

# Petroleum Hydrocarbons And Chlorinated Hydrocarbons Differ In Their Potential For Vapor Intrusion

## Contents

	Page
Background And Purpose	1
Introduction	2
Differences Under Common Subsurface Scenarios	2
Effect Of Biodegradation	3
Influence Of Density	4
Fate And Transport Processes For Vapor-Phase Contaminants	5
Biodegradation Of Petroleum Hydrocarbons In The Unsaturated Zone	6
Conditions With Greater Potential For Petroleum Vapor Intrusion	7
Considerations For Petroleum Site Investigation And Screening	10
Site Investigation Considerations	10
Site Screening Considerations	11
References	11

## Background And Purpose

In November 2002, the U.S. Environmental Protection Agency (EPA), Office of Solid Waste and Emergency Response issued draft vapor intrusion guidance (EPA, 2002), which specifically states that it is not recommended for Subtitle I underground storage tank (UST) sites. EPA's Office of Underground Storage Tanks (OUST) is thus currently developing guidance to address petroleum vapor intrusion (PVI) at UST sites. In September 2009, OUST assembled experts in the field of vapor intrusion and petroleum releases from EPA, state regulatory agencies, private consultants, and industry groups to provide technical and practitioner input for EPA to consider in developing the UST PVI guidance. This information paper<sup>1</sup> describes how petroleum compounds behave differently in the subsurface from other volatile chemicals, in particular chlorinated hydrocarbons (CHCs), and how these behaviors can be considered when evaluating the potential for vapor intrusion at sites contaminated by leaking Subtitle I USTs or other sources of petroleum hydrocarbons (PHCs).<sup>2</sup>

PHCs typically degrade biologically in groundwater as well as in unsaturated soil zones. In many cases, this aerobic<sup>3</sup> biodegradation is substantial and can limit the potential for PVI. In contrast, biodegradation of CHCs is anaerobic (under anoxic conditions), which is generally slower than aerobic biodegradation of PHCs. This limited biodegradability is to some degree responsible for the greater observed prevalence of chlorinated solvent vapor intrusion (CVI) when compared with PVI.

During the 1980s and 1990s, a better understanding of PHC biodegradation in groundwater led to the development of monitored natural attenuation, a remediation approach that involves no external inputs and has now been used successfully to address groundwater contamination at many leaking UST sites (Wilson et al., 1986; Bedient et al., 1994). Based on a review of current literature (e.g., Sanders and Hers, 2006; Davis et al., 2009; McHugh et al., 2010), EPA recognizes that analogous aerobic biodegradation processes are active in the unsaturated zone and that these processes can limit the potential for PVI.

<sup>1</sup> This information paper is intended to communicate the overall concepts of petroleum vapor intrusion. It is not intended to be interpreted as either a technical guidance document or statement of regulatory policy.

<sup>2</sup> Petroleum hydrocarbons are chemical compounds made up of hydrogen and carbon that are constituents of petroleum and various refined products of petroleum, including automotive gasoline, diesel fuel, lubricating oils, and the like.

<sup>3</sup> Aerobic means that the process requires oxygen. In contrast, anaerobic means the process does not require oxygen. Anoxic refers to the absence of oxygen.

## Introduction

This paper discusses the impact on the inhalation exposure pathway from vapor intrusion (VI) of volatile organic chemicals (VOCs).<sup>4</sup> VI occurs when vapor-phase contaminants migrate from subsurface sources into buildings. The primary concerns regarding VI are immediate threats to safety (e.g., explosive concentrations of petroleum vapors or methane) and possible adverse health effects from inhalation exposure to toxic chemicals. This paper focuses primarily on the latter concern, although the reader should recognize that in high enough concentrations, petroleum compounds and methane (a biodegradation product) can collect in buildings, leading to imminent explosive hazards. The information in this paper focuses on small-scale Subtitle I UST sites as opposed to sites with large sources (e.g., refineries and tank farms); however, you can use this information to inform decisions at non-Subtitle I petroleum releases. In addition, this paper does not address sites with comingled plumes such as mixed chlorinated and petroleum hydrocarbon contamination.

There are two classes of VOCs that together account for a large number of soil and groundwater contamination sites in the United States:

- **Petroleum hydrocarbons** (PHCs) such as gasoline, diesel, and jet fuel
- **Chlorinated solvents** such as the dry cleaning chemical tetrachloroethylene (perchloroethylene, or PCE) and the degreasing solvents trichloroethylene (TCE), 1,1,1-trichloroethane (TCA), and PCE

This information paper discusses and compares petroleum vapor intrusion (PVI) and chlorinated solvent vapor intrusion (CVI) with respect to processes that influence whether and how vapors can migrate through vadose zone materials into buildings and other confined spaces as well as some implications for addressing PVI.

