Important Physical Processes For Vapor Intrusion:
A Literature Review

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Abstract
The evaluation of vapor intrusion through the use of VOC concentration measurements in
various environmental media often yields inconclusive results. In many cases, measurements
focusing on the physical processes that affect VOC transport from the subsurface into buildings
can provide more definitive investigation results, potentially at lower cost. Research conducted
over the last 20 years has served to document a wide variety of fate and transport processes that
contribute to the movement of chemicals through the subsurface and into buildings. Fate and
transport processes within three key environmental matrices or interfaces are considered in this
review: i) the groundwater-soil gas and soil-soil gas interfaces, ii) unsaturated zone soils, and iii)
the building foundation. This review of previously published research and field observations
will provide useful guidance concerning the critical physical processes to be considered when
conducting a vapor intrusion evaluation.

Introduction
Since 2000, regulators and the regulated community have become increasingly concerned about
the potential for exposure to volatile organic compounds (VOCs) through vapor intrusion to
indoor air at sites with contaminated soil or groundwater. Detailed investigations at a limited
number of corrective action sites have documented elevated levels of chlorinated VOCs in
houses located above contaminated groundwater (Tillman and Weaver, 2005; DiGiulio et al.,
2006). In response, the USEPA and many state regulatory agencies have issued guidance
specifying screening and field investigation procedures for the identification of vapor intrusion
impacts at corrective action sites. Although the specific recommended investigation procedures
vary significantly between guidance documents, the majority of these documents use a step-
wise evaluation process that includes preliminary screening followed by field investigation, if
needed. Because site-specific factors can contribute up to several orders of magnitude in
uncertainty and variability in vapor intrusion, screening criteria developed to be protective over a
broad range of site conditions are conservative for a majority of sites, and field investigations of
the vapor intrusion pathway are required at many sites with subsurface volatile chemical impacts.

The use of field investigations of shallow groundwater, soil gas, and/or indoor air to evaluate
vapor intrusion brings a separate set of difficulties. VOC concentrations in soil gas (including
sub-slab gas) exhibit high spatial and temporal variability (McHugh, 2007; Luo et al., 2006). As
a result, a larger number of soil gas samples are needed to characterize VOC concentrations in
soil gas compared to groundwater or indoor air. However, if elevated concentrations of VOCs are detected in indoor air, additional evaluation may be required to distinguish vapor intrusion from ambient or indoor sources of VOCs. Because of these challenges, vapor intrusion investigations that focus exclusively on measurements of VOC concentrations in various media often yield inconclusive results.

In some cases, however, the potential for vapor intrusion can be evaluated by focusing on physical or biological barriers that limit VOC migration through the subsurface and into buildings. The most common barriers to vapor intrusion are illustrated in Figure 1.

![Figure 1: Potential Barriers to Vapor Intrusion](image)

A better understanding of the physical and chemical processes of vapor intrusion will support the development of improved screening and field investigation approaches for this pathway. Research conducted over the last 20 years has served to document a wide variety of fate and transport processes that contribute to the movement of chemicals in the subsurface. The goal of this literature review has been to identify the physical processes most likely to affect the migration of VOCs from subsurface sources into buildings. The review is focused on three key environmental matrices or interfaces: i) the groundwater-soil gas and soil-soil gas interfaces, ii)
unsaturated zone soils, and iii) the building foundation. The reviewed papers included field studies, laboratory studies, and modeling analyses. Biodegradation is often an important factor controlling the fate and transport of petroleum hydrocarbon vapors, however, we have chosen not to include biodegradation in this review and, therefore, papers that primarily focused on petroleum hydrocarbon vapor intrusion were not included.

Migration of VOCs from Groundwater to Soil Gas

Many of the published vapor intrusion case studies are sites where dissolved VOCs have migrated through groundwater away from the original release area and into areas containing a large number of individual buildings. To understand the potential for vapor intrusion from VOCs dissolved in groundwater, it is important to understand the processes controlling the migration of VOCs from groundwater to soil gas.

