-1	Allyl chloride	75-00-3	Ethyl chloride
120-12-7	Anthracene (SVOC)	60-29-7	Ethyl ether
11104-28-2	Aroclor 1221	97-63-2	Ethyl methacrylate
11141-16-5	Aroclor 1232	100-41-4	Ethylbenzene (VOC)
103-33-3	Azobenzene	75-21-8	Ethylene oxide
100-52-7	Benzaldehyde	151-56-4	Ethyleneimine
71-43-2	Benzene (VOC)	86-73-7	Fluorene (SVOC)
108-98-5	Benzenethiol	110-00-9	Furan
98-07-7	Benzotrichloride	822-06-0	Hexamethylene diisocyanate, 1,6-
100-44-7	Benzyl chloride	110-54-3	Hexane, N-
92-52-4	Biphenyl, 1,1'-	591-78-6	Hexanone, 2- (VOC)
108-60-1	Bis(2-chloro-1-methylethyl) ether	74-90-8	Hydrogen cyanide
111-44-4	Bis(2-chloroethyl)ether (SVOC)	NA (JP-7)	JP-7
542-88-1	Bis(chloromethyl)ether	7439-97-6	Mercury (elemental)
107-04-0	Bromo-2-chloroethane, 1-	126-98-7	Methacrylonitrile
108-86-1	Bromobenzene (VOC)	79-20-9	Methyl acetate
74-97-5	Bromochloromethane (VOC)	96-33-3	Methyl acrylate
75-27-4	Bromodichloromethane (VOC)	78-93-3	Methyl ethyl ketone (2-butanone) (VOC)
74-83-9	Bromomethane (VOC)	108-10-1	Methyl isobutyl ketone (4-methyl-2-
106-99-0	Butadiene, 1,3-		pentanone) (VOC)
104-51-8	Butylbenzene, n- (VOC)	624-83-9	Methyl isocyanate
135-98-8	Butylbenzene, sec-	80-62-6	Methyl methacrylate
98-06-6	Butylbenzene, tert-	25013-15-4	Methyl styrene (mixed isomers)
75-15-0	Carbon disulfide (VOC)	1634-04-4	Methyl tert-butyl ether (MTBE) (VOC)
56-23-5	Carbon tetrachloride (VOC)	75-09-2	Methylene chloride (VOC)
75-68-3	Chloro-1,1-difluoroethane, 1-	90-12-0	Methylnaphthalene, 1-
126-99-8	Chloro-1,3-butadiene, 2-	91-57-6	Methylnaphthalene, 2- (SVOC)
107-20-0	Chloroacetaldehyde, 2-	98-83-9	Methylstyrene, Alpha-
108-90-7	Chlorobenzene (VOC)	8012-95-1	Mineral oils
98-56-6	Chlorobenzotrifluoride, 4-	64/24-95-6	Naphtha, high flash aromatic (HFAN)
109-69-3	Chlorobutane, 1-	91-20-3	Naphthalene (SVOC)
/5-45-6	Chlorodifluoromethane	98-95-3	Nitrobenzene (SVOC)
07-00-3	Chloronorm (VOC)	75-52-5	Nitrometnane
107 20 2	Chloromethale (VOC)	/9-40-9	Nitropropane, 2-
107-50-2	Chloroparhthalana, Data (SVOC)	924-10-5	Nitroso-ul-in-butylamine, in-
91-38-7	Chlorophanol 2 (SVOC)	00-72-2	Nillololuelle, 0-
95-57-8	Chloropierin	111-64-2	Nonane, n-
70-00-2	Chlorotoluono o (VOC)	75 44 5	Phosenno
106-43-4	Chlorotoluene, $\mathbf{p}_{-}(\mathbf{VOC})$	123_38_6	Propionaldehyde
123-73-9	Crotonaldehyde trans-	103-65-1	Propyl henzene (VOC)
98-87-8	Cumene	115-07-1	Pronvlene
57-12-5	Cvanide (CN-)	75-56-9	Propylene oxide
460-19-5	Cvanogen	129-00-0	Pyrene (SVOC)
506-68-3	Cyanogen bromide	110-86-1	Pyridine
506-77-4	Cyanogen chloride	100-42-5	Styrene (VOC)
110-82-7	Cyclohexane	630-20-6	Tetrachloroethane, 1,1,1,2- (VOC)

