

The Vapor-Intrusion Pathway: Petroleum Hydrocarbon Issues

by Blayne Hartman

It has been four years since my last article in LUSTline on vapor intrusion (LL#53, September 2006). Since then, the vapor-intrusion pathway has continued to be a “box-office blockbuster” throughout the environmental community. Guidance documents have been released by the Interstate Technology and Regulatory Council (ITRC), ASTM, and more than 25 states. USEPA is preparing to update its guidance. However, these documents do not have sufficient distinctions between assessing the vapor-intrusion pathway for chlorinated hydrocarbons (e.g., CHCs, solvents such as TCE, PCE) versus petroleum-related hydrocarbons (e.g., PHCs). As a result, vapor-intrusion assessments are being conducted at many PHC sites when recent evidence suggests they may not be necessary or they are being conducted in a manner that is inappropriate for PHCs. State reimbursement fund managers are concerned that the costs for unnecessary or improperly conducted vapor-intrusion assessments could drain the coffers of already cash-poor funds. So what to do?

In this article, I begin with a brief regulatory update on the vapor-intrusion pathway and then address issues specifically related to PHCs to underscore the distinction between PHCs and CHCs. I refer you to my previous articles written in LUSTline #48 and #53 for more information on some of the topics covered herein.

Regulatory Updates

■ EPA-OSWER

As of this writing, the draft 2002 EPA-OSWER vapor-intrusion guidance has yet to be updated. In 2009, the Office of Inspector General recommended that OSWER identify the portions of the 2002 guidance that need to be updated. A report released by OSWER in August 2010 summarizes the areas they feel need to be updated, including:

- Emphasis on a multiple lines of evidence approach
- Generic attenuation factors for soil gas data
- Collection time period for indoor air samples (days or longer)

(See http://www.epa.gov/oswer/vaporintrusion/documents/review_of_2002_draft_vi_guidance_final.pdf.)

In a footnote, this document states that: “The generalized statements in this document may not pertain to the more readily degradable petroleum compounds.” OSWER will be releasing a draft version of the revised guidance in late 2011, and has committed to releasing a final version by November 2012.

Go to OSWER’s vapor-intrusion website for more information: <http://www.epa.gov/oswer/vaporintrusion>.

■ EPA-OUST

Recognizing the need for vapor-intrusion guidance specific to PHCs, OUST convened a technical workgroup to prepare guidance specifically for PHCs. The workgroup consists of EPA-OUST staff, regulators from several states, and representatives from industry. The group plans to assist with the development of a series of issue papers on various topics throughout 2011, draft guidance by November 2011, and a final version by November 2012 at the same time as the revised OSWER guidance.

Fundamental Differences Between CHCs and PHCs in the Vadose Zone

PHCs behave differently than CHCs in the vadose zone for two primary reasons. First, volatile petroleum compounds biodegrade readily in the presence of oxygen and soil moisture, whereas chlorinated compounds are typically more resistant to biodegradation. The biodegradability of volatile petroleum compounds provides an effective, naturally occurring contaminant-removal mechanism that inherently limits the migration of subsurface petroleum vapors in most cases.

Second, petroleum-hydrocarbon free product is lighter than water, while chlorinated-hydrocarbon free product is denser. These two key

properties (i.e., biodegradability and density) lead to significantly different subsurface source and transport behaviors that greatly influence whether vapors reach the near surface and intrude into structures.

One final difference to keep in mind is that PHC fuel products are mixtures of many hundreds of compounds, many of which are also present in common consumer products other than fuel. Chlorinated solvents are typically only one primary compound with perhaps some degradation compounds.

Biovapor: A New Predictive Model Incorporating Bioattenuation

The most common predictive model currently used for vapor-intrusion applications is the one-dimensional Johnson-Ettinger (J-E) model that USEPA and some states have formulated into Excel spreadsheets (http://www.epa.gov/oswer/riskassessment/airmodel/johnson_ettinger.htm). However, for PHCs this model tends to significantly overpredict the vapor-intrusion risk, primarily because there is no allowance for bioattenuation. Recently, the American Petroleum Institute (API) funded the creation of a new Excel version of the J-E model that incorporates bioattenuation, named Biovapor. Dr. George DeVaul of the Shell Development Company developed the original for-

mulation of this spreadsheet and the new Excel version was developed by GSI Environmental Inc.