The foremost difference between PHC and chlorinated hydrocarbon (CHC) vapors in the subsurface is that PHCs biodegrade readily under aerobic (oxygenated) environmental conditions, whereas CHCs typically biodegrade much more slowly and under anaerobic conditions (Howard, 1991). Because PHC biodegradation is relatively rapid when oxygen is present, aerobic biodegradation can typically limit the concentration and subsurface migration of petroleum vapors in unsaturated soils. In addition, CHC biodegradation can produce toxic degradation products, such as dichloroethylene and vinyl chloride, while petroleum degradation usually produces carbon dioxide, water, and sometimes methane or other simple hydrocarbons. A second primary difference is density: PHC liquids (e.g., gasoline, diesel fuel) are lighter (less dense) than water and when released from a leaking UST, can float on the groundwater surface (water table), whereas chlorinated solvents (e.g., TCE, PCE) are heavier than water and sink through the groundwater column to the bottom of the aquifer. These key differences (biodegradability and density) lead to very different subsurface behavior that often reduce the potential for human exposure.

## Differences Under Common Subsurface Scenarios

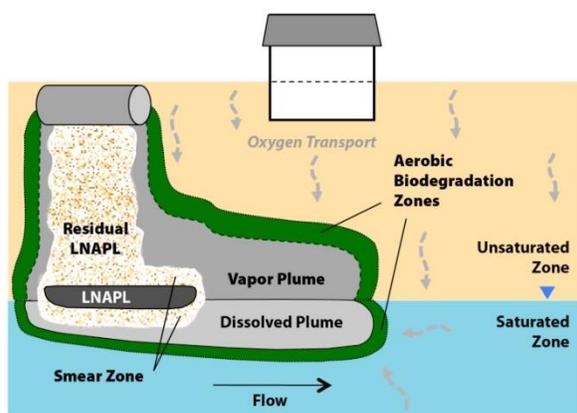
Figures 1 and 2 illustrate differences in subsurface transport behavior for PHC and CHC chemicals under commonly observed subsurface conditions. The conceptual scenarios in these figures are simplified and do not represent the complexity of actual subsurface environments, such as variations in contaminant distribution due to subsurface heterogeneities. Rather, they are intended to illustrate and contrast several

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<sup>4</sup> Vapor intrusion may also occur with inorganic contaminants. One example with well-known public health impacts is radon, an inorganic and volatile radioactive gas that can emanate from some natural soil and rocks.

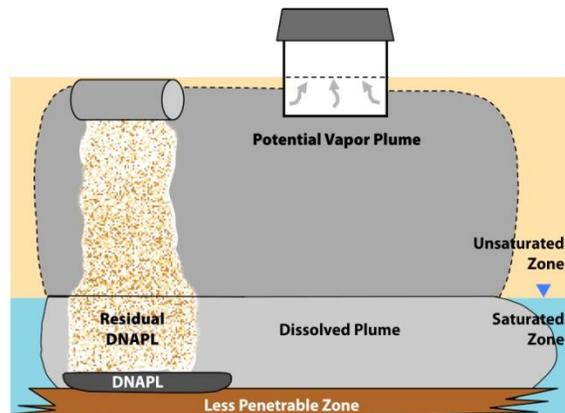
essential behaviors characteristic of petroleum and chlorinated solvent contaminants that are often observed under common site conditions.

The aerobic biodegradability of PHCs can generally limit the potential for subsurface migration of petroleum vapors and PVI. Figure 1 depicts a typical UST release scenario and conceptually illustrates how aerobic biodegradation can limit PVI into an overlying building. In contrast, because CHC biodegradation is anaerobic and proceeds much more slowly, chlorinated vapor plumes (see Figure 2) are often more extensive and generally more likely to result in VI. Although these generalized scenarios are considered representative of most conditions, chlorinated solvent contamination does not always result in VI. Similarly, subsurface biodegradation of PHCs does not always prevent PVI, and PHC vapors can migrate into buildings under some circumstances. For example, PVI would more likely occur in a structure located directly above shallow contaminated soil, such as the area near a buried tank as shown on the left in Figure 1 or in cases where a building is so large that it limits movement of oxygen beneath the center of the building (e.g., Patterson and Davis, 2009). See page 7, *Conditions With Greater Potential For PVI*, for several specific site conditions that are more likely to lead to PVI impacts.



**Figure 1. Typical petroleum hydrocarbon transport conceptual scenario**

Aerobic biodegradation of PHCs along the perimeter of the vapor and dissolved plumes limits subsurface contaminant spreading. Effective oxygen transport (dashed arrows) maintains aerobic conditions in the biodegradation zone. Petroleum LNAPL (light nonaqueous phase liquid) collects at the groundwater surface (the water table, blue triangle).