132-64-9	Dibenzofuran (SVOC)	79-34-5	Tetrachloroethane, 1,1,2,2- (VOC)
96-12-8	Dibromo-3-chloropropane, 1,2- (VOC)	127-18-4	Tetrachloroethylene (VOC)
124-48-1	Dibromochloromethane (VOC)	811-97-2	Tetrafluoroethane, 1,1,1,2-
106-93-4	Dibromoethane, 1,2-	109-99-9	Tetrahydrofuran
74-95-3	Dibromomethane (methylene bromide)	463-56-9	Thiocyanate
	(VOC)	108-88-3	Toluene (VOC)
764-41-0	Dichloro-2-butene, 1,4-	76-13-1	Trichloro-1,2,2-trifluoroethane, 1,1,2-
1476-11-5	Dichloro-2-butene, cis-1,4-	87-61-6	Trichlorobenzene, 1,2,3-
110-57-6	Dichloro-2-butene, trans-1,4-	120-82-1	Trichlorobenzene, 1,2,4- (SVOC)
95-50-1	Dichlorobenzene, 1,2- (SVOC)	71-55-6	Trichloroethane, 1,1,1- (VOC)
106-46-7	Dichlorobenzene, 1,4- (SVOC)	79-00-5	Trichloroethane, 1,1,2- (VOC)
75-71-8	Dichlorodifluoromethane (VOC)	79-01-6	Trichloroethylene (VOC)
75-34-3	Dichloroethane, 1,1- (VOC)	75-69-4	Trichlorofluoromethane (VOC)
107-06-2	Dichloroethane, 1,2- (VOC)	598-77-6	Trichloropropane, 1,1,2-
75-35-4	Dichloroethylene, 1,1- (VOC)	96-18-4	Trichloropropane, 1,2,3- (VOC)
540-59-0	Dichloroethylene, 1,2- (mixed isomers)	96-19-5	Trichloropropene, 1,2,3-
	(VOC)	121-44-8	Triethylamine
156-59-2	Dichloroethylene, 1,2-cis- (VOC)	526-73-8	Trimethylbenzene, 1,2,3- (VOC)
156-60-5	Dichloroethylene, 1,2-trans- (VOC)	95-63-6	Trimethylbenzene, 1,2,4- (VOC)
78-87-5	Dichloropropane, 1,2- (VOC)	108-67-8	Trimethylbenzene, 1,3,5- (VOC)
142-28-9	Dichloropropane, 1,3- (VOC)	108-05-4	Vinyl acetate (VOC)
542-75-6	Dichloropropene, 1,3- (VOC)	593-60-2	Vinyl bromide
77-73-6	Dicyclopentadiene	75-01-4	Vinyl chloride (VOC)
75-37-6	Difluoroethane, 1,1-	108-38-3	Xylene, m- (VOC)
94-58-6	Dihydrosafrole	95-47-6	Xylene, o- (VOC)
108-20-3	Diisopropyl ether	106-42-3	Xylene, p- (VOC)
1445-75-6	Diisopropyl methylphosphonate	1330-20-7	Xylenes (VOC)
121-69-7	Dimethylaniline, N,N-		
Source: EPA	A 2016a. Vapor intrusion screening leve	el calculator.	·

	Groundwater				Soil gas		Indoor air			
Chemical	Maximum detected concentration [*]	Number of samples	Vapor intrusion comparison value	Maximum detected concentration [*]	Number of samples	Vapor intrusion comparison value	Maximum detected concentration [*]	Number of samples	Air comparison value	Background value †

Appendix D. Sample Template Table for Media-Specific Screening of Vapor Intrusion Data

* Include sample dates and data sources in footnote or within table.

[†] See the U.S. Environmental Protection Agency's Background indoor air concentrations of volatile organic compounds in North American residences (1990-2005): A compilation of statistics for assessing vapor intrusion (EPA 2011).