Bio vapor is a user-friendly spreadsheet that allows prediction of indoor air concentrations and associated risk from soil-gas or groundwater data (a version for soil-phase data is being contemplated). It also performs the back calculation of calculating allowable soil-gas and groundwater concentrations from indoor-air screening levels.

The model does the calculations for the individual aromatic compounds (i.e., BTEX, naphthalene), as well as for aliphatic hydrocarbons. The model applies bioattenuation only when sufficient oxygen is present in the vadose zone (i.e., aerobic bioattenuation). It uses a mass-balance approach to ensure that the amount of bioattenuation does not exceed the amount of available oxygen.

Shaw Environmental reviewed the model formulations in January 2010 under contract to USEPA ORD. The formulations were found to be correct. EPA-ORD is planning to do its own evaluation of the model. Meanwhile, Robin Davis of the Utah Department of Environmental Quality has compared the model's predictions to actual field data at a number of sites and found the model's results to be slightly on the conservative side (in other words, the model often underpredicts the amount of attenuation and hence overpredicts the risk). (See Robin Davis's presentation at <http://www.neiwpcc.org/lustline/supplements.asp>.)

The model is currently available on the API website (www.api.org). Instructional classes/webinars are being planned and will be listed on the website.

Exclusion (Screen-Out Sites) Criteria

A primary problem we are facing with petroleum hydrocarbon sites is what criteria to use to decide if a site needs a vapor-intrusion assessment if there is not an obvious situation (e.g., fuel in a basement, petroleum odor in a structure). If existing OSWER Tier 1 screening distances of 100 feet are applied both vertically and spatially, combined with extremely low Tier 2 screening concentration, then the vast majority of

sites will be screened in for further investigation, and few sites will be screened out. While these criteria may be appropriate for recalcitrant compounds, they are not appropriate for PHCs in most scenarios.

Robin Davis has analyzed a database of about 170 sites from the United States, Canada, and Australia in an effort to determine screening criteria for PHCs sites (see *LUSTLine* # 61). Her primary goal was to determine what thickness of clean soil is necessary for various source concentrations to decrease to levels below

LNAPL on groundwater are also completely attenuated with as little as eight feet of clean soil between the source and the receptor, based on a more limited data set of 76 vapor samples collected at 16 different sites (Figure 2).

For soil vapor concentrations, Robin has previously written in two prior PHCs articles (*LUSTLine* #49 and #52) that if three to five feet of clean, aerobic soil (oxygen \geq 5%) exist, vapors are completely attenuated and the vapor-intrusion pathway will not be complete.

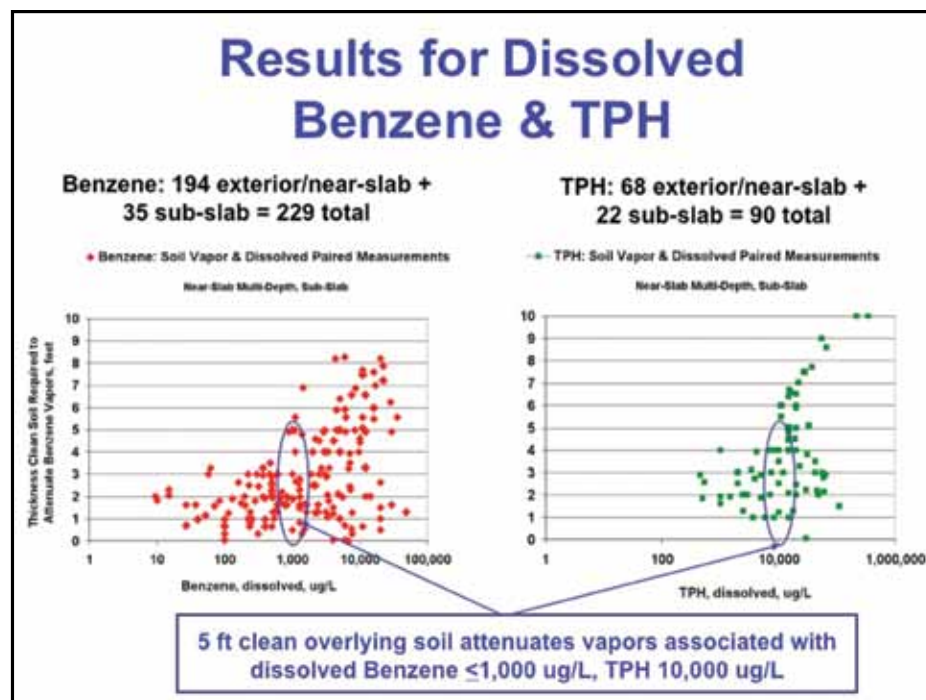


FIGURE 1. Thickness of clean soil required to attenuate benzene vapors from dissolved benzene in groundwater and to attenuate TPH vapors from dissolved TPH in groundwater (Robin Davis, 2010).

accepted risk thresholds due to bioattenuation.