General Partitioning Processes: Many models of vapor intrusion from groundwater sources (e.g., the USEPA Johnson and Ettinger Spreadsheet Model; USEPA, 2003) account for VOC transfer from groundwater to soil gas by equilibrium partitioning between groundwater and deep soil gas. However, available field data indicates that equilibrium partitioning based on Henry’s law is a poor predictor of the relationship between VOC concentrations measured in groundwater and deep soil gas. Paired field measurements commonly show little correlation between measured VOC concentrations in groundwater and deep soil gas. In one study evaluating data from 24 sites, the measured soil gas concentrations ranged from 0.002% to 10% of that predicted by Henry’s law with a mean of 0.66% (Fitzpatrick and Fitzgerald, 1996). At the Endicott, New York site, no clear correlation was observed between measured TCE concentrations in groundwater and deep soil gas (Wertz, 2006). At this site, the measured TCE concentration in soil gas was less than that predicted by Henry’s law for more than 80% of measurements.

When a vertical concentration gradient is present in groundwater near the soil gas interface, then vertical diffusion and dispersion through groundwater may control the migration of VOCs from deeper groundwater to soil gas (McHugh et al., 2003). Barber et al. (1990) conducted detailed field measurements of methane transfer from groundwater to soil gas at a landfill site and found that this transfer was controlled by vertical diffusion of methane within the saturated groundwater zone. Laboratory tank experiments conducted by McCarthy and Johnson (1993) also showed that for a stable (i.e., non-fluctuating) water table, the transfer of TCE from bulk groundwater to soil gas was controlled by vertical diffusion through the groundwater. Modeling results included in the Barber et al. study indicated that when accounting for vertical diffusion in groundwater and in soil gas, the value of Henry’s Law constant for a chemical had little impact on the predicted concentration in deep soil gas. For any chemical more volatile than naphthalene (i.e., $H' > 0.02$), a simplified model including vertical diffusion in groundwater, but not including Henry’s Law constant for equilibrium partitioning, predicted deep soil gas concentrations within 10% of the values predicted by the more complex model incorporating both diffusion and equilibrium partitioning (Barber et al., 1990). For less volatile chemicals, the equilibrium partitioning term was more significant and, therefore, the error associated with the simplified model was greater. These results indicate that for at least some aquifer conditions, the process of
vertical diffusion through groundwater is more important than equilibrium partitioning at the groundwater-soil gas interface for the mass transfer of VOCs from deeper groundwater to soil gas. In these situations, transport models that account for equilibrium partitioning but not vertical diffusion through groundwater would over-predict the mass flux of more volatile constituents from groundwater to deep soil gas relative to less volatile constituents at the same site.

Infiltration and Evapotranspiration: Where infiltration rates are high relative to the magnitude of seasonal water table fluctuations, a sustainable fresh water lens can develop which can be an effective barrier to off-gassing of VOCs from groundwater to the vadose zone (McAlary et al., 2004). In contrast, in areas where tree roots extend to the depth of the water table, evapotranspiration can result in removal of water and VOCs from the top of the water-bearing unit (Doucette et al., 2007), potentially exposing deeper more impacted groundwater. Because evapotranspiration is seasonal in many areas, a clean water lens may form during the winter when the trees are dormant, but may be removed in the summer during the growth season.

