

Investigation and Remediation

The Great Escape (from the UST)

by Blayne Hartman

[Editor's Note: This is the second in a series of articles reviewing some of the physical/chemical properties that are commonly used in environmental assessment and remediation. This article will focus on the property of vapor pressure and how to use it for estimating vapor concentrations in the vadose zone.]

Based on the enthusiastic responses I received to the quiz in the last article on Henry's law, let's start with another quiz:

A site with USTs that contain gasoline has MTBE contamination in the underlying groundwater; however, the cause of the groundwater contamination is not clear. No liquid spills or releases have been recorded or detected, no soil contamination has been detected, and no upgradient sources of MTBE exist. You conduct a soil vapor survey to look for potential vapor-phase MTBE contamination and find nothing. What do you advise your client (a potential buyer of the property) to do?

- There are no on-site MTBE sources of groundwater contamination, so the contamination must be from somewhere else. Buy the property.
- Tell the client not to buy the property and then buy it yourself.
- Question the accuracy of the soil vapor data.
- Retest the soil vapor for different compounds.

Need a hint? Well, it's probably not (a) or (b) because then I would have nothing to write about. Need another hint? It has something to do with vapor pressure (the topic of this article).

To choose the correct answer to this quiz, we need to know the answers to a couple of key questions regarding the potential source of the MTBE contamination in the soil vapor and the potential for MTBE vapor to contaminate groundwater:

- What is the concentration of the MTBE in vapor escaping from an UST containing gasoline?
- What would be the resulting groundwater concentrations if that same vapor contacted groundwater and reached equilibrium with the groundwater?

Step 1 – Determine the Vapor Pressure of MTBE in the Tank Headspace

Since the concentration of MTBE in the escaping vapor will be the same as the concentration of MTBE in the vapor in the tank above the gasoline, the first thing we need to do is compute the concentration of MTBE in the tank headspace. To perform this calculation, we need to consider the vapor pressure of each compound, which gives us a perfect reason to review the concept of vapor pressure.

Vapor pressure is the pressure that a compound exerts in the airspace above the pure compound. Stated another way, vapor pressure is a measure of how a com-

pound distributes, or partitions, itself between its pure form (solid or liquid) and the airspace above it. The higher the vapor pressure, the more a compound prefers to be in the vapor phase (i.e., the more volatile the compound). Some compounds have such high vapor pressures that they evaporate before our eyes (e.g., acetone, or gasoline on warm days). Generally, when we speak of volatile organic compounds (VOCs), we are referring to compounds with vapor pressures that exceed 1 millimeter (mm) of mercury (Hg) at temperatures that are normally encountered (15°C to 20°C).

Vapor pressures have been measured empirically (i.e., in the laboratory) for a wide variety of compounds and are tabulated in many reference books. They can be expressed in many different units. The most common are atmospheres (atm), inches of mercury (in. Hg), or millimeters of mercury. For your reference, there are 760 mm Hg to 1 atm and 30 in. Hg to 1 atm.

For a mixture of compounds such as gasoline, the pressure of each compound in the overlying vapor (e.g., MTBE, benzene, hexane) is equal to its fraction in the mixture multiplied by its individual vapor pressure:

$$P_i = VP * MF$$

where: P_i is the pressure of a compound in the overlying vapor;

VP is the vapor pressure of the pure compound; and

MF is the mole fraction of that compound in the mixture.

Step 2 – Convert Pressure into Concentration

The next step is to convert the amounts of a compound in the vapor from pressure units to concentration units. To make this change, we have to go back to a fundamental concept that we all learned (or were supposed to learn) in freshman chemistry, the good ol' ideal gas law:

$$PV = nRT$$

where: P is pressure (in atm);

R is the universal gas constant (0.0821 L-atm/^oK-mole);

T is temperature in ^oK (^oK = ^oC + 273);