She concluded that five feet of clean soil is all that is required between source and receptor to fully attenuate benzene vapors for dissolved concentrations of benzene up to 1,000 $\mu\text{g/L}$ and TPH vapors for dissolved TPH concentrations of up to 10,000 $\mu\text{g/L}$ (Figure 1), although the latter value is based on a smaller number of data points. Compare her benzene screening value of 1,000 $\mu\text{g/L}$ to the value that you would get from the current USEPA Tier 2 screening value of 1.5 $\mu\text{g/L}$: the difference is a factor of nearly 700 times!

Robin's database also shows that benzene vapors volatilizing from

These exclusion criteria for dissolved groundwater concentrations, free product, and soil-vapor concentrations are being discussed to screen out PHC sites from further vapor-intrusion assessment. California recently included some of them as screening criteria in their new draft *Leaking Underground Fuel Tanks (LUFT) Manual*.

Sampling Issues for PHC Sites

■ Indoor Air Sampling

The August 2010 OSWER review document mentioned previously discusses possibly collecting indoor air samples at the beginning of a vapor-

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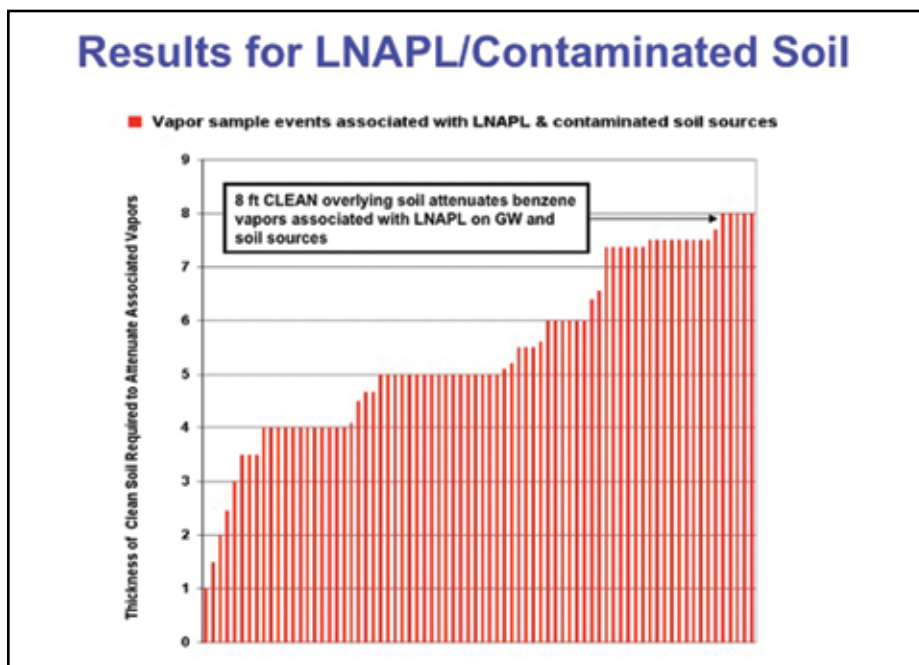


FIGURE 2. Thickness of clean soil required to attenuate benzene vapors from sites with LNAPL (Robin Davis, 2010).

intrusion investigation. Indoor air sampling for PHCs will likely be problematic and confuse, not clarify, the vapor-intrusion pathway for two primary reasons:

- Ambient (outdoor air) levels of benzene exceed the screening levels in most urban areas and can exceed the one in one million residential risk levels in many non-urban areas. Try explaining to the resident why his or her indoor air exceeds the allowable cancer risk value by 10 times, but that it is okay because the air is coming from the outside.
- The indoor sources for benzene and other PHC compounds are ubiquitous and nearly impossible to identify. My favorite recent example that demonstrates this point is Bloonie®, a balloon-making toy for kids. It contains obscene amounts of acetone, ethanol, benzene, and other goodies, and you would never think to remove it from a house if it was lying on the counter. (Read on for another example of a ubiquitous source of benzene in homes.)