Impact of Water Table Fluctuations on VOC Transfer to Soil Gas: In an unconfined aquifer, when the water table falls, capillary forces trap a significant volume of water in the vadose zone. The water saturation of well-drained soils is 20% to 80%, depending on soil type. If this water contains VOCs, then the transfer of the VOCs from groundwater to soil gas will be enhanced under falling water table conditions as water drains from the larger pores and is replaced by air, significantly increasing the contact area between contaminated groundwater and soil gas. This process can result in temporal variations in the mass flux of VOCs from groundwater to soil gas.
with the highest transfer rates occurring during falling water table conditions. McCarty and Johnson (1993) observed this phenomenon in their laboratory tank experiments, noting a threefold increase in TCE concentration in soil gas when the water table was lowered. Similarly, a laboratory column study of cis-dichloroethene (cis-DCE) and three chlorofluorocarbon (CFC) compounds found increased transfer of these compounds from groundwater to soil gas under falling water table conditions (Werner, 2002). The mass flux of cis-DCE from water to soil gas increased by 2-4x under falling water table conditions, and CFC-114 was detected in soil gas under falling water table conditions, but not under stable or raising water table conditions. In this study, the largest increase in VOC concentration in soil gas was observed when a falling water table was preceded by a rising water table. This higher flux was attributed to VOC partitioning into air bubbles trapped below the rising water table. The air bubbles were then released by the falling water table resulting in a rapid mass transfer of VOCs to the bulk soil gas. Silliman et al. (2002) also noted pockets of air trapped below a rising water table that could be released during a falling water table. Thomson et al. (1997) conducted numerical modeling of water table fluctuations and found that these fluctuations could increase mass transfer across the water table by up to 200x compared to a static water table. However, this model assumed a NAPL source below the water table so that the dissolved TCE in water was replenished during each fluctuation cycle.

In summary, a series of laboratory studies suggests that the rate of VOC transfer from groundwater to soil gas may vary temporally at sites with a fluctuating water table with the highest transfer rates occurring with falling water table elevation. As a result, an understanding of recent changes in water table elevation may be important for the interpretation of deep soil gas monitoring results. Specifically, VOC concentrations in deep soil gas may be highest during periods of falling water table elevation. Consideration of changes in water table elevation may be an important for understanding temporal variability in deep soil gas concentration.

Migration of VOCs Through Unsaturated Soils

Within the vadose zone, advective and diffusive transport processes can lead to the migration of VOCs in soil gas from the local source to near-by buildings.

Transport in the Vadose Zone: A number of researchers have investigated the factors influencing the migration VOCs through vadose zone soil gas. Based on the results from laboratory studies, field studies, and model simulations, diffusion (rather than advection) is the primary transport mechanism for VOC migration in the vadose zone under most naturally-occurring conditions (Jellali et al., 2001; Jellali et al., 2003; Conant et al., 1996; Moldrup et al., 2003; Choi et al., 2002; Choi and Smith, 2005). Choi et al. (2002), measured pressure gradients between the atmosphere and vadose zone at the Picatinny Arsenal site in New Jersey, and used the measured pressure gradients along with measured or estimated soil properties to model advective vs. diffusive VOC flux at the ground surface. For two of the three test periods, diffusive flux was much higher than advective flux, but these fluxes were approximately equal during the third test period. Moisture content in the surface soils had a larger impact on diffusive flux than on advective flux with diffusive flux decreasing with increasing soil moisture. Choi
and Smith (2005) used modeling to further examine the importance of advection vs. diffusion on VOC flux at the ground surface (i.e., flux from soil gas to the atmosphere). For this purpose, advection of soil gas was driven primarily by simulated variations of atmospheric pressure. They found that diffusive flux dominated advective flux under all conditions simulated by the model, but that the advective flux was more sensitive to changes in site conditions. While diffusive flux was significantly impacted only by soil moisture content (with flux decreasing with increasing soil moisture), advective flux was sensitive to soil permeability, soil moisture content, temperature, vadose zone thickness, and changes in water table elevation.

Geologic Barriers to VOC Migration: Geologic layers with low-permeability and high moisture content can form a barrier to vapor transport (both advection and diffusion). When groundwater occurs in a confined aquifer (i.e., permeable water-bearing zone overlain by a low-permeability aquitard or aquiclude), the potential for VOCs to migrate from groundwater to soil gas is generally very limited. Similarly, a high moisture content, fine-grained soil layer in the vadose zone can prevent the vertical migration of VOCs if it is laterally continuous. VOC diffusion through soil gas is weakly influenced by soil type, but is strongly influenced by soil moisture (Moldrup et al., 2003). As a result, the impact of a fine-grained soil layer as a barrier to vapor intrusion is likely to be more significant in moist climates where these fine-grained layers typically have a high moisture content. The presence of fine-grained layers is likely to be less significant in arid climates where the air content of these layers is higher. In addition, seasonal changes in rainfall may contribute to temporal variations in both VOC concentration and VOC flux in the vadose zone.

