Investigation and Remediation

The Upward Migration of Vapors

by Blayne Hartman

A Note From The Editor: *Recent changes in environmental cleanup ideology and regulations have led to the increased application of natural attenuation as a remediation strategy and risk-based corrective action (RBCA) as a means for determining the cleanup requirements for contaminated sites. As these approaches are implemented, consideration must be given to the fate and transport of contaminant vapors in the subsurface and the potential risks they pose to human health. In this article, Blayne Hartman examines the processes by which vapors move through the vadose zone and the potential risk caused by the upward migration of vapors into an overlying building. He concludes by recommending a protocol for determining the upward vapor flux in the field.*

While I recognize that the technical nature of this article—not to mention the preponderance of daunting equations—may scare off some of you (it scared me), I also recognize that this type of timely information will be of value to those of you who are struggling with remediation issues. For completeness of information, I chose to retain all of the equations submitted with the article. It is easy enough, however, to skip over the mathematics and still benefit from the discussion. In a future issue of "LUSTLine," Blayne will discuss the potential risk to groundwater resulting from the downward migration of vapors.

How Do Contaminants Move in the Vapor Phase?

A common misconception associated with vapors emanating from a subsurface source of contamination (i.e., soil, fractured bedrock, groundwater) is that the vapors will preferentially rise upward and escape into the atmosphere, much like smoke rising from a smokestack. To understand why this idea is a misconception, you need to understand how the transfer of contaminants occurs in the vapor phase.

There are primarily two types of physical processes by which contaminants are transported in the vapor phase: advection and gaseous diffusion. Advection refers to the bulk movement of the vapor itself (e.g., the movement of vapor by wind). In advective transport, any contaminants in the vapor are carried along with the moving vapor. Advective transport processes can be important in the movement of soil vapor through the vadose zone (e.g., near the surface due to atmospheric pressure variations or near buildings that create pressure gradients due to differential heating).

Gaseous diffusion refers to the motion of the contaminants by molecular processes through a nonmoving vapor column. It is the primary transport mechanism for contaminants in the vapor phase through the soil vadose zone. Contaminant transport by gaseous diffusion is described by Fick's first law as:

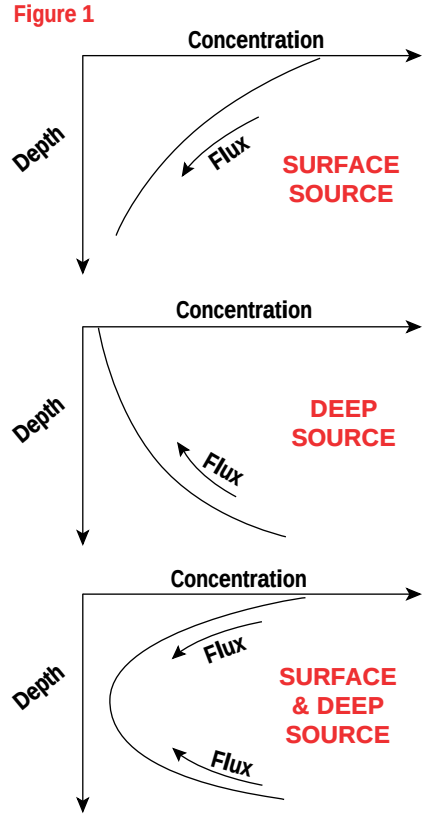
$$\text{Flux} = \frac{D_e * dC_{sg}}{dX}$$

Flux is the rate of movement of a compound per unit area.
D_e is the effective diffusion coefficient in the vadose zone.
dC_{sg} is the contaminant concentration gradient in the soil vapor.
dX is the depth interval in the vadose zone.

Similar to momentum transfer (e.g., water running downhill) and heat transfer (movement from hot to cold), contaminant transfer by gaseous diffusion moves from areas of high concentration to areas of low concentration. The flux will always be down the concentration gradient, regardless of the orientation of the concentration gradient with respect to depth below the surface. In the subsurface environment, diffusional transport occurs in all directions so contaminants move away from a source in all directions, similar to an expanding balloon. The key issues to remember are:

- Contaminant transport by gaseous diffusion does not move preferentially in one direction (e.g., up or down) but spreads out radially in all directions.
- The direction of movement is from high concentration to low concentration regardless of the orientation with respect to depth in the vadose zone. In other words, if high concentrations of a contaminant in the vapor phase are midway between the ground surface and the groundwater, the diffusive flux from the source will move both upward and downward from the source.