In recent presentations at vapor-intrusion-related conferences, USEPA-OSWER is recommending longer indoor air sample-collection

periods, for periods as long as 7 to 30 days, based on lessons-learned from the radon literature. This is not a good idea for PHC sites because of the many potential indoor air sources. The procedure will result in numerous false positives, which will require a lot of time and expense to decipher the actual source of the detections.

For the above reasons, I rarely recommend collecting indoor air samples for PHCs at residences. For commercial/industrial receptors, collection of indoor air samples might be more suitable depending on the allowable indoor levels (allowable indoor levels can be 10 to 50 times higher than residential levels in some states).

■ Groundwater Sampling

Since the existing models and default attenuation factors do not account for bioattenuation, you can expect groundwater data to overpredict the risk for PHC compounds if there are no sources in the vadose zone. Hence, I rarely recommend that groundwater samples be collected for PHC vapor-intrusion assessment if soil-gas data can be collected (sometimes a shallow water table precludes the collection of soil-gas data). However, if groundwater data

already exist and indicate there is no risk, then it is probably a safe bet that the pathway is not of concern, and no further assessment is needed.

■ Soil-Gas Sampling

Sample Depth

PHC soil-gas sampling locations differ from those for CHCs owing to their different fate and transport behavior. For PHCs, if samples at deeper depths (>5ft bgs) exceed allowable values, shallower samples (<5ft bgs) should be collected for slab-on-grade structures, since bioattenuation may be active in the upper few feet and reduce values below acceptable levels. If on-site analysis is available, this decision can be made in real time. However, if on-site analysis is not available, I recommend that my clients collect a sample shallower than five feet bgs in the event that the deeper sample exceeds allowable levels.

The incremental cost of collecting the additional samples is negligible. You can withhold analyzing the shallower sample to see if results from the deeper sample indicate there is a need to analyze it. As far as the representativeness of shallow soil-gas concentrations, EPA-ORD has finished two studies documenting that the temporal variation of soil-gas concentrations as shallow as two feet bgs are less than 50 percent (Figure 3). (See <http://www.epa.gov/nerlesd1/cmb/pdf/270cmb07.pdf>.)

Oxygen data should always be collected to document the presence of the aerobic zone. Carbon dioxide and methane are also useful to confirm the presence of bioattenuation. Soil-phase data may also be needed to document the presence of clean soil.

Sub-slab vs. Near-slab Samples

For CHCs, the current thinking is that shallow soil-gas data (5 to 10 ft bgs) collected outside the building slab may not adequately represent sub-slab soil-gas concentrations in many situations. This thinking is based on modeling simulations as well as data from many CHC sites. But for PHCs, field data currently being presented by Robin Davis and Todd Ririe (BP-Arco) at many conferences (<http://www.neiwpcc.org/tanks-conference/pre-workshops.asp>) and from

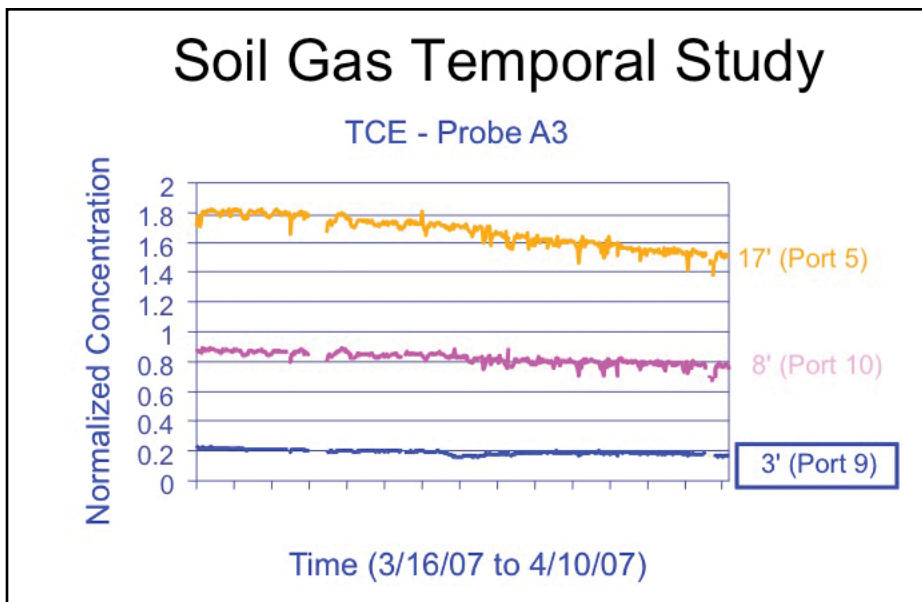


FIGURE 3. TCE concentrations in soil gas for a period of four weeks for three probes at 3' bgs, 7' bgs, and 17' bgs (EPA 2007).

