

Vapor Risks:

If Done Right, it's Not as Bad as You Think

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ABSTRACT

Cancer risks to occupants of residential and commercial establishments from migrating hydrocarbon and solvent vapors are now a major factor in Risk Based Corrective Action (RBCA) studies and the evaluation of long term hazards of existing and former petroleum facilities (refineries, oil fields affected by encroachment of urbanization, etc.). Such risk assessments are a key part of Environmental Justice lawsuits. Acquisition and analysis of migrating organic vapors are not specified in any EPA protocol, and as a result, numerous field and analytical methods are used. However, because of the very low PRGs for such compounds as benzene, vinyl chloride, and DCE, conventional soil gas sampling methods are not adequate for either reproducible sampling or analysis.

More than four years of soil gas projects specifically for vapor risk assessment have led to the development of sophisticated, reproducible, and defensible protocols for both the sampling and analysis of vapors in the subsurface. The methods presented are applicable to virtually any lithology and organic compound, plus sulfur compounds. Most analyses can be conducted on the site, allowing the mapping of vapor plumes and determination of first order risk in the field. As a result, it is not necessary to conduct such vapor studies solely using expensive canisters and TO-14 analyses, waiting weeks for results.

INTRODUCTION

The widespread adoption of Risk Based Corrective Action (RBCA) regulations has added a whole new aspect to evaluation of risks associated with sites contaminated by petroleum and other organic compounds. While each regulatory agency has its own variations on the ATSM RBCA Standard, the estimation of vapor risk is common to all (ASTM, 1999; CDLE, OIS, 1999).

A review of the recent literature and RBCA-type regulations around the country reveals an emerging consensus regarding the estimation of vapor related risk: the use of theoretical physical and chemical properties, plus default geotechnical parameters, with models to calculate vapor levels in the subsurface results in substantially higher risk estimates than if vapors are actually measured (Johnson, et al, 1998). It is common for the measured levels to be from 3-5 orders of magnitude lower than the estimated levels. This has been documented by a number of investigators (Fitzpatrick and Fitzgerald, 1997; McNeel and Dibley, 1998; Viellenave et al., 1999). A number of factors are either ignored or treated very conservatively in the models (Daugherty, 1997):

- ◆ Biodegradation (constant vs. diminishing source)
- ◆ How variations in lithology affect retardation (adsorption)
- ◆ Soil moisture, including capillary fringe treatment

- ◆ Equilibrium conditions are assumed for partitioning

The solution to this problem incorporates several actions. These assume that, first, existing ground water and soil data have been input into the conservative “plug and play” model and the site fails to exhibit vapor risks under the 10^{-6} cancer factor or PRG. Under that scenario, most of the actions involve acquisition of site-specific data. The use of site-specific data, in particular actual soil vapor measurements, will almost always have the effect of significantly lowering the estimated risk due to migrating vapors. The sampling and analysis of vapors is the key element, and is one for which there are no EPA protocols. Instead, there are numerous adaptations of sampling and analytical methods designed for other matrices that are applied to soil vapor samples.

SOIL VAPOR SAMPLING

Before evaluating specific methods, it is important to set some criteria that must be met by any sampling/analytical method in order to deliver data that can be used for decision-making. The decisions being made relate to human health risks, not whether a monitoring well needs installation. Therefore, the data quality objectives are significantly more stringent.

1. Sample acquisition must be reproducible
2. The sample must represent soil vapor, not atmospheric air
3. Vertical profiling can be conducted
4. The minimum detection limit for any compound must be lower than a level that will yield an indoor air concentration exceeding the PRG
5. The analytical method must give confirmed compound identification

Four different approaches have been reportedly used for soil vapor sampling for risk assessment. All have derived from traditional soil gas surveying for reconnaissance purposes (Morrison, et. al, 1998; ASTM, 1998). Each has its own unique set of advantages and disadvantages; unfortunately, some of the disadvantages are fatal—that is, they do not allow the method to meet the criteria listed above.

The four vapor sampling methods are: active; passive; flux chambers; and vapor implants. Each method is summarized below.

Active Sampling

Active sampling (as described here) involves the withdrawal of a small aliquot of whole gas from the subsurface, usually through a hollow probe. The acquisition of the sample is done almost immediately after advancing the probe to the sampling depth. It is possible to sample multiple depths in the same hole. The sample is taken either to an on-site or off-site lab for analysis. This method is derived from techniques used for most reconnaissance soil gas surveys.