**Figure 2. Typical chlorinated solvent transport conceptual scenario**

Biodegradation of CHCs is anaerobic and usually slower than PHC biodegradation, so that the vapor and dissolved plumes often migrate farther than PHC plumes. CHC DNAPL (dense nonaqueous-phase liquid), if present, can sink below the water table, collecting in this case on a less penetrable layer.

### *Effect Of Biodegradation*

An aerobic biodegradation zone (see Figure 1) is typically present along the perimeter of the PHC plumes in groundwater and soil gas. Within this bioactive zone, natural microbial activity can degrade many PHCs into nontoxic end products like carbon dioxide and water (although some biodegradation pathways can produce compounds like methane, as discussed later). Because soil microbes consume oxygen to degrade PHCs, oxygen may become depleted where contaminant concentrations are elevated such as in the interior of a groundwater or vapor plume. The aerobic biodegradation zone generally develops around the perimeter of the contaminant plume, where oxygen transport from the atmosphere or oxygenated groundwater (depicted as dashed arrows in Figure 1) can replenish the oxygen consumed from degradation in this bioactive zone. Atmospheric oxygen migrates into the subsurface through diffusion and advection (e.g., barometric pumping of soil gas into and out of the subsurface in response to changes in barometric pressure), as well as dissolved in infiltrating rainwater.

PHC plumes in the saturated (groundwater) and unsaturated (soil) zones can reach a relatively stable condition, with oxygen replenished and contaminants biodegraded at the same rate chemicals are released from a source through dissolution and volatilization. If the source is removed, this equilibrium is disturbed and biodegradation can reduce the size of the plume, shrinking it back toward the original source area to the point that the plume may dissipate completely over time (Wilson et al., 1986). As documented in monitored natural attenuation guidance and literature (Wilson et al., 1986; EPA, 1999), under favorable conditions biodegradation can provide an effective contaminant removal-and-control mechanism for PHCs in groundwater, which effectively limits contaminant migration and reduces plume extent over time. Given that oxygen is usually more available in soil and unsaturated zones overlying groundwater (where air is present in the soil pore space), it follows that similar processes effectively limit vapor-phase PHC plumes in soil. See page 5, *Fate And Transport Processes For Vapor-Phase Contaminants*, for more information about PHC biodegradation in the unsaturated zone, including typical observed vertical concentration patterns in soil gas profiles.

In contrast to PHCs, CHCs biodegrade much more slowly, often incompletely, and primarily under anaerobic conditions in the subsurface. Although anaerobic biodegradation of chlorinated compounds can effectively limit contaminant migration in the saturated zone in some cases (EPA, 1998), chlorinated plumes (dissolved groundwater and vapor) often extend farther than typically observed petroleum contaminant plumes (see Figures 1 and 2). Other than biodegradation, vapor transport mechanisms for PHCs and chlorinated compounds are similar (see page 5).

### *Influence Of Density*

Petroleum hydrocarbon liquids (e.g., gasoline) and chlorinated solvents are only moderately soluble in water and often form separate phase liquids commonly referred to as NAPLs (nonaqueous phase liquids) when released into the environment. On one hand, when NAPLs are lighter (i.e., less dense) than water, as with PHCs, they are known as LNAPLs (light NAPLs) and can accumulate at the water table interface and spread laterally, as shown in Figure 1. On the other hand, when they are denser (i.e., heavier) than water, as with chlorinated solvents, they are known as DNAPLs (dense NAPLs) and can penetrate the water table, sink in the groundwater, and collect as pools on less permeable interfaces (e.g., clay or bedrock), as shown in Figure 2. When NAPLs of either kind move through soils and aquifer materials, they leave behind immobile, discontinuous droplets of separate-phase liquid referred to as residual NAPL. Residual NAPL (or residual) can be a long-lasting, immobile source of contamination for soil gas or groundwater.

It is important to recognize that NAPL does not occupy the entire pore space; rather, water, NAPL, and often gas/vapor phases are present together in a multiphase configuration controlled primarily by capillary forces and gravity (buoyancy). The continuous NAPL zones may spread, depending on the available volume of NAPL and the soil and liquid properties controlling NAPL mobility (e.g., multiphase permeability and capillary relationships). When a release stops, NAPL zones will eventually reach a dynamic equilibrium and thereafter remain relatively immobile. The formation of continuous-phase NAPL depends on a sufficient release volume large enough to occupy the unsaturated pore space; otherwise all of the separate-phase liquid may be trapped as immobile and discontinuous residual NAPL in the unsaturated or saturated zones without collecting as a continuous-phase NAPL zone.

