Investigation and Remediation

The Downward Migration of Vapors

by Blayne Hartman

*I*n the last issue of LUSTLine,*we discussed potential risk to human health with respect to the upward migration of vapors into overlying structures. In that scenario, the health risk of concern was the inhalation of contaminant vapors from room air. This risk pathway has gained increasing attention over the past several years and has been addressed in a number of published documents, including the 1995 ASTM Risk-Based Corrective Action (RBCA) document.*
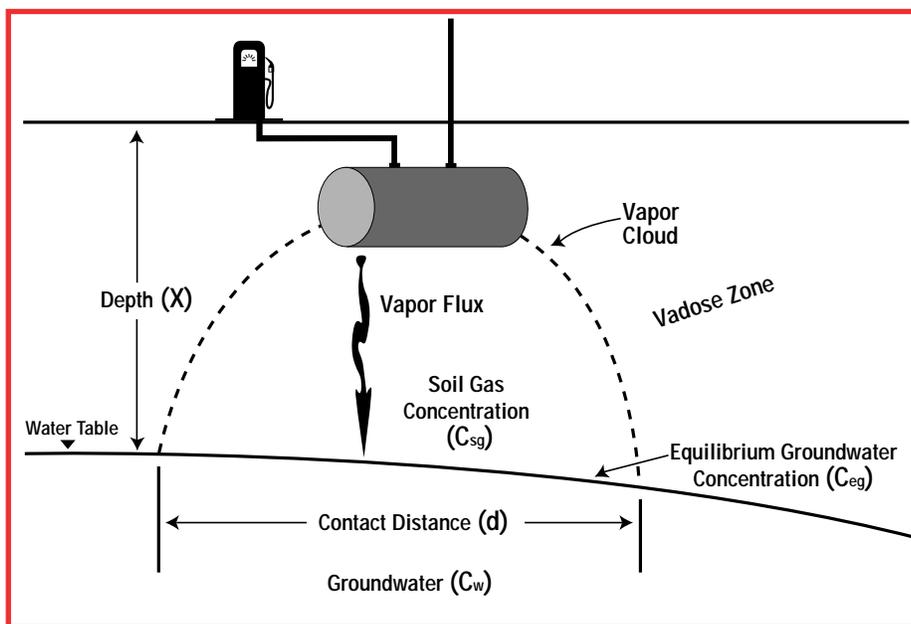
In contrast to the upward vapor risk, potential risk to groundwater associated with the downward migration of vapors has been relatively ignored. The principal reason for this is that it is generally assumed that contaminated soil vapor is the result of contamination in the soil. Therefore, there is the perception that the real risk to groundwater is not the soil vapor, but the contaminant in the soil that makes its way to the groundwater.

So why worry about risk associated with downward vapor migration? Because, over the past few years, more and more sites have been discovered that have high contaminant concentrations in the soil vapor but no corresponding soil contamination. In this article, I'll explore this phenomenon. Is it a problem? If it is, then when should we start to worry?

Vapor Clouds

How can a site have contaminated soil vapor with no corresponding soil contamination? One explanation is that the contamination entered the vadose zone as a vapor. Many compounds in fuels and many chlorinated solvents have relatively high vapor pressures and vapor densities three to six times greater than those of air. Because of these physiochemical properties, vapors may emanate from containers holding gaseous or liquid products that are used or stored in an indoor confined space or from pipe joints and then sink to the floor. If air flow is restricted, such as in a closed room, the dense vapors can penetrate the concrete floor and enter the upper vadose zone.