Passive Sampling

Passive sampling uses a non-polar sorbent contained in, or attached to, a support, which is put into the ground and left for a period of time. The sampler loads continuously while exposed, and once the prescribed residence time is reached, the sampler is retrieved and sealed in a vapor-tight container for transport to the lab. The advantage of passive sampling is that it concentrates the vapor sample, allowing for improved detection levels.

Flux Chambers

Flux chambers are enclosed devices that sit either on the ground or on a floor for a specified exposure period, during which they accumulate migrating contaminants. Vapor samples may be acquired via septum sealed fittings in the container. Flux chambers also allow for lower detection limits by making larger volume samples available for analysis. However, they are used only on the surface, not the subsurface.

Implants

Vapor Implants are perforated devices installed at specific depths in the subsurface, either singly or in nests of several per hole. Each is contained in a sand pack and sealed from each other or the surface by hydrated bentonite. Each implant is connected to the surface using polyethylene tubing and completed as a small monitoring well. Implants allow large volume samples to be taken (> 1L) for very low detection levels and subsequent long term monitoring, if needed.

Sampling Advantages and Disadvantages

Table 1 summarizes the advantages and disadvantages of each of the sampling methods listed above.

Table 1. Advantages and Disadvantages of Vapor Sampling Methods for Risk

METHOD	ADVANTAGES	DISADVANTAGES
Active	<ul style="list-style-type: none"> + Most rapid + Multi-depth available + Least expensive 	<ul style="list-style-type: none"> – Poor to moderate sensitivity – Fails in clay soils – Fair reproducibility – Overstates quantity
Passive	<ul style="list-style-type: none"> + Very sensitive + Non-invasive + Moderate cost 	<ul style="list-style-type: none"> – Not quantitative – Very slow – Single depth only – Not reproducible
Flux Chambers	<ul style="list-style-type: none"> + Good sensitivity + Indoor air comparability 	<ul style="list-style-type: none"> – Very slow – Expensive – May not be representative
Vapor Implants	<ul style="list-style-type: none"> + Multi-depth available + Very sensitive + Reproducible + Applicable in all soils + Long term monitoring 	<ul style="list-style-type: none"> – Moderate speed – Moderate cost

Active sampling will work effectively where lithologic conditions allow acquisition of large volume samples. In silty and clayey environments, instantaneous sampling may fail to acquire a viable

sample. Some practitioners “never fail” to get a sample; beware! In tight clays, if the annular seal is good, it is frequently not possible to get a soil gas sample. If an air sample is obtained, it is likely to be atmospheric, rendering the entire exercise wasted. Because samples are obtained immediately after probing, the vapor concentration is elevated due to the heat generated by probing (Whiticar, 1990). However, this effect is vastly smaller with Direct Push than it is using an auger.

Passive sampling is entirely inappropriate for risk analysis. While it is very sensitive, it does not acquire a volume of gas, essential for reporting concentrations. When using passive, it is necessary to make numerous assumptions regarding the vapor and soil, increasing the collective error so much that the results are valueless. Vertical profiles are very expensive, even if possible.

Flux Chambers may not be representative, particularly over hard surfaces (asphalt and concrete). It is impossible to get a vertical profile to document the decline in vapor concentrations with distance from the source.