Appendix E. Special Considerations for Evaluating Petroleum Vapor Intrusion

Overview

This appendix discusses the physical, chemical, and other characteristics specific to health assessment of petroleum vapor intrusion (PVI) to provide tools for quantitative and qualitative evaluations as part of the multiple lines of evidence approach. The field of PVI research is still very active and will likely provide additional tools and approaches to site evaluations in the future. Evaluating the potential for an urgent public health hazard and completing a <u>checklist</u> are highly recommended as the first steps in developing a conceptual site model and evaluating PVI [ITRC 2014a].

Evaluate the potential for an urgent public health hazard from explosion

Vapor forming components of petroleum products (e.g., methane, propane, and butane) can pose an immediate physical hazard from risk of fire or explosion [Ma 2014; Wilson 2012]. Methane has a lower exposure limit (LEL) of 5% by volume [Cashdollar 2000]. If present at $\geq 10\%$ of its LEL, methane is a hazard and emergency responders or the fire department should be contacted [ATSDR 2001]. Groundwater containing 1–2 mg/L methane can generate LEL conditions [ITRC 2014b]. Methane generally diminishes to less than 5% of the LEL when the light non-aqueous phase layer (LNAPL) is below about 10 feet deep [EPA 2013b], but actual levels should be verified by sampling.

Photoionization detectors (PIDs) or other mobile or laboratory vapor analysis can be used to show PVI. Odors and physiological effects (respiratory irritation, headache, dizziness, nausea, vomiting, or confusion) might also indicate PVI. If characteristic petroleum odors are present, immediate action is recommended to investigate the source. One example of a prompt vapor intrusion investigation arising from odors took place in Wisconsin in 2005 [ATSDR 2005b].

Because detectors have limitations, petroleum vapors might be present even when not indicated by the device. For example, PIDs do not detect methane, and flame ionization detectors (FIDs) do not detect benzene. Nuisance odors below effect levels might warrant mitigation in some cases [ATSDR 2014a]. Free LNAPL product, usually visible as a sheen on the water, can also seep into wet basements and pose risks from direct contact and off-gassing.

Substantial methane generation might induce pressure-driven (advective) soil gas transport and thus increased vertical or lateral soil gas transport rate and distance [ATSDR 2001; EPA 2013b]. Methane can be formed by aerobic biodegradation of ethanol from biofuel or by anaerobic biodegradation of petroleum. Five of the 27 sites in the U.S. Environmental Protection Agency's (EPA's) PVI database had methane above the LEL in soil gas. Because three of those were from releases before the use of ethanol in gasoline, they likely resulted from anaerobic biodegradation [EPA 2013b]. Flammable gases such as propane, butane, and indene might be present from natural gas and manufactured gas plant sites [ITRC 2014a].

Preferential fluid flow (lateral and vertical) occurs through coarser layers such as gravel and sand and can be in directions that differ from groundwater flow. In one example, elevated PID readings were reported in buildings up to 500 meters down-gradient from a sudden tank failure release of 20,000 gallons of gasoline [McHugh 2010]. Carbon dioxide, a possible asphyxiant, is also generated from anaerobic biodegradation and can enhance pressure-driven bulk gas flow [ITRC 2014a]. High plume concentrations (e.g., LNAPL), high soil organic

content (e.g., peat), and large capped areas (e.g., large buildings or pavement) can create anaerobic conditions [<u>ITRC 2014a</u>]. Flammable indoor air levels can result from soil gases being flushed up by rising water tables after heavy rain or flooding [<u>ATSDR 2005c</u>].

Characterize fate and transport

Factors affecting the fate and transport of petroleum in the subsurface include source concentrations and size, surface cover and building size, soil layer properties, and soil oxygen demand [EPA 2013b]. Characterizing the source zone includes defining the vertical and lateral extent of the following:

- Free product in soil
- Residual soil contamination
- Soil gas contamination
- LNAPL
- Dissolved groundwater contamination

It also includes defining

- mobility and variability of the different phases of contamination and assessment of uncertainties;
- chemical composition, physico-chemical properties, and weathering/biodegradation; and
- preferential pathways.

Lateral delineation is usually performed over tens of feet, resulting in greater uncertainty, whereas vertical delineation is often to within a few feet [ITRC 2014a]. EPA provides guidance on methods to characterize changing groundwater flow patterns and irregular migration in heterogeneous media [EPA 2012f]. EPA also describes methods for spatially estimating plume boundaries from peripheral clean and contaminated points [EPA 2012f]. Biodegradation, weathering, and complexities of petrochemical sites make characterizing the source zone challenging. Factors to consider that will help conceptualize and assess the source zone are discussed below.