The integrity of a fine-grained soil layer can be evaluated in the field using permeability testing. Permeability testing in the vadose zone is quick and inexpensive relative to the testing of water-bearing units because vacuum levels respond very quickly (seconds to minutes) to pumping (Johnson et al., 1990). Furthermore, the extracted fluid often does not require storage, waste characterization and disposal, which are commonly expensive components of groundwater pumping tests. A testing scheme for evaluation of low-permeability units is shown in Figure 3. When pumping for well #1, a high vacuum at well #3 compared to well #2 suggests the presence of a low permeability layer.
Figure 3. Example test configuration to evaluate permeability of fine-grained layer in the vadose zone.

Thrupp et al., 1996 also describes a method by which the vertical leakance of air through the low permeability layer can be calculated by fitting the time versus vacuum data from well #1 to a leaky-aquifer model for groundwater pumping test analysis after transforming the data to account for differences between the viscosity and density of water and air. Another method of assessing the presence of a pneumatic barrier is to monitor gauge pressure in a deep soil gas probe (i.e., the difference in pressure between the probe and the atmosphere), and barometric pressure changes over time. If the vadose zone has no low-permeability layers, there will be little or no measurable pressure difference in the probe because as barometric pressure changes, gas will flow readily and the pressure gradient will dissipate rapidly. If there is a laterally continuous layer of low gas permeability, the gauge pressure in the probe will be inversely correlated with the atmospheric pressure changes (i.e., gauge pressure will increase as atmospheric pressure decreases, and vice versa). Note that these tests measure the potential for advective, rather than diffusive flow through the vadose zone. However, a low permeability soil layer that also has a high moisture content will also serve as a barrier to diffusive VOC transport.
Transport of VOCs Through the Building Foundation

The final component in the vapor intrusion pathway is the building foundation. If VOCs are present beneath a building foundation, then the advection or diffusion of VOCs through the foundation relative to the rate of building air exchange will determine the magnitude of the vapor intrusion impact.

Transport Across the Building Foundation: Researchers who have measured cross-foundation pressure gradients report measurable pressure gradients (positive, negative, or varying between positive and negative) at all buildings studied (e.g., Nazaroff et al., 1985; Hintenlang and Al-Ahmady, 1992; Riley, et al., 1996; Robinson and Sextro, 1997; McHugh et al., 2006). This is an unsurprising finding given that pressure gradients can be induced by mechanical ventilation, indoor combustion, ambient wind, temperature gradients, and other factors commonly present in buildings. In addition, several researchers have reported a positive relationship between cross-foundation pressure gradient and soil gas entry rate indicating that the foundations of the buildings studied support advective flow (e.g., Nazaroff et al, 1987; Gabresi and Sextro, 1989; Fischer et al., 1996; Robinson and Sextro 1997). These findings indicate that almost all buildings likely exhibit cross-foundation pressure gradients sufficient to induce advective transport of VOCs through cracks or penetrations that may be present. Diffusive transport could be the dominant transport mechanism when either: i) there is no pressure gradient across the building foundation (which is rare), or ii) there are no cracks or penetrations in the foundation that support advective flow. In the second case, the attenuation factor (i.e., VOC concentration in the building divided by the VOC concentration below the foundation) is likely to be small (i.e., high attenuation) as the limited diffusive transport through the bulk foundation material will be diluted as a result of normal building ventilation. These findings indicate that advective transport of VOCs across the building foundation will dominate diffusive transport in most or all buildings where vapor intrusion is a concern.