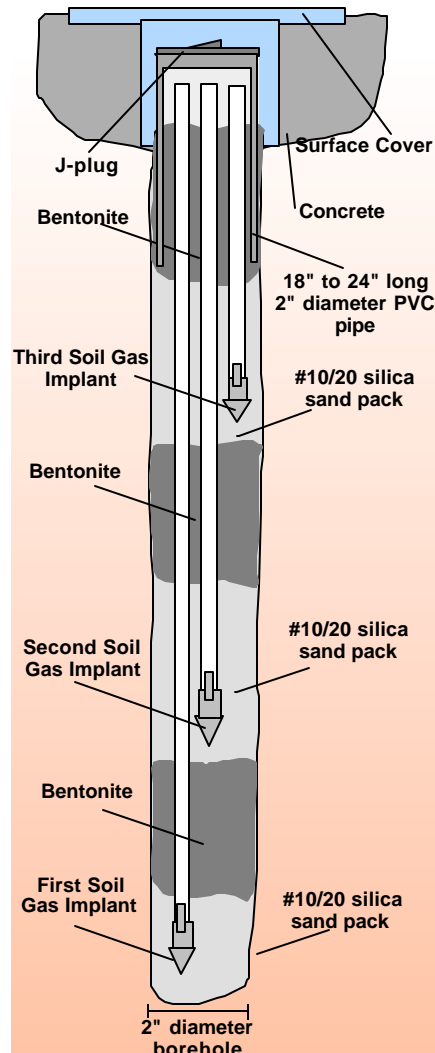


Figure 1. Typical Nested Vapor Implants

Vapor Implants are the preferred method, unless the soil character is ideal (gravels to sandy silts). Using vapor implants, it is possible, even under most clayey conditions, to obtain sufficiently large samples to yield low detection levels for risk calculations. In addition, vapor implants yield highly reproducible samples for years, because they represent close to equilibrium conditions of migrating vapors. As a result, they can illustrate seasonality (when appropriate) and be used for long term monitoring. They are only slightly slower and more expensive than **Active Sampling**.

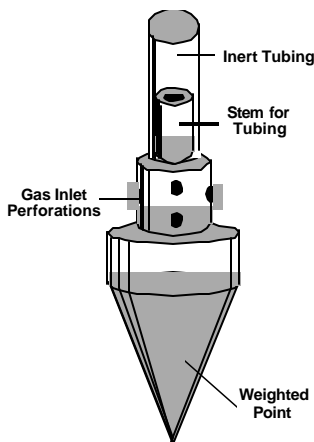


Figure 1a. Soil Gas Point Detail

We recommend the vapor implant approach unless active sampling allows the acquisition of a large volume sample (Viellenave, et. al, 1998). However the sample is acquired, it is essential to isolate the sampling region from the atmosphere. This is easy to accomplish using the implants, but more care must be taken with probing or drilling systems. A typical vapor implant is illustrated in Figure 1.

ANALYTICAL METHODS

Portable and “field” instruments have been used for soil gas surveys for years, but are neither selective nor sensitive enough for vapor risk assessments. Analysis should be done on “Laboratory

Grade” instruments only, with the appropriate settings and QC for the analytes of concern (US EPA, 1997). EPA Level III QC should be implemented for all risk analysis.

Both GCs with applicable detectors and GC/MS analysis are acceptable for most risk analysis. Methods can include both traditional analytical methods run for waters and soils for volatile organics (GC methods 8021 (8010/8020) 8015 and GC/MS method 8260). Depending on the actual instrument and analyte, the GC methods for halogens and aromatic hydrocarbons (8021) may exhibit lower detection limits than can be observed using a GC/MS running 8260. In any event, it is necessary to be able to reproducibly report vapor concentrations into the low ppbv range.

Most traditional soil gas surveys (using Active Sampling) will report as low as 1 µg/L, which depending on the compound, ranges from 100-300 ppbv. Larger volume samples are required in order to detect closer to 1 ppbv. The path most often taken to get low detection limits is to acquire SUMMA canisters ranging from 1-6 L and run such air analyses as TO-3 or TO-14. These are very effective in reaching low detection limits, but impose a high cost and delay in a project. ESN has developed protocols, for both mobile and fixed lab situations, to analyze large sample volumes (up to 1 L) without SUMMA canisters and reach the levels of about 0.1 ppbv running either method 8021 or 8260. The cost is not materially higher than standard 10-day turnaround prices for the same method.

The use of mobile labs allows not only rapid decision-making and vapor plume tracking in three dimensions, but the determination of where and how much of a site or area is subject to potentially high vapor risks. Ideally, the lab operator will have spreadsheets with the local agency RBCA software for input of data directly. In addition, vapor risk assessments may be readily integrated into the more traditional site assessment process as vapors can be run in the same lab as soils and waters, including with appropriate QC.