Assess for the presence and extent of NAPL

LNAPLs can generate considerable anaerobic zones, migrate laterally at a different rate than groundwater, and leave residual LNAPL in the vadose zone after groundwater fluctuations. LNAPLs are likely present when chemicals are at 20% or more of their solubility limits in groundwater [Bruce 1991] or when LNAPL is directly observed from well water [ITRC 2014a]. LNAPL is often present within 20 feet of leaking underground storage tank or fuel dispenser areas and below large petroleum industrial sites [EPA 2013b]. Coal tars and creosotes can form dense non-aqueous phase layers (DNAPLs) and continually release naphthalene and smaller amounts of benzene, toluene, ethylbenzene, and xylene (BTEX) into groundwater and soil gas [ITRC 2014a; Misquitta 2004]. Direct indicators identified 80% of LNAPLs [EPA 2013b]. Direct LNAPL indicators [EPA 2013b; ITRC 2014a] include the following:

• Groundwater sheen or soil stains near water table

- Groundwater benzene concentrations greater than about $1-5 \text{ mg/L}^*$
- Groundwater total petroleum hydrocarbon (TPH) greater than about 30 mg/L
- Soil benzene concentrations greater than about 10 mg/kg
- Soil TPH greater than about 250 mg/kg
- Soil gasoline range organics greater than 100–200 mg/kg and diesel range organics greater than 10–50 mg/kg
- Visual identification in soil using fluorescent techniques (i.e., ultraviolet (UV), laser induced fluorescence (LIF), or ultraviolet induced fluorescence (UVIF))[†]
- PID readings greater than about 500 ppmV
- Anaerobic zone identified using vertical soil gas profiling (hexane greater than 100,000 μ g/m³, oxygen less than 2%, methane above detection limit)

These indicators will identify most of the risk hazards, but they are not absolute predictors of LNAPL contamination. The predominant focus on benzene might rule out spills where benzene has degraded or decreased by weathering. Benzene is one of the most volatile and soluble petroleum contaminants and uniquely degrades compared with the remaining petroleum vapor-forming contaminants. Heterogeneous conditions might also affect LNAPL distribution.

LNAPL presence or thickness in wells is not always directly correlated with LNAPL in the subsurface and can depend on groundwater fluctuations and hydrogeology [ITRC 2009b]. In addition to being present in the area of release LNAPL can migrate laterally along perched aquifers or confining soil layers such as tills and clays or vertically through karst and fractured bedrock [CL:AIRE 2014]. LNAPL viscosity and interfacial tension can affect the movement into soil pore channels (saturation).

Bulk removal (excavation, skimming) of NAPL can decrease the footprint and duration of contamination. Soil vapor extraction enhances removal of more volatile contaminants and might change the overall composition of remaining LNAPLs [ITRC 2009a]. Dispersion modeling might be needed to evaluate inhalation hazards from venting of soil vapor extraction systems.

Evaluate the nature and extent of weathering

Weathering of NAPLs occurs by evaporation, dissolution (water-washing), and soil sorption of petroleum contaminants. Methods of evaluating weathering include measuring soil gas, groundwater, and LNAPL concentration profiles up/down gradient or vertically over time [EPA 2013b; ITRC 2009a]. Component movement out of the LNAPL phase and into soil gas and groundwater phases are largely determined by the physico-chemical properties of the components: vapor pressure, Henry's law constant (H), molecular weight (MW), and solubility (Table E.1) [ITRC 2011]. Density, viscosity, and organic carbon-water partition coefficient affect the movement and affinity of NAPL in soil.

Chemicals with unitless Henry's law constants less than 4.1×10^{-4} , molecular weights less than 200 grams/mole and vapor pressures less than 0.13 kilopascals are generally considered to be volatile. BTEX compounds are

^{*} Two sites with benzene up to 12 mg/L were classified in EPA's PVI database as groundwater sources without LNAPL. <u>Bruce et al.</u> found that LNAPL was likely present when individual components were present at 20% of the solubility limit or more (1991).

