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Quantitative Passive Soil Gas and Air Sampling in Vapor Intrusion Investigations

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ABSTRACT

Vapor intrusion - the intrusion of volatile and semi-volatile compounds into structures potentially creating a health risk to occupants - has become a dominant environmental topic. Vapor sampling of soil gas and air provides a direct measurement of these compounds in order to evaluate health risks. Numerous published procedures and guidance documents discuss air and soil gas sampling techniques, sample analysis, and interpretation of data.

Most of these publications discuss well-known active vapor sampling techniques. An alternative technique, passive sampling of air and soil gas, involves the deployment of an adsorbent that collects compounds in the vapor state over time. Discussions of passive sampling in procedural documents are often limited in scope and fail to recognize the quantitative capabilities and benefits of passive sampling. Passive sampling can provide soil gas, sub-slab soil gas and air data simply, effectively and accurately for volatile- and semi-volatile organic compounds, under a wide range of challenging site conditions. Sampler deployment is simple and inexpensive. When properly characterized, passive samplers yield valid data. This approach has been used for decades in industrial hygiene applications for sampling indoor and ambient air.

This paper discusses the calculation of vapor concentrations for a membrane-based, adsorbent, passive sampler based on the sampler's uptake rate, time of exposure, and sorbed contaminant mass. Additionally, this paper presents soil gas data collected by multiple active methods and this passive method at a site in the Midwestern US, showing that passive sampling techniques can deliver quantitative values.

INTRODUCTION

Chemicals intentionally or accidentally deposited into subsurface soils and groundwater, if able to volatilize, will migrate as a gas through the subsurface soil pore space, and potentially enter into overlying buildings. Accumulation and exposure to the chemical vapors can pose a human health risk. The US EPA defines this process - vapor intrusion - as the migration of volatile chemicals from subsurface sources, such as contaminated soils and groundwater, into overlying buildings.[1] The topic of vapor intrusion is complex and ever-evolving. While the industrial hygiene community has been grappling with indoor air and health concerns of employees for decades, vapor intrusion, in the context of contaminated soil and groundwater acting as a vapor source, has become a critical issue in the past eight to ten years.

Technology developers, service providers, environmental consultants and state and federal regulators continue to struggle to define acceptable sampling, investigation, interpretation and mitigation techniques and procedures for vapor intrusion. While some states simply refer to the US EPA federal guidance, approximately half of the US states have issued independent guidance documents addressing vapor intrusion.[1,2,3,4] New York, has gone a step further by challenging the validity of vapor intrusion numerical modeling and reopening regulatory closed sites, to re-evaluate the vapor intrusion pathway. Multi-state consortiums, such as the Interstate Technology Regulatory Council (ITRC) as well as, the American Society for Testing and Materials (ASTM), have released guidance or method documents on the topic of vapor intrusion.[5,6,7] Since 2003, the US EPA and the AWMA have hosted several workshops and specialty conferences on a wide variety of vapor intrusion topics.[8,9,10,11]

Generally, the documents and workshops focus on active sampling techniques to collect soil gas, subslab soil gas or air samples. These methods forcefully or mechanically extract a known volume of vapor, or hopefully a representative sample, from the soil pore space or from free air (e.g., indoor air), and are analyzed on-site or at fixed off-site laboratories following a variety of accepted sampling and analytical methods.[12,13,14]

Alternatively, passive sampling relies on the diffusion of compounds in the vapor state to adsorbent(s) housed in a chemically-inert container designed to protect the sample integrity. This approach has been used for years to monitor the concentration of workplace contaminants for industrial hygiene applications. For environmental site assessment, passive soil gas sampling has been used for decades to assess the distribution of volatile and semi-volatile organic compounds (VOCs, SVOCs). This cost-effective site assessment approach reports soil gas data in relative units (mass), and is used to focus subsequent invasive and more expensive sampling.[15,16] Due to mass unit reporting, beyond its use for conventional site assessment, passive sampling is usually not discussed in great detail in the context of vapor intrusion,. However, recent documents, workshops and conference presentations are including sections on the role and benefits of passive vapor sampling in vapor intrusion investigations.[5,6,9-11,17-24]

Vapor sampling provides a direct measurement of the chemicals of concern (COCs), and is the preferred technique to assess the direct exposure route to humans via inhalation. Historically, in the industrial hygiene community, passive sampling has been widely used to sample workplace air and assess chemical exposure and risk to humans. Numerous methods which describe the use of passive, adsorbent-based samplers, and the reporting of vapor concentration data, have been developed, validated and accepted in both the US and Europe.[25-33] The body of literature is quite extensive.[34]

Passive sampling provides a less complicated, high-resolution, cost-effective, alternative to other forms of soil gas, subslab soil gas and air sampling. Though design dependent, passive samplers perform well under challenging site conditions and for a broader range of compounds than active techniques, and are generally easy to use.