Figure 1

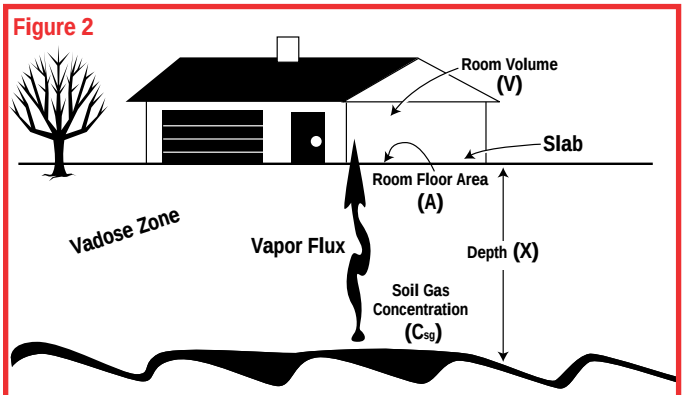


Common soil vapor profiles in the vadose zone for different locations of contaminant sources.

The Upward Migration of Vapors Into Enclosed Spaces

Benzene is the principal contaminant of concern at most sites because of its proven carcinogenity and common occurrence at gasoline-contaminated sites. Other common compounds of concern at fuel-contaminated sites

Figure 2



Upward migration of vapors into building.

include chlorinated solvents (e.g., vinyl chloride and tetrachloroethylene from oil sumps) and methane.

A simplified environmental fate and transport model for evaluating the inhalation exposure pathway for a contaminant is summarized in the 1995 ASTM Risk-Based Corrective Action (RBCA) Standard. The model assumes that contaminant vapor transport is by gaseous diffusion, that the contamination source is constant and nondiminishing, and that equilibrium conditions exist. Buildings with basements or subterranean structures, however, can create pressure gradients that initiate advective transport, which requires different assumptions than those presented in the following discussion. With these limitations in mind, the indoor air concentration of a contaminant (C_i) is computed as:

$$C_i = \frac{\text{Slab} * \text{Flux} * A}{V * E} = \frac{\text{Slab} * \text{Flux}}{\text{Height} * E}$$

C_i is the concentration in the room in µg/m^3.
Slab is the slab attenuation factor (unitless).
Flux is the contaminant flux into the room (µg/hr-m^2).
A is the room floor area in m^2.
V is the room volume in m^3.
Height is the room height in m.
E is the indoor air exchange rate (exchanges per hour, 1/hr).

As you can see, the indoor air concentration is dependent upon the flux, the height of the room, and the indoor air exchange rate with outdoor air. For residential buildings, an indoor air exchange rate of one room volume every 2 hours (or 12 exchanges per day) is typically used. Commercial buildings typically have faster exchange rates, which are obtainable from the architect or engineer.

In addition, the vapor flux is considered to be attenuated by the presence of a concrete slab or wall. The net result of the concrete is to decrease the soil vapor flux. For new or relatively new concrete slabs, an attenuation factor of 0.01 is typically used on the basis that approximately 1 percent of the slab consists of cracks that offer unrestricted vapor flow. For older slabs in poor condition, an attenuation factor of 0.10 gives a more conservative estimate of the reduction in vapor flux caused by the slab.

As described previously, the upward contaminant vapor flux into a building is computed by Fick's first law, using the gaseous diffusivity, corrected for porosity.

$$\text{Flux} = \frac{D_e * \Delta C_{sg}}{X} * 1{,}000$$

Flux is the rate of movement of a compound per unit area (µg/hr-m^2).
De is the effective diffusion coefficient in the vadose zone (m^2/hr).
ΔC_{sg} is the contaminant concentration gradient in the soil vapor (µg/L).
X is the depth below the surface (m).

For most cases, the contaminant concentration in the room air is negligible compared with the soil vapor concentration, so the measured soil vapor concentration (C_{sg}) can be plugged directly into the equation.

Calculation of the flux requires knowledge of the soil vapor concentration. In the absence of actual soil vapor data, soil vapor concentrations can be calculated from soil and groundwater data, assuming equilibrium conditions, using equations based upon Henry's law constants and soil-to-water partitioning constants. These equations (summarized below) can be found in the 1995 ASTM RBCA standard.

- **Calculating Soil Vapor Concentration from Soil Data**

  The soil vapor concentration (C_{sg}) is computed based upon the equilibrium partitioning between the soil, moisture, and vapor phases as:

$$C_{sg}(\mu g/L) = \frac{H * C_{soil} * BD}{P_w + (K_s * BD) + (H * P_a)} * 1{,}000$$

C_{soil} is the concentration in the soil for the contaminant of concern (e.g., benzene). If the concentration values for the specific contaminant are not known, then the value may be estimated from its concentration in the fuel product as the mole fraction times the product concentration. For example, the concentration of benzene in soil may be estimated from TPH-gasoline data as the mole fraction of benzene (2.5 percent) times the TPH concentration.