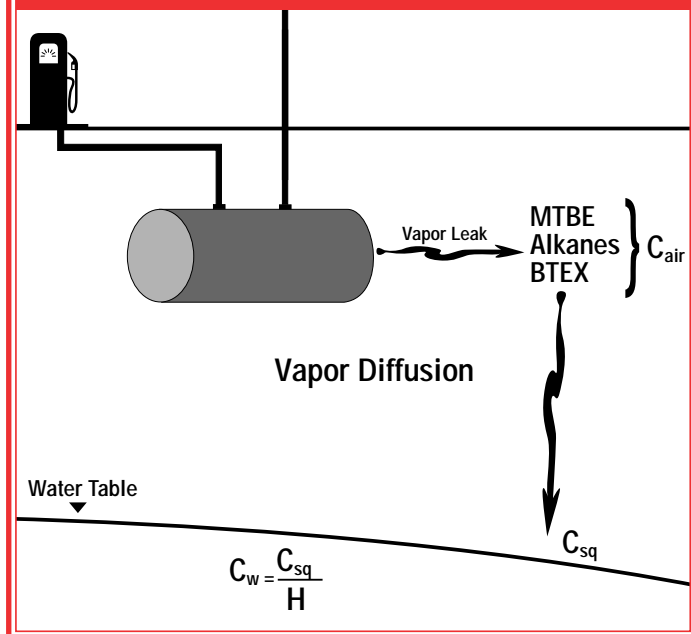
n is moles of a compound; and

V is volume in liters.

By rearranging this expression, we can convert pressure into concentration:

$$P/RT = n/V$$

Potential Pathways of Escaped UST Vapors to Groundwater



Note that moles (n) multiplied by the molecular weight of a compound gives mass (in grams) and V is volume, so the ratio (n/V) is equivalent to concentration.

Putting it all together, the concentration of a compound in the headspace can be computed from its vapor pressure, molecular weight, and mole fraction as:

Concentration in the headspace (C_{air}) = $VP * MW * MF / RT$

where: C_{air} is in units of grams per liter (g/L);

VP is the vapor pressure of the pure compound (in atm);

MW is the molecular weight of the compound (in g);

MF is the mole fraction of the compound in the mixture; and

RT is the universal gas constant times temperature (~24 L-atm/mole at 20°C).

Using the above equation, the concentrations of various compounds in the headspace (C_{air}) in an UST that contains gasoline can be easily calculated (Table 1). You can see that the headspace is dominated by the alkanes

Table 1. Summary of relevant physical properties and calculated airspace concentrations of various compounds in gasoline. Mole fractions of the various compounds were selected to represent an "average gasoline." An average molecular weight was used for the lower alkanes (C4-C8). Vapor pressures have been rounded off for simplicity.

	VP (atm)	MW	MF	C_{air} ($\mu\text{g/L}$)
Benzene	0.1	78	0.025	7,800
MTBE	0.3	88	0.125	130,000
Lower alkanes	0.2	100	0.50	400,000

and MTBE, but benzene, due to its lower mole fraction and vapor pressure, makes up a relatively small fraction.

The key point to recognize from the values in Table 1 is that if there are vapor leaks from an UST—from loose bungs, loose fittings on vapor return lines or vent pipes, or pinhole leaks—the concentration of the vapor in the vadose zone immediately outside the tank (i.e., the soil vapor) will contain large amounts of alkanes and MTBE, but relatively small amounts of benzene (I'll leave it to you to calculate the relative amounts of the other common aromatics).

Step 3 – Determine the Equilibrium Groundwater Concentration

Now let's allow the escaped vapor to impinge on groundwater. What's the resulting groundwater concentration? Well, flush with your knowledge after reading the article on Henry's law in the last issue, you know that the resulting equilibrium groundwater concentration can be easily computed from the vapor concentration using the dimensionless Henry's constant:

$$H = C_{air} / C_{water} \text{ or } C_{water} = C_{air} / H$$

Table 2 summarizes the calculation of the groundwater

Table 2. Equilibrium water concentrations for several compounds in contact with vapors escaping from an UST with gasoline. Values for Henry's constants and resulting water concentrations have been rounded off for simplicity.

	C_{air} ($\mu\text{g/L}$)	H	C_w ($\mu\text{g/L}$)
Benzene	7,800	0.2	40,000
MTBE	130,000	0.02	6,500,000
Lower alkanes	400,000	50	8,000

concentration in equilibrium with the escaped vapor.