This paper continues to update the reader on the use of passive sampling in vapor intrusion investigations, explores the adaptation and development of a vapor concentration reporting method for a membrane-based passive sampler, and provides new case study results.

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APPLICABILITY AND BENEFITS OF PASSIVE SAMPLING

Passive samplers can be placed in exterior unsaturated soils, beneath basement floors, building slabs and parking lots, and in the air - indoors, in crawlspaces and outdoors - to help determine if a health risk exists from subsurface chemical vapors. Passive samplers should consist of a chemically and biologically inert housing, containing hydrophobic adsorbents. The housing must facilitate vapor diffusion to the adsorbent. This inert housing should not off-gas or react chemically with the other materials present in the sampler or the environment, therefore protect the integrity of the adsorbent and the sample. The hydrophobic adsorbent must have sufficient attractive and binding forces to hold onto the vapor molecules, while minimizing the uptake of water vapor, which would compete for adsorbent sites. The forces hold the compounds until they are released during laboratory sample preparation and analysis.

Passive sampler configurations currently consist of, but are not limited to:

1. adsorbent adhered to a wire, housed in a glass vial or tube, open on one end;
2. adsorbent contained in metal screen “pouches,” adhered to metal strips, or loose; housed in glass vials, usually with a metal screened or permeable cap covering the open end;
3. adsorbent housed in narrow-diameter metal tubes open or with a permeable cap covering on one or both ends;
4. adsorbent housed in industrial hygiene badges constructed with a variety of materials and forms;
5. adsorbent housed completely in vapor-permeable, membrane tubes.

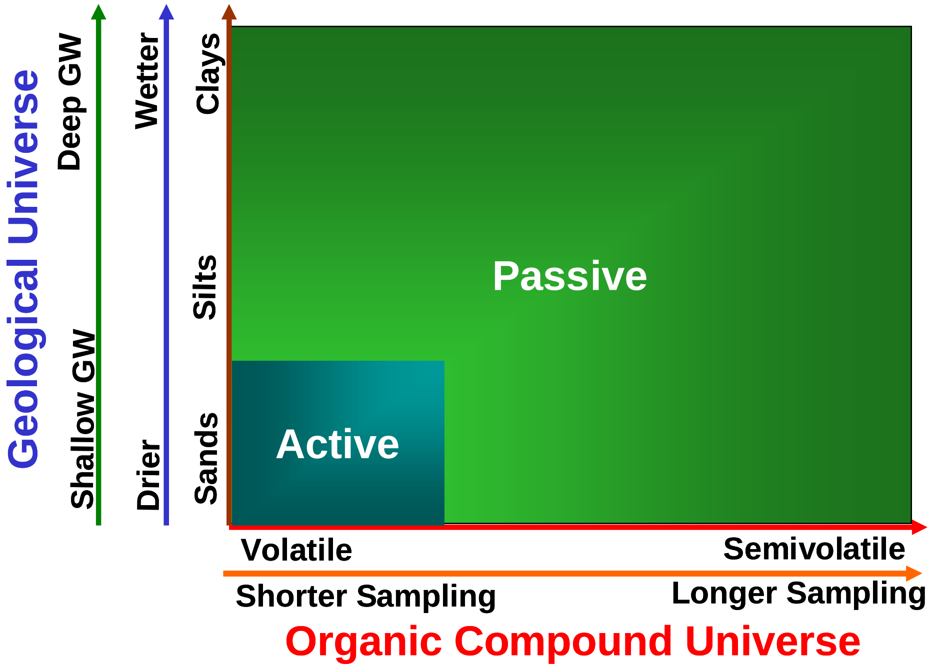
Sufficient chemical volatility is required to partition the compound from source (i.e., free phase, groundwater dissolved, and/or soil adsorbed) to the vapor state for a passive sampler to work. Once volatilized, migration to the sampler is a function of the chemical’s diffusivity in air, concentration gradient, convective and advective forces, and preferential pathways of least resistance, natural or anthropogenic.