⁺ The aromatic components of petroleum mixtures produce fluorescent emissions when stimulated with ultraviolet light.

very volatile and soluble. So they will evaporate into the air and dissolve into the water. Once in the air or water, they migrate relatively quickly. As shown in the table, benzene is the most soluble and most volatile compound in BTEX: benzene is more than three times more soluble and volatile than toluene and about ten times more volatile and soluble than ethylbenzene and xylene. So based only on the physico-chemical properties, benzene will decrease the most from weathering. Chemicals with very high vapor pressures can migrate through highly porous soil layers or drainage or utility lines lined with gravel [ITRC 2014a].

"Lighter" petroleum products such as gasoline tend to have higher concentrations of BTEX and light aliphatics that undergo weathering [Lekmine 2014] by evaporation based on the partial pressure exerted by each component of the mixture [Lahvis 2013]. Weathering tends to enrich heavier aliphatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) in the LNAPL phase while decreasing the BTEX concentrations by evaporation and dissolution into the water phase [EPA 2013b]. PAHs from middle and heavy distillates generally have low solubility and high affinity for soil organic carbon, which decreases their mobility [ITRC 2014a].

Table E.1.	Physico-chemical	properties of commo	on petroleum hy	drocarbons (darker colo	rs indicate
greater val	lues)					

Cl	Vapor pressure (kPa)	Н'	Molecular weight (g/mol)	Solubility (mg/L)	Density (g/cm ³)	
В	enzene	12.7*	0.22*	78.11	1767*	$0.88^{\$}$
Т	oluene	3.79*	0.27*	106.2	547*	$0.86^{\$}$
m,j	p-xylene	1.15*	0.29*	106.2	172*	$0.86^{\$}$
0.	-xylene	0.88*	0.21*	106.2	172*	$0.88^{\$}$
Ethy	lbenzene	1.26*	0.32*	106.2	184*	$0.86^{\$}$
Nanhthalanas	Naphthalene	0.11*	0.018*	128.2	108*	$1.0^{\$}$
Inaphthalenes	2-methylnaphthalene	<u>0.00733</u> *	0.021 [¶]	142.2	36*	1.0 [§]
1,3,5-trin	nethylbenzene ²	0.32*	0.36 [¶]	120.2	48*	$0.86^{\$}$
1,2,4-trin	nethylbenzene ²	0.27*	0.25*	120.2	65*	$0.88^{\$}$
1,2,3-trin	nethylbenzene ²	0.19*	0.18*	120.2	69*	$0.89^{\$}$
	4-carbon aliphatic (nC4)	<u>243</u> *	39 [¶]	58.12	61*	0.57^{\P}
	5-carbon aliphatic (nC5)	68.3*	51 [¶]	72.15	38*	0.63 [§]
	6-carbon aliphatic (nC6)	20.2*	74 [¶]	86.18	10*	$0.66^{\$}$
Aliphatics	7-carbon aliphatic (nC7)	6.09*	74 [¶]	100.2	3.4*	0.68^{\P}
	8-carbon aliphatic (nC8)	1.72*	130 [¶]	114.2	0.7*	0.70^{\P}
	9-carbon aliphatic (nC9)	0.46*	140 [¶]	128.2	0.2*	0.72 [¶]
	10-carbon aliphatic (nC10)	0.12*	<u>210</u> ¶	142.3	<u>0.05</u> *	0.73 [¶]
Ethylene dibromide (EDB)		1.47 [‡]	0.029^{\ddagger}	<u>187.9</u>	4300 [‡]	<u>1.2</u> §
1,2-dichlor	8.10 [‡]	0.050 [‡]	98.97	8700 [‡]	<u>1.2</u> §	
E	Ethanol	7.9 [†]	0.00026^{\dagger}	46.07	<u>infinite</u> [†]	0.79^{\P}
Methyl tertiary	butyl ether (MTBE)	33*	0.024*	88.15	51,000*	$0.74^{\$}$

* <u>EPA 2016a</u>

† <u>ITRC 2011</u>

[‡] <u>EPA 2013b</u>

§ <u>EPA 2016d</u>

[¶] <u>NIH 2016b</u> (Henry's law constant, H (atm-m³/mol) converted to H' (unitless) by multiplying by 41)