When water tables fluctuate because of seasonal changes, tidal influences, nearby pumping wells, or rainfall events, a LNAPL layer, if present, will move up and down with the water table. These fluctuations leave behind residual NAPL throughout the zone of water table fluctuation, resulting in a smear zone above and below the water table (see Figure 1). Chemicals dissolve into groundwater from the LNAPL source (the continuous LNAPL, as well as the discontinuous residual LNAPL smear zone), forming a mobile dissolved plume that can migrate with flowing groundwater. Volatile contaminants can

emanate from the LNAPL source, residual contamination in the smear zone, and the dissolved plume to form vapors that can migrate through unsaturated soils and preferential pathways.

## Fate And Transport Processes For Vapor-Phase Contaminants

Several fundamental fate and transport processes influence the behavior of subsurface vapor-phase contaminants:

- **Diffusion** refers to the process whereby molecules move from an area of higher concentration to an area of lower concentration. Diffusion will lead to chemical migration within unsaturated soils away from the highest concentration source area (i.e., NAPL or a dissolved plume). Diffusion can also lead to chemical migration into buildings directly through a dirt floor and crawlspace or through cracks, pores, and other openings in the building slab and foundation such as passages for utility lines and sumps. Diffusion is faster in the gaseous phase than in the aqueous phase, so that a layer of clean recharge water above a contaminant plume can decrease the rate of volatilization of contaminants from the plume. Although chemical-specific diffusion rates vary somewhat, in general PHCs and CHCs behave similarly with respect to diffusion.
- **Advection** refers to the movement of soil gas in response to pressure gradients. Advection can be an important mechanism for drawing soil gas and contaminant vapors into or out of (beneath) a building. Heating and cooling systems can create differential pressures inside the building. When the pressure inside the building is lower than the pressure in the subsurface, vapors are drawn into the building. When the pressure inside the building is greater than the pressure in the subsurface, air within the building may be forced into the subsurface causing some degree of reoxygenation. Barometric pressure changes or wind may also drive advection of soil gas. For example, pressures upwind from a building may exceed pressures downwind, leading to advection of soil gas beneath the building (Lundegard et al., 2008). PHCs and CHCs behave similarly with respect to advection.
- **Biodegradation** refers to the process by which chemical compounds are altered through the biological activity of microorganisms in the subsurface. As discussed above, many PHCs degrade readily in the subsurface under typical, aerobic environmental conditions. In contrast, CHCs biodegrade much more slowly and under anaerobic conditions. In addition, CHC biodegradation can produce toxic degradation products such as dichloroethylene and vinyl chloride, while petroleum degradation usually produces carbon dioxide, water, and under certain conditions methane or other simple hydrocarbons.
- **Sorption** refers to the partitioning of chemicals onto the solid phase. Both petroleum and chlorinated solvent compounds tend to preferentially adsorb onto soil organic matter. Although chemical-specific sorption characteristics (partitioning coefficients) vary somewhat, in general PHCs and CHCs behave similarly with respect to sorption. Therefore, in soils with high organic carbon content, movement of organic compounds is retarded.
- **Mixing** refers to the blending of intruding vapors with ambient indoor air, which if free of volatile chemicals may dilute the concentration of intruding vapors. However, if the ambient indoor (or outdoor) air itself contains volatile chemicals, for example resulting either from off-gassing of building materials or products stored within the building, or if there are industrial sources of contaminants in ambient outdoor air, you may find it difficult to distinguish between VI and other sources of these other chemicals. This is especially true for chemicals that may originate from several sources simultaneously. The most common chemicals associated with PVI (e.g., benzene, toluene, TPH) and CVI (e.g., PCE, TCE) are components of products found in many homes and attached garages; examples include glues, cleaners, solvents, dry-cleaned clothes, and gasoline (EPA, 2011). Although EPA (2011) presents information on typical background levels of both PHCs and CHCs in indoor air resulting from sources other than vapor intrusion, this information should not substitute for site-specific data.