Passive samplers are deployed for a set period of time and then retrieved. There is no forced extraction of the vapor and minimal disruption of the vapor equilibrium during installation. The minimally disruptive nature of passive sampling allows for time-integrated sampling even during short exposure periods (i.e., hours to a single day). Time-integrated sampling allows for an accumulation of mass and therefore, is highly sensitive to compounds in a broad vapor-pressure range (VOCs, SVOCs, and PAHs), as well as a wide range of concentrations (ppt-ppm). Figure 1 summarizes some of the benefits passive soil gas sampling provides relative to active soil gas sampling.[35]

In addition, though passive sampler design dependent, several other advantages can be realized with passive sampling:

- Simple, inexpensive deployment, with minimal training and installation equipment;
- Less data variability; reduced potential for human error or sampling bias;
- No mechanical parts, or energy required to operate during sampling;
- Ability to sample soils having low to high permeability and/or low to high soil moisture;

Figure 1. Conceptual figure illustrating compound volatility, sample exposure period, and geological setting, impacting passive and active soil gas sampling.



- Ease of use in areas of limited access, e.g., high traffic areas; buried utilities;
- Deployable in vadose zone soils, beneath slabs, in crawlspaces, and indoor and outdoor air environments;
- Rapid, high resolution sampling and datasets;
- Estimated concentration reporting by statistical or physically-based methods for comparison to regulatory screening levels - a “first look” at the severity;
- Estimated concentrations that can be used as input to the Johnson-Ettinger model;
- Applicable to early “tier” and “phase” investigative steps as outlined in vapor intrusion guidance documents;
- Can achieve regulatory risk levels when coupled with an appropriate analytical method;
- Proven in Triad investigations to focus subsequent rapid, on-site sampling and analysis;
- Proven line of evidence in conceptual site model development;
- Characterizes spatially the compound presence, type and extent (i.e., vapor pathway);
- Focuses subsequent more invasive and expensive sampling techniques;
- Applicable to site conditions which preclude or prevent active sampling techniques.

Cost Considerations

When examining the cost-effectiveness of using a passive sampler to collect a soil gas or air sample, one should consider the total costs involved in collecting and reporting the sample, and not simply compare analytical costs. A comparison of the total costs involved in collecting the sample will help in the decision point in which approach to use. The total costs should also be examined in the context of the capability of the equipment to collect a sample at the site under investigation, for the given data quality objectives. For example, collecting a soil gas sample by a method that is not functional under the given site conditions will lead to erroneous data and ultimately a waste of money. More specific to the actual field collection of the sample and its analysis, by either an active or passive technique, the total costs include but are not limited to:

- Actual sampling equipment,
    - Active: canisters, pumps, bags, controllers, fittings, valves, power
        - Flow calibration
    - Passive: sampler
- Hole drilling,
    - Hand tools (shallow depths)
    - Power, direct push tools (greater depths)
- Temporary or permanent port installation and materials,
- Sealing/securing holes,
    - Active – leak prevention, testing
- On-site sampling and analysis,
    - Active - leak testing, sample analysis
- Decontamination,
- Hazardous waste disposal,
- Fixed-lab analysis, standard or expedited
- Shipping (weight, hold times)
- Labor
    - Depends on skill level required,
- Overall project management.

A 58% cost savings was realized at a dry cleaner vapor intrusion investigation, when both passive and active soil gas sampling were employed, when compared to an active sampling program alone, when all costs were considered.[9,10] With regulatory approval, a passive soil gas survey was conducted first to screen the site and provide a higher resolution initial dataset. The results focused the more expensive, and fewer, subsequent active soil gas sampling locations.

At a large military site investigation (not for vapor intrusion), site geology was problematic for active soil gas sampling.[15] Instead, a high resolution passive soil gas survey was utilized to screen the site initially. Around 950 passive soil gas samplers were deployed over 800 acres. The results guided a 25 point active soil gas sampling program. Costs to collect and analyze an active soil gas sample were approximately three times the cost to collect a passive soil gas sample.