Such bulk-dense vapor movement will continue to drive the vapor downward through the vadose zone until it is diluted to low enough concentrations (<1 percent) that density is no longer an important factor in the vapor transport process. "Vapor clouds" reaching tens of feet into the uppermost vadose zone have been documented and attributed, at least in part, to density-driven flow. Business and commercial operations that are most susceptible to this situation include perchloroethylene (PCE) washing units at dry cleaners, vapor degreasers at machine shops, and spray booths at inking or painting facilities where chlorinated solvent-based inks or paints are used. As far as USTs are concerned, underground vent pipes are typically filled with high concentrations of MTBE and

Figure showing: Depth (X), Water Table, Vapor Cloud, Vadose Zone, Vapor Flux, Soil Gas Concentration (C_{sg}), Equilibrium Groundwater Concentration (C_{eg}), Contact Distance (d), Groundwater (C_w)

gasoline vapors that can conceivably migrate through pipe joints and create vapor clouds.

As vapor clouds are discovered in the vadose zone at more and more sites, we must try to determine whether they are a potential risk to groundwater. If they are, at what soil vapor concentrations should we start to worry? I'll start with a quick review of the basic processes by which vapors move through the vadose zone. (Refer to *LUSTLine* Bulletin #27 for a more complete discussion.) Then I'll discuss, compute, and summarize in a table the potential risk that results from downward vapor migration. I'll conclude with a recommended protocol for collecting soil vapor data for assessing the downward vapor risk. Like my article

on the upward migration of vapors, this one will also be somewhat technical; however, I have attempted to keep the subject understandable and have refrained from including so many "daunting" equations.

How Do Contaminants Move 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. The process of 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

an important factor in the movement of soil vapor. This phenomenon is especially true where vapors are near the ground surface, where atmospheric pressure variations come into play, or near buildings, which can create pressure gradients because of differential heating or density-driven flow.

The second type of transport process, gaseous diffusion, refers to the motion of the contaminants by molecular processes through a non-moving vapor column. Gas diffusion is the primary transport mechanism for contaminants in the vapor phase through the vadose zone down to groundwater. Contaminant transport by gaseous diffusion is described by Fick's first law as:

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

Where:

- 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 (i.e., 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.

How Fast Do Contaminant Vapors Move?

An approximation of the mean distance that contaminant vapors can move by gaseous diffusion can be made as:

$$\text{Distance} = (2 \times D_e \times t)^{1/2}$$

Where:

- D_e is the effective diffusivity.
- t is time.

Through the Vadose Zone
The effective diffusion coefficient for contaminant vapor transport through the vadose zone is the gaseous diffusion coefficient corrected for soil porosity. For many vapors, the gaseous diffusion coefficient is approximately 0.1 cm²/s. The effect of soil porosity varies depending on the type of soil. Several equations are available to calculate the effect of air-filled and total porosity on the diffusivity. A conservative approximation is that the porosity reduces the gaseous diffusivity by a factor of 10. Thus, for vapors, D_e can be approximated as 0.01 cm²/s.

The mean distance that contaminant vapors can move through the vadose zone in a year, assuming no adsorption, can be estimated as:

$$\text{Distance} = (2 \times 0.01 \text{ cm}^2/\text{s} \times 31{,}536{,}000 \text{ s})^{1/2}$$
$$\sim 800 \text{ cm} = \sim 25 \text{ feet.}$$

This calculation shows that contaminant vapors can move long distances through the vadose zone in a short period of time. Within a few years, vapor contamination can move laterally underneath a neighboring room or building, or downward to the groundwater surface.

Into or Out of Groundwater
In contrast to movement through the vadose zone, the movement of contaminant vapors into or out of groundwater is controlled by the rate at which vapors partition into and move through the liquid. Because groundwater movement is so slow, the water interface remains relatively undisturbed (laminar flow), and vertical mixing of the water is minimal. The primary exchange process is again molecular diffusion, but in this case the exchange rate is controlled by liquid diffusion, not gaseous diffusion. A general value for the liquid diffusion coefficient for compounds is approximately 0.00001 cm²/s. Using the same factor of 10 reduction to account for soil porosity, D_e for most liquids can be approximated as 0.000001 cm²/s.