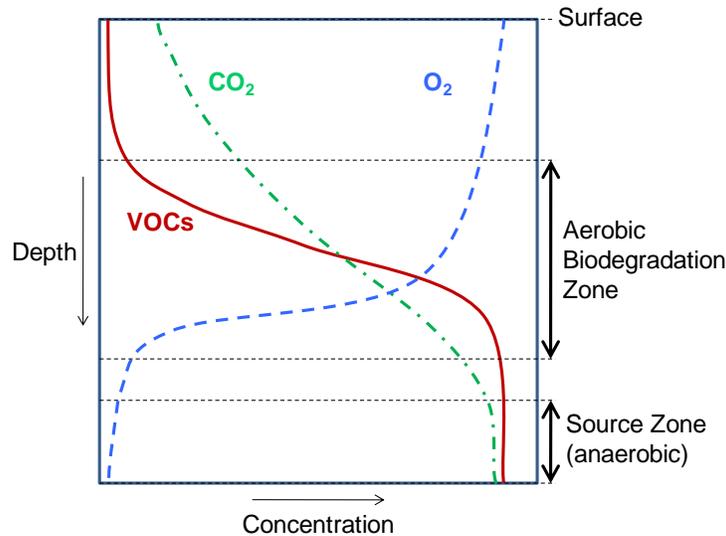
The chemicals that pose the most significant potential inhalation risks (sometimes called risk drivers) in PVI and CVI, such as benzene and PCE, respectively, generally have similar physical-chemical properties controlling diffusion and sorption in the vapor phase; advection, in contrast, is unaffected by chemical properties. Fundamentally though, these processes (diffusion, sorption, and advection) have a similar influence on the subsurface distribution of vapor-phase contaminants for both PHC and CHCs. If biodegradation is excluded, one generally would expect PHC and CHC vapors to behave similarly. However, investigations from sites across the United States and other countries have shown that vapor plumes of PHCs are typically less extensive than vapor plumes of chlorinated solvents, providing empirical evidence that aerobic biodegradation can effectively limit the migration of petroleum vapors in many situations (McHugh et al., 2010).

### **Biodegradation Of Petroleum Hydrocarbons In The Unsaturated Zone**

Scientific research and site investigations going back decades have demonstrated conclusively that microorganisms capable of aerobically degrading PHCs are present in nearly all subsurface soil environments (Zobell, 1946; Atlas, 1981; Wilson et al., 1986; Leahy and Colwell, 1990; Bedient et al., 1994; EPA, 1999). Effective aerobic biodegradation of PHCs depends on the soil having sufficient oxygen and enough soil water to provide a habitat for adequate populations of active microorganisms. If oxygen is present, these organisms will generally consume available PHCs. Furthermore, aerobic biodegradation of petroleum compounds can occur relatively quickly, with degradation half lives as short as hours or days under some conditions (DeVaul, 2007). Some petroleum compounds can also biodegrade under anaerobic conditions; however, above the water table, where oxygen is usually available in the soil zone, this process is less important and generally much slower than aerobic biodegradation.

Figure 1 depicts key processes for the biodegradation of PHCs in the unsaturated zone under common conditions: downward oxygen transport from the atmosphere, upward hydrocarbon vapor migration from the contaminant source, and aerobic biodegradation along the perimeter of the contamination zone where PHCs are consumed by microbial activity. Important factors influencing aerobic biodegradation in the vadose zone include source concentration, oxygen demand (the oxygen required to biodegrade the available hydrocarbons and any ambient soil organic matter that is present), distance between the source and the building, and soil type.

Aerobic biodegradation consumes oxygen and generates carbon dioxide and water. This leads to a characteristic vertical concentration profile in the unsaturated zone in which oxygen concentrations decrease with depth and VOCs (including PHCs and methane from anaerobic biodegradation) and carbon dioxide concentrations increase with depth. Figure 3 depicts a characteristic vertical profile, which will vary in shape depending on site-specific conditions (Roggemans et al., 2002).



**Figure 3. Typical vertical concentration profile in the unsaturated zone for VOCs, CO<sub>2</sub>, and O<sub>2</sub>**

With aerobic biodegradation in unsaturated soils, VOCs (red) degrade, carbon dioxide (green) is produced, and oxygen (blue) is consumed. The aerobic biodegradation zone extends over the area of active biodegradation. The source zone, which is anaerobic, is characterized by the maximum VOC concentrations and little biodegradation.