VAPOR PERMEABLE, MEMBRANE TUBE PASSIVE SAMPLERS

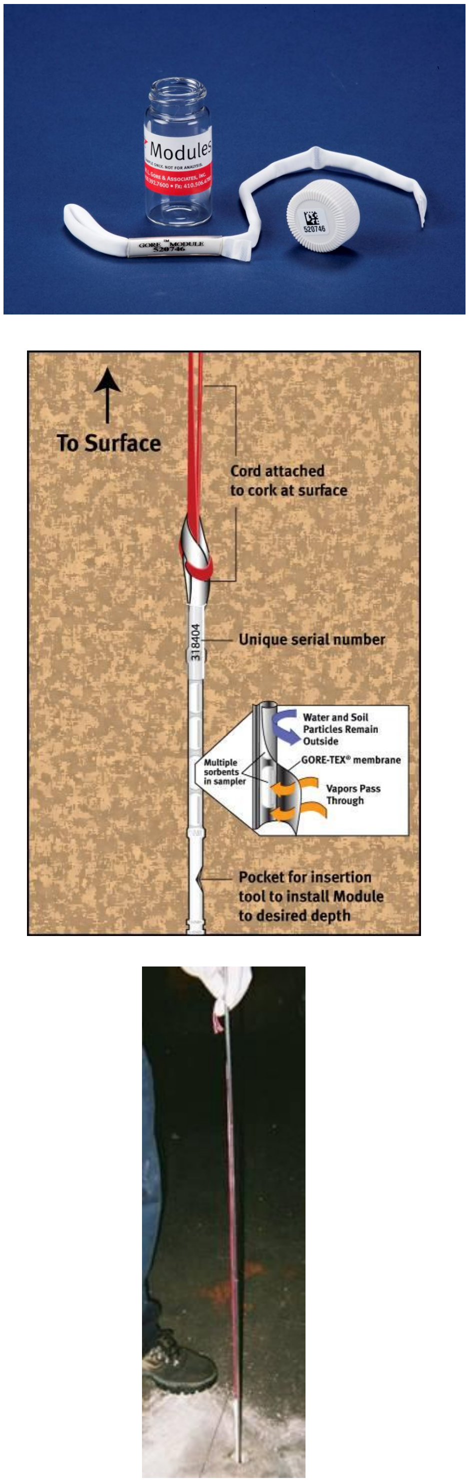
Vapor permeable membrane-based samplers are often considered the most versatile passive samplers. The membrane facilitates compound diffusion to the adsorbent, under a wide range of geological and chemical conditions. One such sampler, the GORE™ Module, is constructed of a chemically- and biologically-inert, microporous, waterproof, vapor-permeable membrane (GORE-TEX® membrane) tubes, containing engineered, hydrophobic adsorbents (Figure 2). The GORE-TEX membrane is designed to diffuse vapors, not adsorb them. The membrane protects the adsorbent, and maintains the sample integrity by protecting it from soil, liquid water, and other site or ambient interferences.

The unique membrane construction allows for sampler placement in both saturated and unsaturated soils, placed in groundwater (to determine compounds dissolved in water and partitioning into soil gas), and deployed in air. The adsorbents have a strong affinity for a broad range of compounds, minimal water vapor uptake, and the ability to release the compounds during analysis.

Soil gas migration theory suggests that compounds in soil gas migrate away from the source and due to concentration gradients and natural fluxes, move upward to the atmosphere, if no obstacles impede this migration. The GORE Module, with its vapor permeable membrane encasing the adsorbent, allows relatively free migration of the vapors onto the adsorbent. Surface area of adsorption for glass vial and solid-metal tube samplers is restricted to the diameter of their openings, thus limiting the rate of adsorption. The design of the GORE Module allows for greater sensitivity and more accurate contaminant delineation in areas with low concentrations, deep sources, contaminant plume edges, and challenging site conditions.

For a cost-effective vapor intrusion investigation using a passive technique, a typical scenario involves collecting a comprehensive set of samples using one kind of passive sampler. The high-resolution dataset

Figure 2. GORE™ Module

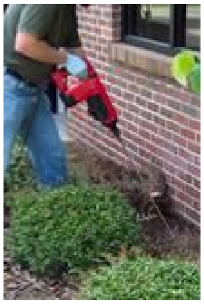


reported provides a valuable line of evidence of potential vapor migration from a subsurface source(s) to the indoor air environment of a structure for a broad range of organic compounds and concentrations (ppt to ppm).