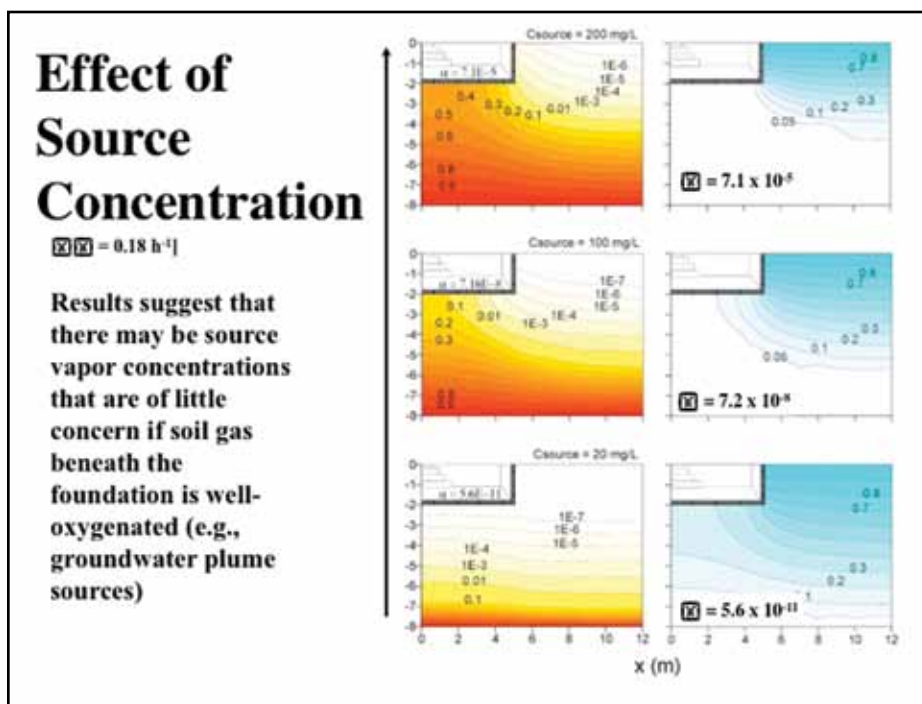


FIGURE 4. 3-D modeling of hydrocarbon vapors showing the effects of bioattenuation (Abreu & Johnson, 2006).

modeling simulations suggest that exterior shallow soil-gas samples are representative, so long as sufficient oxygen is present ($\geq 4\%$) and three to five feet of clean soil exist under the receptor (Figure 4). So, near-slab sampling for PHCs should be a viable approach at most sites, unless contaminated soils or low oxygen is suspected under the structure.

Including Petroleum Aliphatics as a Compound of Concern?

Some states (e.g., MA, CA, WA, HI) have published indoor air screening levels for the petroleum aliphatic range and require that they be included as a compound of concern (COC) for the vapor-intrusion pathway at PHC sites. There is currently considerable debate as to whether

this compound group does represent a potential health threat. I am not a regulator making policy, but I will caution those that do—if aliphatics are included as a COC, it is likely that many more sites will require a vapor-intrusion assessment. The reason for this is that the aliphatics have much higher Henry's constants and higher vapor pressures than the aromatics, resulting in much higher concentrations in the soil gas (by 10x to 50x) over free product, near dirty soil, and even near dissolved contamination.

The fundamental problem is that petroleum is made up of many different aliphatic compounds, but the toxicity data exist for very few of them. Hence, applying the limited existing toxicity data to the total aliphatic fraction is an extrapolation. To better understand the true risk of these compounds, it is necessary that the toxicity of the individual aliphatics be reviewed so that the risk-driving compounds, or compound groups, are identified and appropriate chemical-specific screening levels (meaning not too conservative) are determined.

If you are going to measure the aliphatics, be sure that the laboratory does the appropriate compound-group speciation and that it uses calibration standards for those compounds. Some labs are quantifying all the aliphatics using one or two compounds, such as hexane, rather than purchasing the expensive aliphatic mixture standards.