The mean distance that contaminants can move into and through the groundwater in a year, assuming no absorption, can be estimated as:

$$\text{Distance} = (2 * 0.000001 \text{ cm}^2/\text{s} \times 31{,}536{,}000 \text{ s})^{1/2}$$
$$\sim 8 \text{ cm} = \sim 3 \text{ inches}$$

These calculations show that although contaminant vapors can move through the vadose zone relatively quickly, they partition into and move through groundwater extremely slowly. The reverse situation is also true; the partitioning of contaminants out of groundwater into the soil vapor is also extremely slow and very unlikely to reach the equilibrium values predicted by Henry's law constants. The reason equilibrium is not reached is because the mixing processes between the soil vapor and the groundwater are extremely slow (i.e., there are no blenders or mixers in the vadose zone mixing things up).

Can the Downward Transport of Vapors Contaminate Groundwater?

The calculations summarized in the preceding section indicate that although contaminant vapors can move quickly down to groundwater, they do not partition into the groundwater very quickly. Using a modification of Fick's first law, the transfer of a contaminant from the soil vapor into the groundwater can be estimated. The flux is calculated as:

$$\text{Flux} = K_L (C_{eq} - C_w)$$

Where:

- K_L is the gas exchange coefficient (length/time).
- C_{eq} is the equilibrium water concentration at the interface.
- C_w is the background groundwater concentration.

C_{eq} represents the groundwater concentration in equilibrium with the overlying soil vapor at the interface between the soil gas and groundwater. It is easily calculated from the measured soil gas concentration as:

$$C_{eq} = C_{sg}/H$$

Where:

- H is the dimensionless Henry's law constant.
- C_{sg} is the soil vapor concentration.

The gas exchange coefficient has units of velocity and essentially represents the distance that contaminants move vertically through the

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groundwater per unit time. This exchange coefficient is primarily dependent upon two transfer processes: dispersion caused by advective mixing and molecular diffusion at the interface. A full discussion of the relative importance of these processes is beyond the scope of this article; however, for groundwater velocities less than 100 ft/yr and soil grain sizes less than 0.5 mm, diffusional transport dominates over dispersion and K_L can be approximated as:

$$K_L = 1.1 \times (D_e \times d/v)^{1/2}$$

Where:

- d is the horizontal distance (downgradient) over which the soil vapor plume and groundwater are in contact.
- v is the horizontal groundwater flow velocity.

Using this equation to estimate the gas exchange coefficient, estimates of the expected contaminant concentration in the groundwater that results from contamination in the overlying soil vapor can be calculated. The computed groundwater values are dependent on the depth into the groundwater that the contamination is mixed. The assumption used in these calculations is that the typical well-purging process mixes (homogenizes) the contamination in the groundwater uniformly over the entire well screen interval. Table 1 summarizes expected groundwater concentrations (C_w) for various equilibrium concentrations (C_{eq}).

In order to use Table 1, you must convert equilibrium groundwater concentrations (C_{eq}) into the corresponding soil vapor concentrations. Remember that the corresponding soil vapor values will vary for different compounds because Henry's law constants are compound-specific. Table 2 summarizes the soil vapor concentrations (C_{sg}) for various equilibrium concentrations (C_{eq}) for four common compounds (at 20°C).

Table 1 shows that for equilibrium concentrations up to 500 µg/L, the resulting groundwater concentration after 5 years will be low if liquid molecular diffusion is the only

Table 1

Expected contaminant concentration in groundwater for various equilibrium concentrations (C_{eq}) at the groundwater interface.

Calculations assume equilibrium partitioning at the soil vapor/groundwater interface, transfer by molecular diffusion only ($D_e = 10^{-6}$ cm^2/s), and uniform mixing of the contaminant into the groundwater over a well screen interval of 5 meters.