Deployment of this membrane-based passive sampler is simple, quick and requires minimal training and equipment. For soil gas sampling, the samplers can be placed on the surface or to any depth, in uncased or cased holes, and can include vertical profiling of the subsurface soil gas. The installation hole is sealed effectively with a cork. The prescribed practice is to place the passive sampler (i.e., the adsorbent) at the desired sampling depth. This is similar to collecting an active soil gas sample where the probe tip is advanced and opened at the desired sample depth. The degree of simplicity and install depth will depend on the vendor's passive sampler construction and installation requirements. Generally, for soil gas sampling, depths of three feet or more are favored to minimize the effects of near surface and surface variables (e.g., soil temperature, barometric pressure, air pollution) on the soil gas signal of interest.

Subslab soil gas can be collected by placing the sampler at the slab/soil interface, at depth beneath the slab, or both, in permanent or temporary installation holes. The passive sampler can also be placed beneath slab-on-grade construction, by inserting the sampler into holes drilled diagonally beneath the slab from the outside (Figure 3). For soil gas and subslab soil gas sampling, the installation is flush with the surface with no sampling equipment remaining on the surface. For outdoor, crawlspace or indoor air sampling, the GORE™ Module is simply suspended from building structural components (e.g., ceiling tile grid, wiring or piping), or push-pinned to a wall. Field deployment of passive samplers in general and for the vapor-permeable membrane based sampler in particular, is summarized in Hodny and Whetzel.[36]

Figure 3. Exterior subslab soil gas sampling.

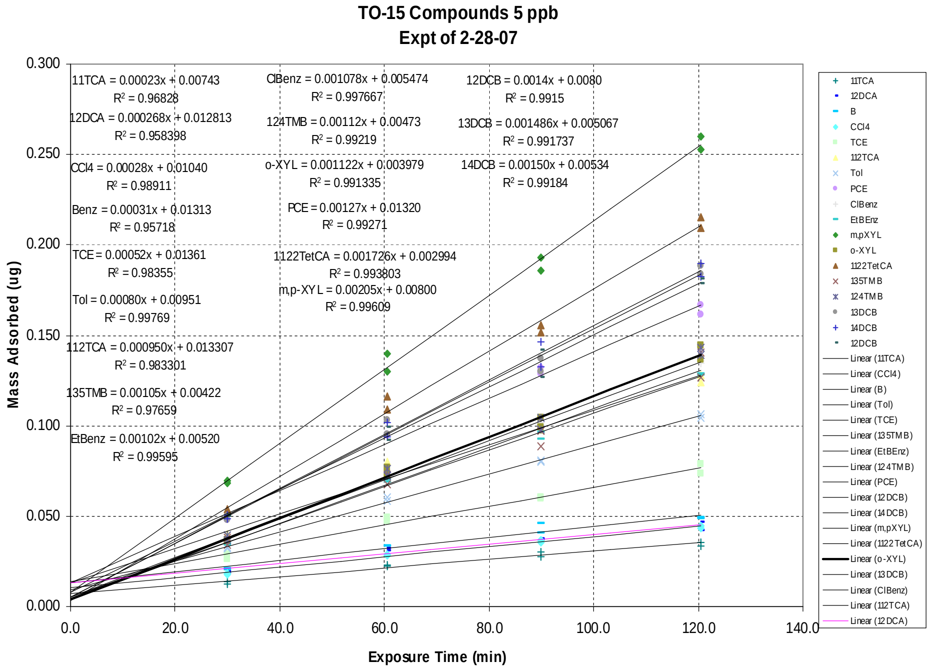


Deriving Concentrations

Depending on the vendor, sampler design and performance, and the analytical method used, vapor data collected with passive methods are reported in qualitative (presence/ absence), semi-quantitative (mass of compound collected), or quantitative units (vapor concentration, e.g., ppbV). For semi-quantitative reporting, the mass of the compound adsorbed by the passive sampler is measured (quantified). The measured mass from one location can be compared to the results from other locations to determine the relative spatial distribution of the compound. Generally, elevated mass levels correlate with elevated subsurface source concentrations.[15, 16, 37]

Vapor concentrations can be estimated by comparing datasets, active and passive, and establishing a correlation or statistical model between the two, which can be used to estimate concentrations for the other passive sample locations. This method assumes that

Figure 4. Linear uptake of compounds by the GORE™ Module.



the modeled relationship is valid, consistent at all sample locations, and is based on data collected by robust systems with the required sensitivity, and with minimal sampling and analytical error.

Alternatively, concentrations can be derived more accurately by characterizing the sampling rate of the passive device. Just as the flowrate through a TO-17, sorbent tube must be known or measured to determine concentration, so to must the uptake rate or sampling rate of a passive device be characterized.