- **From Groundwater with Floating Free Product or Soil with Free Product**

  It is assumed that the vapor immediately above the groundwater is in equilibrium with the free product, based upon the contaminant's mole fraction and vapor pressure:

$$C_{sg}(\mu g/L) = \frac{VP * MW * MF}{RT} * 1{,}000{,}000$$

- **From Groundwater with Dissolved Contamination (No Free Product)**

  It is assumed that the vapor concentration immediately above the groundwater is in equilibrium with the groundwater, and the concentration is given by the water concentration times the dimensionless Henry's law constant:

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$$C_{sg}\ (\mu g/L) = (C_{water} * H)$$

For the preceding equations:

VP is the contaminant vapor pressure in atmospheres.
MW is the molecular weight of the contaminant in g/mole.
MF is the mole fraction of the contaminant in the free product.
RT is the universal gas constant times temperature equivalent to 22.4 µL/µmole at 0 °C & 24 µL/µmole at 20 °C.
H is the dimensionless Henry's law constant.
C_{soil} is the contaminant soil concentration in mg/kg.
C_{water} is the contaminant water concentration in mg/L.
BD is the bulk density in g/cm^3.
P_w and P_a are the water porosity and air porosity, respectively (unitless).
K_s is the soil water distribution coefficient in cm^3/g.

Using these equations, it is possible to compute the maximum soil concentrations, water concentrations, and soil vapor concentrations versus depth from the surface that will yield room concentrations that meet acceptable EPA levels. These values are shown in the following table for benzene.

Depth bgs (ft)	Soil (µg/kg)	Water (µg/L)	Soil Vapor (µg/L-vapor)
5	20	120	25
10	40	240	50
20	80	480	100
50	200	1200	250
100	400	2400	500

bgs = below ground surface

Assumptions used in computing the tabulated values:

Air porosity:	0.2
Total porosity:	0.3
Bulk density:	2.0 (g/cm^3)
Slab factor:	0.01
Exchange rate:	0.5 (1/hr)

Acceptable room concentration for benzene at the 1 in 1 million cancer risk level: 0.24 µg/m^3.

This summary demonstrates that, based upon the assumptions used in the upward risk calculation, only modest concentrations in the soil, soil vapor, or water are required to result in room air concentrations that fail the acceptable levels. For some compounds with lower acceptable room concentrations (e.g., vinyl chloride ~11 pptr), the allowable soil and groundwater values can approach laboratory detection levels.

You must recognize, however, that the equations used to calculate the soil vapor concentration from soil phase data, water phase data, or free product assume equilibrium partitioning between the phases. Equilibrium partitioning is obtained only if a system is well mixed. This condition is very rarely accomplished in the subsurface, because there are no blenders or stirrers present to homogenize the vapor, soil, and groundwater.

A common analogy used to illustrate this mixing concept is the preparation of a salad dressing using oil and vinegar. When the ingredients are initially added to a container, they fall into separate layers; the container must be shaken to mix the ingredients. If the container is not shaken, the oil and vinegar mix very slowly, "equilibrium is not reached," and the resulting salad dressing does not taste very good.

In addition to the issue of equilibrium partitioning, the equations do not account for other processes that are operative in the vadose zone, such as bioattenuation, advective flow, and soil heterogeneity.

For these reasons, calculated soil vapor concentrations generally do not accurately represent actual soil vapor concentrations, and, in the case of fuels, calculated values often overestimate actual soil vapor concentrations by 10 or 100 times. The potential error in the calculated vapor flux introduced by the incorrect vapor concentration is likely to be greater than errors introduced by other parameters, such as porosity. Thus, in the event that a site fails the upward risk calculation from existing soil or water data, direct measurement of actual soil vapor concentrations near the surface is likely to be the easiest and fastest way to verify whether concentrations will pass acceptable levels.

Which Soil Vapor Method to Use?

A number of states are currently trying to decide which soil vapor method is the best one to employ for determining upward migration risk. Three methods are commonly employed to measure soil vapor contamination: active, passive, and surface flux chambers. A full discussion of the various measurement techniques is beyond the scope of this article. I will, however, present some summary thoughts here.

- **Active soil vapor methods** (withdrawal of the soil vapor from the subsurface and subsequent analysis of the vapor) give concentration data, which are required for calculating the contaminant flux using Fick's first law. Further, vertical profiles of the soil vapor concentrations can be obtained to aid in determining the direction and magnitude of the flux. Active soil vapor data can be collected and measured in real time, enabling decisions to be made in the field.

  The problem most often raised with active soil vapor data is whether the concentrations measured at any given time and day are representative of normal conditions (i.e., how "stable" are active soil vapor data?). Variations caused by factors such as barometric changes or building pressures are known to exist; however, they are difficult to quantify. These effects are known to lessen with increased depth below the surface (or away from the building), and it is generally considered that data collected from 3- to 5-foot depths are fairly stable.