Taken alone, the numbers shown in Table 2 indicate that enormously high concentrations of MTBE could be created in the groundwater because of escaping vapor. Don't panic! The fact that this calculated value is so much higher than values we observe in groundwater is proof that our simple calculation is not representative. Why?

Keep in mind that these calculations assume that equilibrium between the phases exists. While equilibrium concentrations may be likely for the partitioning of compounds from the gasoline into the tank vapor, they are extremely unlikely for the partitioning of compounds into the groundwater from the vapor because of the extremely slow process of contaminant transport into groundwater (as discussed in the LUSTLine #28 article, "The Downward Migration of Vapors").

In addition, these calculations assumed that the concentration of the vapor impinging on groundwater was identical to the concentration of the tank headspace. This scenario is extremely unlikely because processes operative in the vadose zone (e.g., dispersion, sorption, biodegrada-

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tion) are likely to create significantly lower vapor concentrations as the vapor travels from the tank leak to groundwater.

The more reasonable conclusions to be drawn from these calculations are that if a vapor leak from an UST containing gasoline exists:

- The lower alkanes (C4 through C8) will remain in the soil vapor.
- If water is around, MTBE will preferentially partition into the water (i.e., soil moisture or groundwater).
- Benzene will exist in both the soil vapor and water but will not be the major contaminant in either phase.

In areas with shallow groundwater, high rainfall, or other sources of flowing water in the vadose zone (e.g., irrigation), MTBE vapor could be a contributor to groundwater contamination. In areas with deep groundwater and not much rainfall, the MTBE transfer rate from the vapor is likely to be too slow to cause an appreciable effect.

Now Back to the Quiz

Since no MTBE was detected in the soil vapor, and no other sources for MTBE were detected on the site, it appears that choice (a)—buy the property—would be the correct answer. But wait—if a vapor leak does exist, MTBE, due to its high affinity for water, might have already “left the scene of the crime” (the leak), while its companions in the escape (the alkanes), are still around. If all you did was measure the soil vapor for the MTBE, it is possible that a vapor leak exists, but that it was missed, because you failed to measure for the alkanes.

So what was the correct answer to the quiz? Choice (d)—retest for different compounds. You need to measure the alkanes in addition to MTBE to ensure the detection of tank vapor leaks and interpret the MTBE values (or lack thereof). Because all of the compounds escape together from the tank, high levels of alkanes in the soil vapor mean that MTBE must be escaping as well, even if it was not detected. If no MTBE is detected in the soil vapor at the same location where high levels of alkanes exist, it indicates that MTBE is being preferentially lost once in the vadose zone. For this scenario, vertical profiles of the soil vapor with depth to groundwater, as well as knowing the concentration ratio of MTBE to the alka-

nes in the soil vapor, will aid in the determination of whether MTBE vapor has impacted groundwater.

One last point to remember if you elect to measure the soil vapor. MTBE is often measured on a photoionization detector (PID) by EPA method 8020. While they are plenty sensitive to MTBE and the aromatics, PIDs are not particularly sensitive to many of the lower alkanes. So analysis of the soil vapor for the alkanes should be done with a flame ionization detector (FID) to ensure sufficient sensitivity.

Did you get the correct answer? This quiz was a tricky one, but I hope you enjoyed it. ■

Blayne Hartman is a regular contributor to LUSTLine. This article is taken from a presentation on physical/chemical properties that he gives as part of a training course on environmental geochemistry. For details on the course, either e-mail Blayne directly at bh@tegen.com, or check out the information on his Web page at <http://www.tegen.com>.

Oops...

In last issue's article titled "Oh Henry," the text describing the conversion from the dimensionless to dimensional form was incorrect. The conversion given was for computing the dimensional Henry's constant in units of atm-L/mole, not units of atm-m³/mole as printed. To compute the dimensional Henry's constant in units of atm-m³/mole, multiply the dimensionless Henry's constant by the universal gas constant (0.000082 atm-m³/mole-°K) times the temperature in degrees kelvin, which is equal to 0.0224 at 0°C and 0.024 at 20°C. ■