Lead scavengers ethylene dibromide (EDB) and 1,2-dichloroethane (1,2-DCA) are highly soluble and can separate from the BTEX portion of groundwater plumes because of their higher densities [EPA 2013b]. EDB and 1,2-DCA also have stringent cancer-based risk criteria in air [EPA 2013b] and might require using EPA method TO-15 SIM to achieve sufficient detection limits [Rejzek 2015]. Methyl tertiary butyl ether (MTBE) and ethanol served as fuel oxygenates in gasoline. MTBE is a gasoline-specific additive that is sufficiently volatile and toxic to pose a vapor intrusion concern. It might be present in gasoline sourced before 2006 [EPA 2014d]. Ethanol has a fairly high vapor pressure, but does not tend to evaporate profusely from groundwater because of its high affinity for water (solubility).

Assess biodegradation

Petroleum biodegradation is the break-down of petroleum contaminants by aerobic (fastest) and anaerobic (slower) microbial activity in the subsurface over time. Petroleum biodegradation occurring in the near-surface zone of soil where oxygen is easily replenished is referred to as natural source zone depletion. Clean, biologically active soil with oxygen content greater than 2% [ITRC 2014a] and sufficient soil moisture are necessary for rapid aerobic biodegradation. Oxygen soil gas profiles show that the transition from aerobic to anaerobic zones typically occur over less than 2 feet (Figure E.1) [Davis 2009; ITRC 2014a]. Modeling predicts a transitional range of conditions where oxygen recharge is on par with oxygen consumption and attenuation is highly susceptible to small differences in source concentration and depth [Hers 2014; ITRC 2014a].

Vertical soil gas profiling of petroleum vapors is necessary to confirm aerobic biodegradation, but the data can be difficult to evaluate. A variety of site-specific conditions (discussed below) can inhibit the supply of oxygen and the reaction. ATSDR vapor intrusion and hydrogeology subject matter experts are available to help review and interpret these and other types of complex fate and transport data.

Oxygen recharge can be hindered by high soil moisture content, low soil permeability, large building foundations, paved surfaces, or ice or snow caps [EPA 2013b; ITRC 2014a; Lutes 2014]. Methane can consume vadose-zone oxygen and inhibit benzene and other petroleum biodegradation [Ma 2014]. Large diesel and gasoline sites have been found to exhibit high methane generation potential [EPA 2013b]. High petroleum source concentrations and high soil organic carbon content (greater than 4% by weight) can consume oxygen and contribute to the formation of anaerobic conditions [ITRC 2014a]. In one case study, vapor intrusion occurred from a 30-foot deep gasoline range organics (purgeable hydrocarbons) LNAPL. The silt/clay zone exhibited low permeability and high oxygen uptake likely caused by anaerobic conditions [Luo 2010]. Anaerobic biodegradation occurs at slower rates than aerobic biodegradation. Other factors that can slow biodegradation include low soil moisture content from arid environments, low nutrient content, low soil temperature, and the presence of heavy metals [ITRC 2014a].

Figure E.1. Conceptual model of aerobic biodegradation



Aerobic biodegradation first-order rate constant averages were from about 0.7 hours to 6 hours⁻¹ for BTEX, 3 hours⁻¹ for naphthalene, and 8–200 hours⁻¹ (fastest) for aliphatics [ITRC 2014a]. Benzene biodegrades slower than other BTEX compounds [Edwards 1992; Schreiber 2002]. Trimethylbenzene hydrocarbons were the slowest to biodegrade averaging around 0.3 hours⁻¹ [ITRC 2014a]. The range of rate constants for each chemical varied by factors of 10 to 100, so the actual biodegraded at slower or different rates than benzene. Biodegradation of MTBE, EDB, and 1,2-DCA can occur under favorable conditions, but BTEX might degrade more quickly [EPA 2013b]. The fuel component MTBE was measured in indoor air at a site where BTEX had biodegraded below detection limits [Sanders 2006].