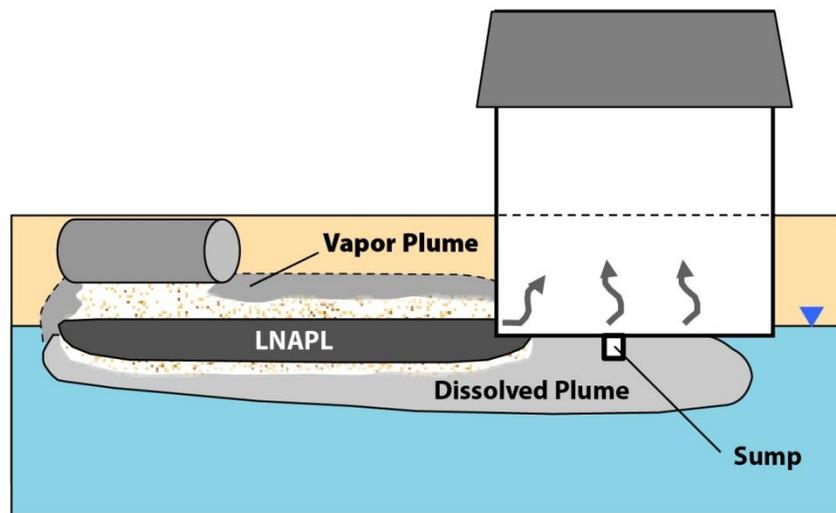
PHC vapor concentrations will almost always be much greater adjacent to a LNAPL hydrocarbon source than adjacent to a dissolved hydrocarbon plume. If PHC concentrations are high enough, available oxygen may be depleted, which in turn limits aerobic biodegradation. When oxygen is limited, anaerobic biodegradation of LNAPL or other organic sources can produce methane. Significant anaerobic biodegradation and methane generation can occur in some situations within anoxic zones of the plume interior and adjacent to the LNAPL source. Methane readily biodegrades under aerobic conditions and, when present, will create an additional oxygen demand. Importantly, methane also creates an explosion hazard if it accumulates within confined spaces (e.g., utility vaults and passages, basements, garages) in sufficiently high concentrations (and there is sufficient oxygen present and a source of ignition).

A number of well-characterized field studies demonstrate extensive aerobic biodegradation of PHC vapors in unsaturated soils (Ostendorf and Kampbell, 1991; Ririe and Sweeney, 1995; Ririe et al., 1998; Ostendorf et al., 2000; Hers et al., 2000; Roggemans et al., 2002; Sanders and Hers, 2006; Davis et al., 2009; Patterson and Davis, 2009). Several of these studies document vapor concentrations at least two to three orders of magnitude lower than would be predicted, through modeling of simple diffusion, in the absence of biodegradation.

### Conditions With Greater Potential For Petroleum Vapor Intrusion

Although aerobic biodegradation of PHC vapors can reduce the potential for PVI, certain site conditions can reduce the effectiveness of biodegradation and increase the potential for PVI. The potential for PVI depends on a number of factors including the characteristics of the source of PHCs and the volume of the release. In general, there is a greater potential for PVI when the source of the contamination is more volatile. For example, a release of gasoline, which has a high percentage of VOCs, has a greater potential for PVI than a release of a heavier, less volatile source material such as #2 fuel oil. Likewise, there is a greater potential for PVI when the volume of the VOC source is larger. Additional factors include proximity of the receptor to the contaminant source, presence of preferential transport pathways, and insufficient oxygen to support aerobic biodegradation.

- **Insufficient Separation Distance.** In order for biodegradation to limit the potential for PVI, a sufficiently thick layer of biologically active soil<sup>5</sup> is needed between the building foundation and the contamination to allow biodegradation to occur. Conditions leading to an insufficient separation distance may include high PHC concentrations, shallow or fluctuating water tables, or nearby petroleum sources in the unsaturated zone. Note that when the water table fluctuates, seasonal variability can bring contaminated groundwater or LNAPL close to or in contact with the building foundation during the wetter parts of the year.
- **Direct Building Contact.** Direct contact between a contaminant source (groundwater or LNAPL) and a building foundation may result from shallow water tables or perched zones (less-permeable materials above which water or LNAPL may collect). This direct contact may lead to contaminant vapor migration through the foundation or actual penetration of contaminated water or LNAPL into the building. For example, a basement dewatering system with an associated sump (see Figure 4) may draw contaminated groundwater into the building, resulting in PHC vapor impacts to indoor air. Many documented cases of PVI involve actual contact of petroleum LNAPL or petroleum-contaminated water with the building foundation (McHugh et al., 2010).



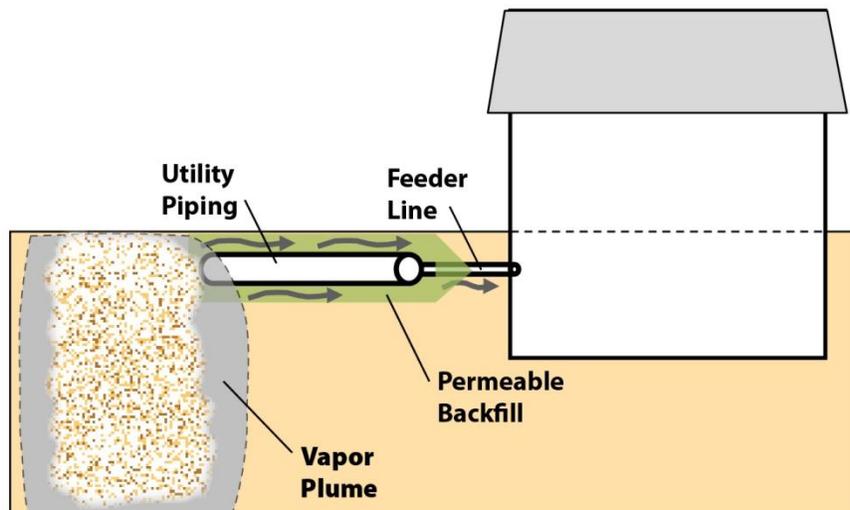
**Figure 4. Vapor intrusion from direct building contact**

A very shallow or perched water table can bring contaminants (LNAPL or contaminated groundwater) into direct contact with a building foundation. Foundation cracks or basement drainage systems (e.g., a sump) can bring source materials into the interior space. Volatilization from these sources likely results in PVI.