When a clean adsorbent is exposed to a media containing a contaminant or analyte, the concentration is high in the media and effectively zero at the surface of the adsorbent. This creates a driving force moving the analyte from the media to the adsorbent for capture following Fick's Law. If the device is operating under Fick's law, its mass collection over time, dm/dt, will increase linearly with time with the sampling rate, S, equal to D(A/l). Figure 4 shows this linear uptake for several analytes at a concentration of 5ppbV.

Equation 1.

$$dm/dt = D(A/l)(C_x - C_0) = dm/dt = Sx(Cx)$$

where:

dm/dt is the mass flow rate (mg/sec)

D = diffusion coefficient for the analyte of interest (cm^2/sec)
A = total area of the diffusion channel (cm^2)
l = length of the diffusion channel (cm)
Cx = environmental concentration of the analyte x (mg/m^3)
C_0 = concentration of the analyte at the surface of the adsorbent ~ 0 at low mass levels
Sx = Dx(A/l) = analyte specific sampling rate (L/hr)

If this analyte transfer causes minimal lowering of the concentration from the media or if the media is replenished in the vicinity of the sampler, the driving force and hence flux or sampling rate remains constant. The mass increase on the adsorbent with time will be linear and the sampling rate, S, is equal to D*A/l.

Equation 2.

$dm/dt = S(Cx - C_0)$

During this time, the concentration can be calculated based on the sampling rate and the exposure time according to:

Equation 3.

Concentration = (dm/dt)/Sx = mass/t/Sx

where:

mass = the measured mass of analyte x desorbed from the passive sampler (µg)
t = the exposure time (hours)
Sx = the measured or estimated sampling rate for the specific analyte, x (L/hr)

While S can be computed using D, A, and l, it is often easier and more accurate to measure it directly, rather than relying on D values in the literature. S was quantified for this sampler for a wide variety of analytes in a temperature- and humidity-controlled sample chamber. The chamber used calibrated gas cylinders mixed with dry or humidified nitrogen to vary concentration and humidity. The true concentrations in the chamber were preset using calibrated flow controllers on both the certified calibration gas and dilution gas, and were verified using the TO-17 method. The sampling rate is calculated using the slope of the mass uptake rate for each compound as follows:

Equation 4.

S = slope/concentration = (ug/hr)/(ug/L) = L/hr

An adjustment must be made to the sampling rate for sampling in soil due to the additional flow resistance of the soil. This flow resistance can be determined by using a soil effectiveness factor, E, which accounts for changes in permeability due to the soil porosity and water blocked pores.

$S_{soil} = S_{air} * E$

where:

S_{soil} = the sampling rate of the passive sampler in soil gas

S_{air} = the sampling rate of the passive sampler in air

E = soil effectiveness factor

In tight soils, diffusion is retarded, which lowers the effective sampling rate. Millington and Quirk[39] demonstrated that the permeability of soil is reduced with lower porosity and with more water-filled pores. These two terms are also found in the Johnson-Ettinger model and based on the research of Millington and Quirk.[38, 39, 40] This permeability reduction from free air can be estimated using the fraction of pores and the fraction of pores filled with water by:

Equation 5.

$E = D_{eff}/D_{air} = \theta^{(4/3)}(1-\varepsilon)^{(10/3)}$

where

D_{eff} = effective diffusivity in soil

D_{air} = compound diffusivity in air

θ = soil porosity

ε = fraction of pores filled with water,

APPLICATIONS

The following discussion presents active and passive soil gas datasets collected with four different active techniques and the vapor-permeable membrane-based passive sampler, respectively.

Midwest Site - Active and Passive Soil Gas Comparison

At an industrial site in the mid-western United States, permanent vapor sampling points provided an opportunity to collect active and passive soil gas data for site evaluation and comparative purposes. Two phases of passive soil gas sampling were conducted. The first phase (December 2006) was limited in scope in order to compare soil gas concentrations from the active methods to the passive soil gas concentrations computed using the method. Active soil gas samples were collected from the ports by three different sampling and capture techniques, TO-15 - Tedlar bags with vacuum box or Summa canisters, and TO-17 - pumped sorbent tubes (June 2006). In addition, a vacuum bottle technique, Bottle-Vac^{TM} sampler, was used at some locations (December). The second phase of sampling (March 2008) involved a site-wide passive soil gas investigation to focus subsequent, more intrusive sampling. To date, no additional active soil gas data have been collected for comparison with the second phase of passive sampling. Soil and groundwater data were collected during the permanent vapor point installation, but have not been compared rigorously to the soil gas results.