A three-dimensional model estimates that benzene vapors from an unweathered source at 200 mg/L in groundwater takes 23 vertical feet to fully biodegrade [ITRC 2014a]. The Interstate Technology and Regulatory Council (ITRC) guidance on natural source zone depletion provides methods and examples for assessing biodegradation reaction rates over space and time [ITRC 2009a]. Biodegradation can also be enhanced by air

sparging. Air sparging can flush soil vapors into nearby buildings if the radius of influence of soil vapor extraction systems are not designed to capture pressure-driven air flow from injection wells.

EPA analyzed many underground storage tank sites without precluding characteristics. The analysis reveals 95% of those sites with LNAPL deeper than 13.5 feet and dissolved groundwater deeper than 5.4 feet will have biodegradation sufficient to attenuate benzene in subslab gas to less than 100 μ g/m³ [EPA 2013b]. Similar assumptions could not be made for fuel terminals, refineries and petrochemical industry releases from EPA's database [EPA 2013b]. Industrial sites were found to have releases with sufficient quantity to overwhelm the oxygen supply within the subsurface, limiting the biodegradation that can occur before soil gases reach surface structures. Defining the nature and extent of industrial release sites can also present more uncertainty because of the added complexities of those types of sites.

Many PVI site evaluations focus on subsurface characterization for possible screening out of sites. ATDSR recommends caution in assessing sites based solely on subsurface data because indoor air measurements are the only way to detect preferential pathways at some sites [Holton 2014, Pennell 2013].

Consider indicator compounds and petroleum mixtures

Petroleum sources generally exist as mixtures of aromatic and aliphatic compounds with additives included to improve performance or cost [ITRC 2014a]. Quantitative risk assessment information is available for noncancer effects from the low, medium, and high carbon fractions of aliphatic and aromatic components of TPH [EPA 2009d, 2014b,d]. TPH can present significant risk at diesel or middle distillate fuel sites in particular [Brewer 2013]. Middle distillates include diesel, kerosene, home heating fuel, jet fuel, and Stoddard solvent [ITRC 2014a] and tend to contain higher levels of PAHs and C5-C9 hydrocarbons, but lower levels of BTEX and less volatile (C8-C25) hydrocarbons [ITRC 2014a]. The World Health Organization (Table AI.9) has published toxic potency factors for evaluating health effects from PAH mixture exposures [WHO 1998]. The volatile fraction of PAHs (e.g., naphthalenes) are also included in EPA's vapor intrusion screening level calculator [EPA 2016a].

Many petroleum chemicals can be grouped by similar characteristics, such as BTEX, naphthalenes, trimethylbenzenes, PAHs, and TPH. ATSDR's webpage on hydrocarbons contains toxicity and exposure information on BTEX, fuel oils, gasoline, jet fuels, naphthalenes, n-hexane, PAHs, and TPH [<u>ATSDR 2008</u>]. ATSDR's interaction profile for BTEX indicates a common pathway of neurotoxicity and shows how to evaluate combined effects [<u>ATSDR 2004b</u>]. ATSDR reviewed health assessments of 121 vapor intrusion sites and found benzene was greater than the cancer screening value at all 28 sites at which it was detected, but was only declared a health hazard at two of those sites [<u>Burk 2013</u>]. N-hexane was detected in nine of the ATSDR sites but did not result in any health hazards.

Hydrogen sulfide and carbonyl sulfide are gases naturally present in petroleum products. They produce a rotten egg smell that is generally detectable below health-based screening levels but can cause irritation at low levels and more serious effects at high levels [ATSDR 2014d]. At high concentrations of hydrogen sulfide and carbonyl sulfide, a person might lose their ability to smell either gas. Chlorinated vapor-forming contaminants, such as chlorobenzene, are sometimes found with petroleum products [Udoetok 2008]. EDB and 1,2-DCA were added to leaded gasoline from the 1920s to the 1980s and are still used in aviation gas (avgas) and automobile racing fuel [EPA 2013b].

Use modeling appropriately

The Johnson and Ettinger model does not account for the rapid biodegradation of petroleum compounds. Models that do incorporate aerobic biodegradation, such as BioVapor, are available and might be useful for

- verifying conceptual site models,
- approximating bounding conditions,
- assisting in remedial design and selection, and
- attempting to predict future conditions where buildings might be constructed.