- **Preferential Transport Pathways.** If preferential transport pathways connect sources of volatile chemicals with buildings, the associated chemical transport may be faster and extend farther than transport through the surrounding soils. Preferential pathways may be geologic features, such as fractures or coarse-grained channels, solution channels in carbonate rock (karst), or engineered features, such as utility lines, drains, and sumps. The resulting transport patterns can be complex. For example, petroleum vapors (or LNAPL) may migrate along the permeable fill surrounding a

<sup>5</sup> Biologically active soil in the context of a PVI investigation means the subsurface soil environment will support populations of microorganisms that are present in sufficient quantities to aerobically biodegrade PHC vapors before they intrude into a confined space. Effective aerobic biodegradation of PHCs depends on the soil having sufficient oxygen and enough soil water to provide a habitat for adequate populations of active microorganisms. Although most soils contain indigenous microorganisms capable of degrading PHC vapors, typically there is an acclimation period between when they are exposed to the PHC vapors and when they begin to biodegrade (metabolize) the vapors. This is why it is critical to demonstrate, through collection of on-site samples, that biodegradation of PHC vapors is occurring.

main utility line (see Figure 5). Gasoline stations often present a special preferential pathway. As the tanks are backfilled with clean, well-sorted pea gravel, vapors emanating from the tank pit can migrate rapidly and without significant biodegradation due to the absence of microorganisms. The pavement is typically on a layer of gravel, which if continuous over the site, could allow relatively unimpeded vapor migration and intrusion into buildings on site.



**Figure 5. Preferential transport through a utility trench**

PHC vapors migrate preferentially within the permeable backfill of a utility trench that intersects contamination. Vapors may migrate preferentially through the more permeable backfill (arrows); however, oxygen may also migrate more readily through these materials, allowing aerobic biodegradation to counter the preferential vapor migration.

- **Anaerobic Conditions.** As described on page 6, *Biodegradation Of Petroleum Hydrocarbons In The Unsaturated Zone*, aerobic biodegradation requires sufficient oxygen to be an effective contaminant-removal mechanism. Some site conditions are relatively less conducive to oxygen transport from the atmosphere. For example, concrete foundations and pavement adjacent to buildings is relatively less pervious to oxygen than an open soil surface. Available data from a few sites suggest these surfaces may not reduce oxygen levels under buildings enough to inhibit biodegradation significantly (Lundegard et al., 2008). However, data from other sites (e.g., Patterson and Davis, 2009) suggest oxygen may be limited if the building footprint is very large, the building foundation is relatively impervious to vapor flow, and high hydrocarbon source vapor concentrations are in close proximity to the building foundation. Natural conditions can also limit oxygen availability, as evidenced by low oxygen concentrations found in the presence of some highly organic soils (e.g., peat). Thus, the presence of highly organic soils can be a marker for limited oxygen availability and potential limits to petroleum biodegradation.
- **Production Of Methane.** Methane may be produced through anaerobic degradation of PHCs in zones with relatively large release volumes and high levels of contamination (e.g., in the presence of LNAPL). Methane occurrence might be more significant at sites where large volumes of ethanol-blended gasoline (and higher ethanol content fuels) have been released into the subsurface. As the ethanol content increases, so does the potential for creating larger volumes of methane. Methane production can increase soil gas volume and pressures and result in advective soil gas flow toward receptors. PHC vapors may also migrate with the methane. In addition, aerobic biodegradation of methane may deplete oxygen that otherwise could be used for biodegradation of the PHC contaminants. Moreover, in situations where intrusion of methane into

confined spaces results in the accumulation of very high concentrations, there can be a risk of explosion.

## **Considerations For Petroleum Site Investigation And Screening**

The preceding discussion highlights how aerobic biodegradation can limit the migration of PHC vapors in many cases. Thus, you should consider biodegradation for investigating and screening sites with PHC contamination. This section discusses some key considerations for site investigation and screening, which regulators and other practitioners may take into account as they address potential PVI at sites with subsurface petroleum contamination.