C_{eq} (µg/L)	Flux (µg/yr-cm^2)	1 yr GW Conc (µg/L)	5 yr GW (µg/L)
10	0.08	0.006	0.28
20	0.16	0.01	0.55
30	0.24	0.02	0.83
40	0.32	0.03	1.1
50	0.40	0.03	1.4
100	0.80	0.06	2.8
500	4	0.3	14
1000	8	0.6	28

Table 2

Soil gas concentrations (C_{sg}) for four common compounds for various equilibrium groundwater concentrations (C_{eq}) at the groundwater interface (values at 20°C).

C_{eq} (µg/L)	MTBE Csg (µg/L)	Benzene Csg (µg/L)	PCE Csg (µg/L)	Vinyl Cl Csg (µg/L)
10	0.1	2	6	10
20	0.2	4	12	20
30	0.3	6	18	30
40	0.4	8	24	40
50	0.5	10	30	50
100	1	20	60	100
500	5	100	300	500
1000	10	200	600	1000

exchange process. Table 2 shows that C_{eq} values of 500 µg/L correspond to soil vapor concentrations exceeding 100 µg/L for most compounds. In most situations, contaminant vapor concentrations at the groundwater surface are far below 100 µg/L, and the contact time of the vapor contamination with groundwater is less than 5 years (the time it takes the groundwater to move across the site).

Thus, in areas with low groundwater flow velocities, contamination of the groundwater by downward vapor transport is not likely to be significant. In areas with higher groundwater flow velocities (>100 ft/yr), large variations in the water table, coarse soil, or high recharge, the gas exchange rate may be higher because of dispersive mixing. Groundwater contamination by vapor transport could be significant.

Does the conclusion that downward vapor transport into groundwater is a slow process make intuitive sense? The concept can be illustrated if you think of what is happening with air bubbles in a fish tank. If the air bubbler is turned off, the fish will go to the surface to gulp air; without the bubbles, they'll eventually die. Air contains nearly 21 percent oxygen, so there is plenty of oxygen sitting on the surface of the fish tank water. However, despite the large supply of oxygen at the surface, the transport mechanism into the water (liquid diffusion) is too slow across the laminar interface to supply enough oxygen to the water for the fish to live. So, the air must be bubbled through the water to increase the oxygen transfer process (by creating turbulent mixing).

Protocol for Determining Risk Caused by the Downward Migration of Vapors

With Table 1 in hand, we can make reasonable judgments on whether measured soil vapor concentrations are likely to be a threat to groundwater. In order to use Table 1, we need to collect soil vapor data using the active soil gas technique and collecting data from as close to the groundwater interface as possible. (See the last issue of *LUSTLine* for a review of the different sampling methods.) In some situations (e.g., where the source of

the soil vapor contamination is unknown or the depth to groundwater is uncertain), vertical profiles of the soil vapor may prove useful for determining the source of the contamination and the values at depth.

Based on the discussion presented in this article, I recommend the following procedure for collecting soil vapor data that will be used to determine risk to groundwater as a result of downward vapor flux:

1. Collect active soil vapor data near the water table at the location of highest contaminant concentration. If the location of highest contaminant concentration is unknown, collect soil vapor data at 5 feet below ground surface (bgs) across the site to identify the location of highest concentration.

2. Calculate C_{eq} from the measured soil vapor values using the Henry's law constant for the contaminant of concern (or use Table 2). Use Table 1 to estimate the impact to groundwater. If Table 1 indicates that downward vapor poses no threat to groundwater, then this risk pathway need not be considered further, assuming the source of the soil vapor contamination is mitigated.

3. If Table 1 indicates that downward vapor may pose a threat to groundwater, then collect additional soil vapor samples near the water table across the entire soil vapor plume.

4. Calculate an average C_{eq} for the entire plume. Use Table 1 to estimate the impact to groundwater. If Table 1 indicates that downward vapor poses no threat to groundwater, then this risk pathway need not be considered further, assuming the source of the soil vapor contamination is mitigated.

5. If Table 1 still indicates that downward vapor may pose a threat to groundwater, then both the soil vapor contamination *and* the contamination source likely need to be mitigated. ■

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