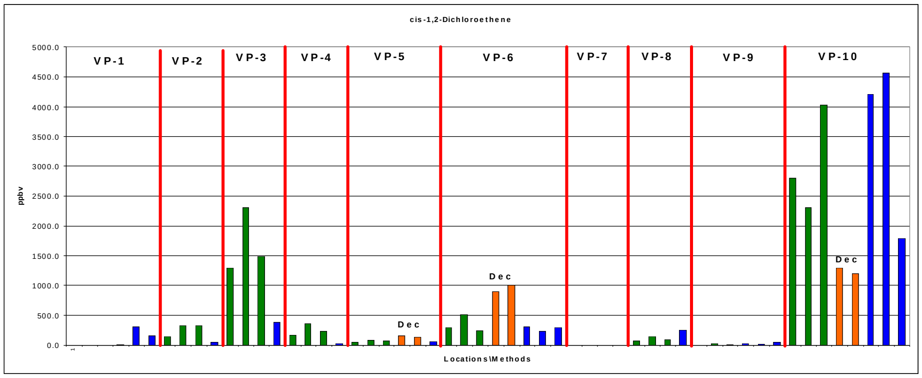
Soil Gas Results

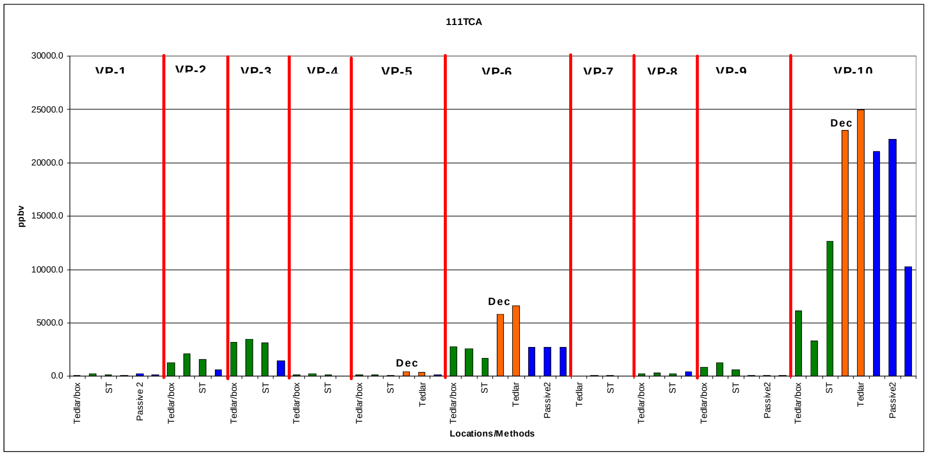
In June 2006, several permanent vapor ports were installed and sampled with the methods mentioned above, except by the vacuum bottle method. Correlation between the active soil gas data and groundwater data was moderate ($R^2 = 0.5$). In December 2006, some ports were sampled again using the Tedlar bag and box and the vacuum bottle approach. The December sampling also included a round of passive soil gas sampling at these ports.

To assess seasonal differences, the Tedlar bag data from the two active sampling events were compared for three locations. There was a general trend to higher concentrations in the December sampling. Percent changes in concentrations ranged from -79% to 2374%. Duplicate data from the vacuum bottle data also showed a wide variance from 0% to 111%.