However, heterogeneous soil layers and nonuniform contamination sources can affect the representativeness of models [ITRC 2014a]. Information on oxygen supply, respiration rate, and demand are among the parameters needed for the BioVapor model. Qualitative sensitivities are provided in ITRC 2014a and Hers 2015b. Modeled attenuation factors for an idealized site with homogeneous sandy soil are provided in one reference for a range of biodegradation rates, source concentrations and depths [Abreu 2009]. PVIScreen is a probabilistic model that is expected to be available for the public soon [Weaver 2013].

Consider the type of site

Different types of petroleum sites tend to vary in the composition, total amount, fate, and transport of chemicals present [ITRC 2014a]. Some sources are more likely to have releases close to occupied buildings, such as home heating fuel oil tanks and dry cleaners [ITRC 2014a]. ITRC suggests increased concern for PVI from dissolved sources within 5 feet vertically of buildings, LNAPL within 15 feet of underground or above-ground storage tank (AST) sites, and LNAPL within 18 feet at industrial sites [ITRC 2014a]. Manufactured gas plants tend to have small release areas. Refineries, creosote, storage, and processing facilities tend to be much larger in scale and require more investigation into the source type, amount, and distribution [ITRC 2014a]. Sanborn Fire Insurance Maps showing historical site features are available from many historical document repositories or paid information services and can often provide location information for structures at facilities from the early 1900s.

Five industrial and three underground storage tank petroleum sites from the 74 sites reviewed in EPA's PVI database had confirmed or likely vapor intrusion [EPA 2013b]. Aerobic biodegradation interrupts the vapor intrusion pathway at many sites. Factors that contributed to PVI at these sites included large fuel releases and extensive LNAPL contamination. Two sites had PVI from sources approximately 25–30 feet deep, one resulting from a geological capping effect, the other from a sharp water table rise after heavy rain [EPA 2013b]. EPA's data sets from PVI sites other than underground storage tank sites are not as robust to make generalizations about contaminant zones and biodegradation.

Note preferential pathways

Although biodegradation can reduce PVI in many cases, preferential pathways could allow soil gas to bypass this pathway of attenuation and result in active vapor intrusion. Preferential pathways include fractured bedrock, karst terrain, gravel lenses, faults, utility conduits, sewer lines, and lateral drains connecting zones of contamination. Preferential pathways are difficult to identify and characterize for sites with complex hydrogeological formations and no utility or construction schematics [EPA 2013b]. Local government offices

might have maps of public utility corridors. Geological classification (sand, clay, till, limestone, etc.) is one indicator of heterogeneity in soil migratory pathways [CL:AIRE 2014].

Include uncertainties and limitations to PVI assessment

The potential health effects of sites lacking robust indoor air data sets can be difficult to determine with certainty. Additional lines of evidence are needed to gain insight into the potential for spatial and temporal variability. Characterizing uncertainties and limitations in PVI is highly site-specific and frequently incorporates a combination of qualitative and quantitative assessments. The complexity of sources, evaluation of biodegradation, and mixture effects are key elements of uncertainty and data limitations in PVI assessments.

The rate and occurrence of biodegradation present substantial uncertainty in PVI assessments. Even though biodegradation usually occurs at sites with clean biologically active aerobic soil, sufficient information might not be available to confirm this determination with high certainty.

The presence of complex mixtures that change composition and migratory properties complicate PVI investigations. Evaluating the potential for health effects from exposures to mixtures with imprecisely characterized and transient characteristics contributes to uncertainty.

Petroleum releases, fate, and transport can be challenging to characterize. Conceptual site models with high data point density defining the periphery of contamination, including clean monitoring points, are key to defining the lateral inclusion zone [EPA 2013b]. More robust data sets tend to more tightly define the areas of concern and decrease the area requiring further investigation. Whether plumes are stable, receding, expanding, or fluctuating vertically affects vapor intrusion over time. Preferential pathways and background sources are often only identified in studies with data density much greater than the few typical 24-hour samples collected at vapor intrusion sites. Groundwater benzene concentrations poorly correlate with soil gas data and are not recommended for screening out sites [EPA 2013b]. Limited soil gas data are available for lead scavengers EDB and 1,2-DCA [EPA 2013b]. Biodegradation assumptions might be inappropriate for petroleum sources with lead scavengers or containing more than 10% by volume of ethanol [ITRC 2014a].