Since advection is driven by the pressure gradients, the evaluation of advective transport across the building foundation can be divided into three main categories according to building pressure:

- **Net Positive Pressure:** Large buildings commonly have rooftop air-handling units that heat or cool air according to the seasons, and blow air into the building. For commercial buildings, these systems are often designed to maintain a small positive building pressure, a design that improves that ability to control dust, humidity, and other indoor air quality factors. Recent recommended building practices applicable to both residential and commercial building ventilation also requires that the heating ventilation system maintain a positive air intake over exfiltration when the system also provides humidity control (ASHRAE, 2004). In buildings with positive building pressure, the pressure gradient will favor the downward migrations of air across the building foundation. Abreu and Johnson (2005) showed that even a very small interior pressure (i.e., <1Pa) is sufficient to decrease the attenuation factor by several orders of magnitude.

- **Variable Pressure Gradient:** Many single-family dwellings with radiant heat or central heating and air-conditioning have little net mechanical (i.e., fan-assisted) flow of air into
or out of the building. For these buildings, building pressure typically fluctuates by a few pascals and varies between positive and negative building pressure. These transient pressure gradients will cause bi-directional flow across the building foundation (McHugh et al., 2006). For these buildings, the “average” pressure gradient may be close to zero due to the variation between positive and negative building pressure. However, the transport of VOCs across the building foundation is still driven by advection rather than diffusion because a pressure gradient (either positive or negative) is present at most times.

- **Net Negative Building Pressure:** Exhaust fans in bathrooms and kitchens, and thermal convection associated with combustion can draw air out of a building resulting in negative building pressures. In cold climates, the stack effect can also result in negative building pressures in the lower floors, in proportion to the height of the building and the magnitude of the temperature difference from inside to outside (Wilson and Tamura, 1968). When these conditions are present, the negative building pressure will favor upward migration of soil gas into the building.

The pressure condition for an individual building (i.e., net positive, variable, or net negative) can be estimated based on an evaluation of the HVAC system operation, other mechanical ventilation, and local climate. Alternatively, cross-foundation pressure gradients can be measured using a portable pressure transducer or digital micro-manometer.

**Impact of Building Pressure on Vapor Intrusion:** For buildings where pressure-driven advection is the primary transport mechanism across the building foundation, one might expect vapor intrusion to be greatest during periods of lowest building pressure. At least partly based on this consideration, several vapor intrusion guidance documents recommend measuring indoor VOC concentrations during the winter heating season when temperature gradients and indoor combustion sources are most likely to induce a negative building pressure (e.g., NYDOH, 2006).

However, several published studies have found little or no relationship between building ventilation rates or building pressure and indoor radon concentrations. Because the physical processes controlling the migration of radon across the building foundation are also applicable to VOC vapor intrusion, the results of these studies should be applicable to VOCs. Nero et al. (1983) measured radon concentrations and building air exchange rates in 98 homes. The purpose of this study was to evaluate whether energy efficient homes with lower air exchange rates had higher radon concentrations. However, they found no correlation between the air exchange rate and radon concentration. This finding suggests that low building air exchange rate is not a good predictor of vapor intrusion problems.

Fischer et al. (1996) used radon and tracer gas concentration measurements to evaluate the effect of building pressure on soil gas entry rates, and found a linear relationship between negative building pressure and soil gas entry rates. However, no corresponding increase in radon or VOC concentrations in indoor air was observed, suggesting that the increase in soil gas entry was balanced by an increase in ambient air entry. Based on a study of two houses in Portland, Oregon (Nazaroff et al., 1987) reported that depressurization of only the basement by 25 to 50 Pa
relative to ambient pressure resulted in a 2 to 4 fold increase in basement radon concentrations. However, a five-month study of a house near Chicago found no relationship between natural fluctuations in whole building pressure, air exchange rate, indoor to ambient temperature gradient, wind speed, or other parameters and indoor radon concentration (Nazaroff et al., 1985). Specifically, five episodes of fireplace use during this study period resulted in a decrease in building pressure and an increase in air exchange rate, but had no impact on the indoor radon concentration.