- **Passive soil vapor methods** (burial of an adsorbent in the ground with subsequent retrieval and measurement of the adsorbent) provide a time-integrated measurement and, therefore, reduce the uncertainty associated with the temporal variations described above. Passive methods also are generally easier to

implement. However, passive soil vapor methods yield soil vapor data only in terms of mass, not concentration. Therefore, a "conversion" of the data from mass units to concentration units needs to be performed prior to determining the health risk. The primary assumption required in making the conversion from mass to concentration is the volume of vapor that passed by the buried adsorbent during the burial time period. There is no easy way to estimate this volume. Thus, the resulting values have a high degree of uncertainty. Further, because passive collectors are buried so close to the surface (generally 2 feet or less), the measured values are highly influenced by any near-surface effects.

- **Surface flux chambers** are enclosures that are placed directly on the surface (e.g., ground, floor) for a period of time (e.g., generally a few hours to a few days), and then the resulting contaminant concentration in the enclosure is measured. By dividing the measured concentration by the incubation time, a direct value for the flux is determined. This method offers advantages over the other two methods because it yields the actual flux of the contaminant out of the ground, which eliminates some of the assumptions required when calculating the flux by Fick's first law (e.g., effective diffusivity, influence of a cement slab). This technique, however, is not as fast or easy to implement as the other methods, is subject to near-surface effects (e.g., the stability of the measured fluxes), and provides no clues about what may be "hiding" below.

The bottom line is that each of the soil vapor methods has advantages and disadvantages for determining upward vapor risk; however, all are potentially applicable. Which method to use on a given site depends on the site-specific goals and the logistical limitations. In my view, the active soil vapor method offers less uncertainty and more versatility than the other methods in most situations.

A Protocol for Determining the Upward Migration Risk by Soil Vapor Measurement

Based on the discussion above, I recommend the following procedure for collecting soil vapor data near the surface for the purpose of determining the upward vapor flux into a room or enclosure.

1. Collect active soil vapor data at 5 feet below ground surface (bgs) at the location of highest contaminant concentration. If the location of highest contaminant concentration is unknown, collect soil vapor data at 5 feet bgs spatially, across the site, to identify the location of highest concentration.
2. Calculate the health risk as outlined above. If the risk calculation indicates that upward vapor poses no threat to human health, then this pathway may be eliminated as an exposure route, assuming the plume remains stable or diminishes.
3. If the risk calculation indicates that upward vapor migration may pose a threat to human health, then collect soil vapor samples at 5 feet bgs at the corners of the building or room to determine the spatial variation of the flux across the area of concern.
4. Recalculate the health risk using the average flux from all of the soil vapor locations. If the risk calculation indicates that upward vapor migration poses no threat to human health, then this pathway may be eliminated as an exposure route, assuming the plume remains stable or diminishes.
5. If the risk calculation indicates that upward vapor migration may pose a threat to human health, then repeat steps 1 through 4 at 3 feet bgs.
6. If the risk calculation still indicates that upward vapor migration may pose a threat to human health, then the soil vapor concentration at a shallower depth (i.e., <3 feet bgs) needs to be determined. Measured concentrations this close to the surface can be greatly influenced by soil vapor collection technique and atmospheric air infiltration caused by barometric pumping. Thus, "time-averaged" data may be appropriate to ensure that the measured soil vapor values are representative.

Time-averaged data may be collected using either active or flux chamber soil vapor techniques. With active methods, a sampling tube should be left in the ground and the soil vapor analyzed multiple times to demonstrate consistency in concentrations over time. I recommend that data be collected at 1-foot intervals and from 1 to 3 feet bgs to ensure that vertical variations are characterized adequately. Alternatively, a flux chamber may be emplaced to measure the flux directly. The time duration for the flux chamber should be long enough to enable adequate measurement of the contaminant.

For subsurface enclosures, such as basements or utility trenches, the same protocol can be used; however, soil vapor samples should be collected from 3 to 5 feet below the floor, rather than below ground surface. It may also be necessary to consider the potential flux through the walls as well as through the floor. In this case, the total flux into the room would be equal to the flux through the floor times the combined surface area of the floor and the walls. Alternatively, a soil vapor measurement may be made on each side of the wall (3 to 5 feet away from the wall) so that the flux through the wall can be computed separately. The total flux into the room would then be computed by summing the individual fluxes through the floor and walls.

Soil vapor data should be collected and analyzed using protocols that satisfy the local regulatory agency. Required detection levels are contaminant-specific and depend on acceptable room air concentrations. For example, for benzene, vinyl chloride, and tetrachloroethylene, detection levels of 0.1 µg/L-vapor (~30 ppbv), 0.05 µg/L-vapor (20 ppbv), and 1.0 µg/L-vapor (144 ppbv), respectively, are required. ■

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