### *Site Investigation Considerations*

A key consideration in a PVI site investigation is whether sufficient oxygen is available and whether there is a sufficiently thick biologically active soil layer between the source and the receptor for aerobic organisms to biodegrade the PHC vapors before they could conceivably reach indoor air. With sufficient oxygen, soil moisture, and an acclimated population of microorganisms the soil column will act as a natural biofilter within which PHC vapors are degraded at sufficiently fast rates, effectively eliminating the potential for PVI.

When evaluating the potential for aerobic biodegradation, it is important to consider how readily oxygen can move through shallow soils around and under buildings to replace oxygen consumed during biodegradation. Oxygen replenishment beneath a building may be influenced by: size of the building; construction type and integrity of the building foundation; type of surface cover beside the building (e.g., pavement versus landscaping); soil properties (e.g., air permeability); weather; and other site-specific factors. By observing and measuring these factors, along with soil gas oxygen, carbon dioxide, and PHC vapor profiles, you can determine and confirm when subsurface oxygen levels may be too low to support an adequate rate of aerobic biodegradation.

As with any investigation of a leaking UST site, you must fully characterize the site in three dimensions to develop a conceptual site model (CSM) based on all available data.<sup>6</sup> The CSM is continually updated as new data become available. Because vapors migrate more easily than NAPL or dissolved contamination, determining soil transport properties and preferential migration pathways is especially important. It is especially critical to assess whether unsaturated soils under a building have elevated PHC concentrations. In some cases where PHC vapors appear to be migrating from a deeper source (e.g., LNAPL at the water table or a groundwater plume), the shallow soil may be contaminated as well and may be contributing to PHC vapors entering the building. In addition, biodegradation of PHCs consumes oxygen and can limit biodegradation processes at sites where soil concentrations of hydrocarbons are elevated.

When biodegradation is active in the unsaturated zone, soil gas concentrations (PHCs, methane, carbon dioxide, and oxygen) usually vary with depth in characteristic patterns (see Figure 3). Accordingly, soil gas samples collected at different depths (vertical profiles) can provide evidence of whether or not aerobic

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<sup>6</sup> Federal regulations (40CFR280) require determination of the full extent of the contamination from a leaking UST release. Section 280.62 paragraph (a)(5) directs owners and operators to "measure for the presence of a release where contamination is most likely to be present..." It goes on to say that sample types, locations, and methods must be appropriate for identifying the presence and source of the release. There are no limits placed on the extent of the investigation; if contamination is likely to be present somewhere, then its presence should be determined. This applies to NAPL, residual, vapor, and dissolved phases. State action levels would come into play to determine whether a contaminant level was actionable. Section 280.65, paragraph (a) requires owners and operators to "determine the full extent and location of soils contaminated by the release and the presence and concentrations of dissolved product contamination in the groundwater", and further that the investigation must extend to "the surrounding area possibly affected by the release." "Full extent" implies delineation of contamination in three-dimensions outward from the source area to non-detect levels, even when this means going "off-site".

biodegradation at a site is occurring. Developing vertical profiles requires a series of soil gas samples at different depths. In some cases, you may need relatively shallow soil gas samples (less than five feet) to characterize active biodegradation zones in the shallow soil (e.g., in the presence of shallow contamination sources). Some state-level regulatory programs do not allow soil gas sampling at depths less than five feet based on the belief that accurate sampling may not be possible at shallow depths because air from the surface may leak into the sample. However, research has shown that accurate shallow-soil gas samples are possible at depths of up to two feet below ground surface using appropriate field methods (e.g., leak testing), such as those documented in EPA (2010). Particularly in cases with shallow contamination, site investigation should evaluate whether an active biodegradation zone is present below the building.

With respect to indoor air investigations at PVI sites, background hydrocarbon concentrations from indoor and outdoor sources unrelated to PVI can make indoor air samples difficult to interpret. In some situations indoor air sampling can provide valuable exposure information, although you may find it difficult to distinguish whether contaminants derive from PVI or an unrelated indoor or outdoor source.

### *Site Screening Considerations*

As highlighted in the discussions above, aerobic biodegradation can limit the potential for PVI under many conditions. We attribute most of the known, documented cases of PVI to one or more of the site conditions discussed on pages 7-9; for example, see the published sites compiled by McHugh et al. (2010). Therefore, site-screening criteria may effectively identify sites where PVI is unlikely to occur (i.e., deep sources with sufficiently low concentrations; sufficiently thick, aerobic soil zones) as well as when petroleum sources are strong enough and in such close proximity to a building that PVI might occur. By quickly identifying cases where biodegradation is unlikely to result in significant petroleum vapor attenuation, you can use financial resources (e.g., state trust funds) most effectively to protect public health by addressing sites where PVI is more likely.

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