A U.S. Department of Defense (DoD)-sponsored study investigated the impact of induced negative building pressure on vapor intrusion (GSI, 2007). In this study of three single-family residences, the induction of a negative building pressure resulted in an increase in soil gas flow across the building foundation, but no increase in the indoor concentration of radon or VOCs associated with subsurface sources. For these residences, the increase in soil gas flow was balanced by an increase in the overall building air exchange rate, preventing an increase in the magnitude of vapor intrusion with the increased negative building pressure. Together, these studies support the suggestion that VOC transport across the building foundation is best represented as a ratio of soil gas entry to total building ventilation, which appears to be independent of building pressure in many cases.

Although many studies have found that the magnitude of vapor intrusion is independent of building pressure, a few studies have found a relationship between building pressure and vapor intrusion under defined conditions. Robinson and Sextro (1997) reported a correlation between cross-foundation pressure gradient and indoor radon concentration in a house in Florida used for radon research. This house was constructed on low permeability soils that responded slowly to changes in atmospheric pressure. As a result, during periods of falling barometric pressure, the cross-foundation pressure gradient was higher than the indoor-ambient pressure gradient resulting in an increase in soil gas entry into the building that was not balanced by an increase in ambient air exchange.

Another situation where building pressure has a clear impact on vapor intrusion is when the building HVAC system creates a positive building pressure. Rydock et al. (2001) reported a diurnal variation in indoor radon in a school building associated with operation of the HVAC system. Indoor radon concentrations were near ambient background during weekdays when the HVAC system created a positive building pressure. However, the radon concentration was elevated well above background during weeknights and weekends when the HVAC system was not in operation. A similar effect was observed in a commercial building at a site with VOCs in the subsurface (Berry-Spark et al., 2005). Under normal building operating conditions, indoor VOC concentrations were similar to values predicted using the Johnson and Ettinger (1991) model based on measured soil gas concentrations. However, when the HVAC system was adjusted to increase the air-flow rate into the building, creating a positive building pressure of about 10 Pascals, the VOC concentrations in indoor air decreased by an order of magnitude or more. The change in HVAC system operation increased the air exchange rate by 2x compared to the >10x reduction in VOC concentration, indicating that the positive pressure induced by the air handling units resulted in a significant reduction in sub-surface vapor intrusion.
In summary, for most passively-ventilated buildings (such as most single-family residences), fluctuations in building pressure may change the soil gas entry rate, but this change is likely to be balanced by the overall change in building air exchange rate resulting in little or no change in the magnitude of vapor intrusion. In buildings where the cross-foundation pressure gradient is decoupled from the indoor-ambient pressure gradient, fluctuations in the cross-foundation pressure gradient are more likely to affect vapor intrusion. Finally, in buildings with mechanical ventilation, an induction or increase of positive building pressure is likely to reduce or eliminate vapor intrusion.

**Summary and Conclusions**
A review of the available literature addressing VOC transport processes along the vapor intrusion pathway supports many aspects of the current vapor intrusion conceptual model. However, the following key findings may support refined approaches for the investigation of vapor intrusion:

**VOC Transfer from Groundwater to Soil Gas:** Although equilibrium partitioning describes the relationship between VOC concentrations in groundwater and soil gas at the water table interface, diffusion through groundwater likely controls the mass transfer from deeper groundwater at many sites with a stable water table. Based on laboratory studies, a falling water table can cause a transient increase in VOC transfer to soil gas. Water table fluctuations may explain some of the temporal variability observed in deep soil gas VOC concentrations, and should be considered when interpreting deep soil gas monitoring results.

**VOC Transport in the Vadose Zone:** Diffusion is the most important transport process for VOCs in the vadose zone under most site conditions. VOC diffusivity in soil is dependent on soil moisture. As a result, the moisture content of fine-grained soil layers in the vadose zone may be an important factor in their effectiveness as a barrier to vapor intrusion.

**VOC Transport through Building Foundations:** Advection is the most important transport process for VOC migration through building foundations. In most buildings with continuous or periodic negative pressure, the magnitude of the negative pressure will not affect the magnitude of vapor intrusion because the increase in soil gas entry will be balanced by an increase in overall building air exchange. However, an induction or increase in positive building pressure is likely to reduce the magnitude of vapor intrusion impacts.

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**References**


Rydock et al., 2001