Beware Natural Gas

Earlier this year, while on a vapor-intrusion investigation, we discovered 90 percent methane and benzene in the thousands of $\mu\text{g}/\text{m}^3$ under a garage at a home far removed from the suspected service station source. Using real-time analysis, we collected additional soil-gas samples and honed in toward the culprit—a built-in barbeque in the adjoining courtyard plumbed directly to the public natural gas. We next collected and analyzed a sample of the natural gas itself and were astonished to find benzene concentrations exceeding $1,000 \mu\text{g}/\text{m}^3$!

All of the houses in the community had natural gas fireplaces in the living rooms, gas furnaces, and

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many had gas ovens/stoves. It turns out that most natural gas supplied by gas companies across the country has 0.1 to 1 percent “impurities,” meaning hydrocarbons other than methane. Take-home lesson: if the receptor has natural gas, analyze a sample of the natural gas for the target compounds. This should be done if indoor-air, sub-slab soil-gas, or exterior soil-gas data are being collected, since underground gas lines can also leak.

Parting Thoughts

■ The Two Most Common Errors in Vapor Intrusion

Vapors and vapor intrusion are an unfamiliar territory for many practitioners in this field (i.e., regulators, stakeholders, consultants, subcontractors, attorneys). Here are two of the most common errors that I see being made in this subject area:

• Confusion with Units

One common error that people make with soil-gas data is thinking a ppbv is equivalent to a $\mu\text{g}/\text{L}$ or a $\mu\text{g}/\text{m}^3$. The units are not equivalent, and the conversion depends on the molecular weight of the compound. Converting between units (e.g., $\mu\text{g}/\text{L}$ to $\mu\text{g}/\text{m}^3$, percent to ppmv) is also causing headaches. Make your life simpler by:

- Instructing your lab in which units and detection levels you want the data reported.
- Going to www.handpmsg.com for a handy-dandy and easy-to-use unit conversion spreadsheet.

• Required Soil-Gas Target Levels

The other error I see too often is the regulator or consultant using incorrect soil-gas target levels. Residential values are erroneously applied at commercial sites, incorrect attenuation factors are being used to determine target values, or values determined from predictive models are incorrect. The soil-gas target level ultimately determines the required analytical method and the need for additional assessment. Determining the proper value is often an unfa-

miliar exercise for both regulator and consultant. So, consultants need to ensure that regulators are asking for the proper values, and regulators need to ensure that consultants are proposing the proper values.

Vapor-intrusion assessments are being conducted at many PHC sites when recent evidence suggests they may not be necessary or they are being conducted in a manner that is inappropriate for PHCs. State reimbursement fund managers are concerned that the costs for unnecessary or improperly conducted vapor-intrusion assessments could drain the coffers of already cash-poor funds.

■ Experience: The Key Ingredient for Vapor-Intrusion Solutions

The most important ingredient needed for cost effective, and cost-efficient vapor-intrusion investigations is the experience of the consultant and the subcontractors (e.g., sampling firm, laboratory). This is a growing problem as many practitioners are jumping into vapor intrusion due to the opportunities that exist.

Sampling errors include such basics as not opening containers, incorrect seals, over-tightening swage lock fittings, wrong tubing, using contaminated parts and sealants, and more. Laboratory issues consist of sending out incorrect or faulty hardware, using the wrong method for the required detection levels (typically at higher cost), and more. These mistakes result in bad data that only further confound the interpretation.

I advise responsible parties to use consultants experienced with this pathway. In turn, I advise consultants to use firms experienced in soil-gas collection and use labs experienced in indoor-air/soil-gas analysis. The stakes are simply too high with vapor intrusion to do anything else.

Want to Know More?

- The Nielsen Field School will be giving a course on “Soil Gas Sampling for Vapor Intrusion Applications” in January 2011 in San Diego. Go to: <http://www.envirofielddconference.com>.
- API is offering free training entitled “Assessing Vapor Intrusion at Petroleum Hydrocarbon Sites” covering the topics discussed in this article and more at the AEHS conference in San Diego in March 2011.
- As mentioned previously, API will be offering training on the Biovapor model throughout 2010 and 2011. Go to www.api.org to find dates or e-mail me if you are interested in such training.
- ITRC continues to offer a two-day vapor intrusion course. San Antonio in January 2011, and three other locations (TBA) in 2011. Go to www.itrcweb.org for details.
- EPA-OSWER will be holding a 1-day workshop on vapor intrusion at the AEHS conference in San Diego in March 2011. Go to: <http://www.aehsfoundation.org>. ■

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