At a minimum, the following QC should apply to all vapor risk analyses:

- ◆ 5 point Initial Calibration
- ◆ Daily Continuing Calibrations (or every 12 hours)
- ◆ At least two surrogates on every sample
- ◆ Analytical and field duplicates
- ◆ Lab and site ambient air samples
- ◆ System blanks
- ◆ Standards certifications and prep logs
- ◆ Supply of chromatograms (and mass spectra)

CASE STUDY

ESN has undertaken dozens of vapor risk projects across the Rocky Mountain and Midwest U.S. In each case, ground water concentrations and geologic data were first input to ASTM-type models for risk estimation. As a result, the sites “failed” the ASTM model or were sufficiently close to the PRG that the acquisition of real data was advisable. Among the projects were such sites as dry cleaners, gasoline stations, manufacturing facilities, gas storage reservoirs, oil and gas fields, highway department labs, military facilities, refineries and tank farms, and housing developments. Compounds of concern included benzene, vinyl chloride, DCE, TCA, methane, and other volatiles. With almost no exceptions, the concentration of the Compounds of Concern declined exponentially as the distance from the known source increased.

The models generally predict a very high initial concentration of contaminants in vapor, declining linearly with distance. Instead, the initial concentration of contaminant in vapor is moderate to low, and the decline thereafter is exponential. The pattern demonstrates that the partitioning of contaminants into the vapor phase is far less than predicted under equilibrium conditions and that retardation processes (physical and biological) frequently operate more efficiently than the models predict.

A representative example involved a housing development in Denver, proposed to be near a petroleum tank farm. Gasoline and other petroleum products were known to be in ground water at concentrations approaching 1 mg/L. Input of benzene data into the Colorado RBCA model yielded benzene concentrations in indoor air above the PRG for benzene.

The contaminant plume was known to underlie nearly 2/3 of the proposed development, meaning that more than 40 homesites were potentially at risk. To firmly establish the pattern of vapor presence and migration, we first installed three vapor profiles, measuring the concentration every 5 feet from the surface to just above ground water. Given the PRG for benzene, it was determined that a reporting limit of 1 ppbv at depths from 5' and deeper below ground surface would be necessary to establish the vapor profile and risk. Measurements of benzene in vapor samples reached the 1 ppbv level at between 15 and 20 feet below grade in all three profiles. Table 2 shows a typical profile, comparing benzene concentrations predicted by the RBCA model from ground water concentrations and measured in the vapor risk investigation.

Table 2. Vapor Migration Example, Denver, Colorado

Predicted by ASTM Model	Vapor Sample Depth	Actual Measurements
279	0	<1
335	5	<1
419	10	<1
568	15	1
839	20	6
1,840	25	8
6,500 ppbv	30	9 ppbv

Note: 100 µg/L BTEX (in ground water)

Following the development of the profiles, we acquired a vapor sample at 20 feet in the center of the proposed building envelope for each home in the development and analyzed the vapor. Site-specific data for soil and other geotechnical data were also obtained. The actual vapor concentrations were then input to the RBCA model and the ratio of predicted indoor air to PRG calculated, resulting in a Risk Factor. Values less than 1 predict risk less than the PRG. All of the Risk Factors were 3-5 orders of magnitude less than 1. Table 3 shows the results of vapor sampling at the sites studied. On the basis of these findings, the Colorado Department of Public Health and Environment issued its No Further Action determination and the project proceeded. During the past two years, monitoring of vapor from a limited number of implants left at the development has confirmed the vapor risk values obtained in the initial study.

Table 3. Benzene Vapor Risk at Housing Development, Denver, CO

Lot Number	Concentration PPBV	Depth	Risk Factor
1	1.45	20	0.000160361
2	8.38	20	0.000926778
3	7.5	20	0.000829455
4	3.62	20	0.00040035
5	2.58	20	0.000285333
6	2.29	20	0.00025326
7	5.4	20	0.000597208
8	3.04	20	0.000336206
9	9.04	20	0.00099977
10	3.64	20	0.000402562
11	3.95	20	0.000436846
12	1.05	20	0.001161237
13	1.36	20	0.000150408
14	1.32	20	0.000145984
15	0.9	20	9.95346E-05
16	2.05	20	0.000226718
17	0.9	20	9.95346E-05

Conclusions

Soil Gas contaminant measurements are necessary at sites that “fail” the theoretical Vapor Risk calculations using RBCA models at petroleum and other sites due to the extremely conservative nature of the models. However, while many techniques are available for acquiring vapor measurements, only a few produce accurate, reproducible values considered valid for Risk Assessment. The ideal method involves installation of vapor implants, including at least a limited number of vertical profiles. Traditional active sampling can be used if lithologic conditions permit easy acquisition of large sample volumes without breakthrough from the surface.

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