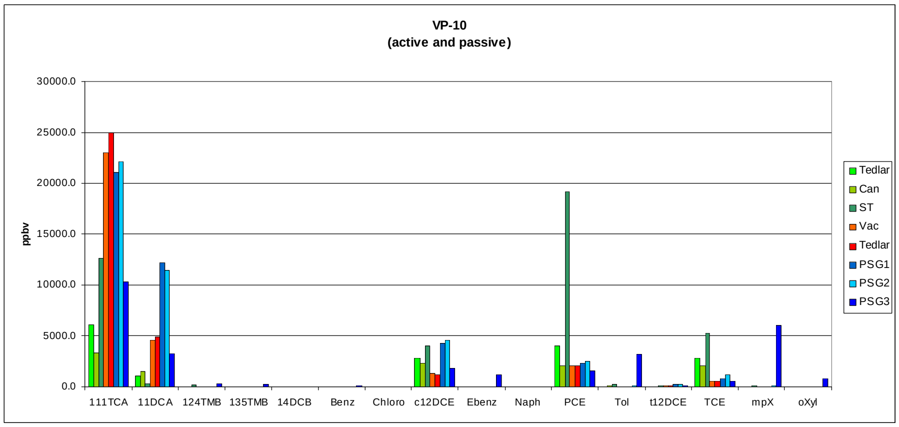
To facilitate this data discussion, a subset of the results is presented. The active sampling was conducted at up to three depths, one foot, five foot and eight foot depths. The passive soil gas data were collected at depths of 2.5 feet. The active soil gas data from the five foot depths were used in the data comparison. Compounds reported in common between the active and passive methods were examined. Compounds such as naphthalene that could not be reported by some active methods are not discussed, though naphthalene is clearly present in the subsurface at the site as seen in the passive and sorbent-tube sampler results. Figure 5 illustrates examples of the soil gas results observed from the active sampling for each technique, regardless of sample period, along with the calculated passive soil gas concentrations. It is readily apparent that variability exists in the active method results. In general, at most locations each technique identified the compounds of interest when present in the soil gas. However, there were considerable differences in the measured concentrations at some locations and for some compounds. While most of the levels do not exceed threshold industrial screening criteria for this state, the measured levels are well in excess of analytical reporting limits. If one is to assess human health risk in the context of vapor intrusion, one would have to ask which accepted method’s results are correct.

Figure 5. Active and passive soil gas concentrations. Top two figures - all methods, June and December sampling, one compound. Bottom figure – all compounds, all methods, one sample location.





Left to right, Tedlar, canister, pumped sorbent tubes (green, June); vacuum bottle, Tedlar (orange, Dec); passive in blue (Dec).



A more appropriate comparison of passive and active soil gas data was obtained by reviewing the soil gas data collected in the December only event (Figure 6). Again, there is variability observed, between the active methods, though not nearly as significant as with the June data. Of additional interest, at locations where multiple passive samplers were deployed and separated by a few feet, spatial variability was also observed. This is likely a function of the site heterogeneity. In general, the passive data compared well with the active data, validating the approach to report soil gas concentrations by the method described above. In some cases, the compounds of interest were only reported with the passive sampler.

In March of 2008, a site-wide passive soil gas survey was conducted to identify additional soil, groundwater and permanent vapor sampling locations. Figure 7 illustrates the soil gas results for PCE. Since then, additional vapor points have been installed and soil and groundwater data have been collected. Initial results suggest that the site assessment using the passive technique generally correlates with the soil and groundwater data, providing a cost-effective site investigation (Figure 7).

CONCLUSIONS

The sampling tool kit used in a vapor intrusion investigation should be expanded to include passive sampling techniques for soil gas, subslab soil gas, and air sampling. This approach provides an accurate, cost-effective, high resolution look at compound presence in the vapor at a site. The easy deployment, minimal operating requirements, and applicability to a broad range of compounds and a wide range of geological site settings, makes this approach an attractive sampling alternative in vapor intrusion investigations. Passive air and soil gas sampling provides a line of evidence on the kinds of compounds present and their relative distribution. These results allow investigators to focus more invasive and expensive sampling in areas requiring further investigation while eliminating other areas from further consideration.

One perceived limitation on passive sampling is the inability to report a vapor concentration through direct measurement of the volume of gas sampled. The industrial hygiene community has developed accepted methods to report air concentration data from passive, sorbent-based vapor samplers. The methods described and published in the industrial hygiene literature were applied to the vapor-permeable membrane-based passive sampler discussed here. By extending the capability of a passive sampler to report concentration values, the applicability of the technique in vapor intrusion investigations increases markedly. The approach can not only assess the distribution of compounds at a site, provide information on the vapor pathway, and aid in conceptual site model development, but can also provide an initial look at the vapor concentrations present at the site. The concentrations can shed light on the potential risk present at the site by comparing the results directly to regulatory vapor intrusion screening levels, and then focus more invasive sampling techniques if the decision is to collect more data.

The site sampling example presented demonstrated variability observed in multiple, accepted active soil gas sampling techniques, and asks the question as to which dataset is correct when it comes to assessing human health risk due to vapor intrusion.

Figure 6. December active and passive soil gas sampling results.

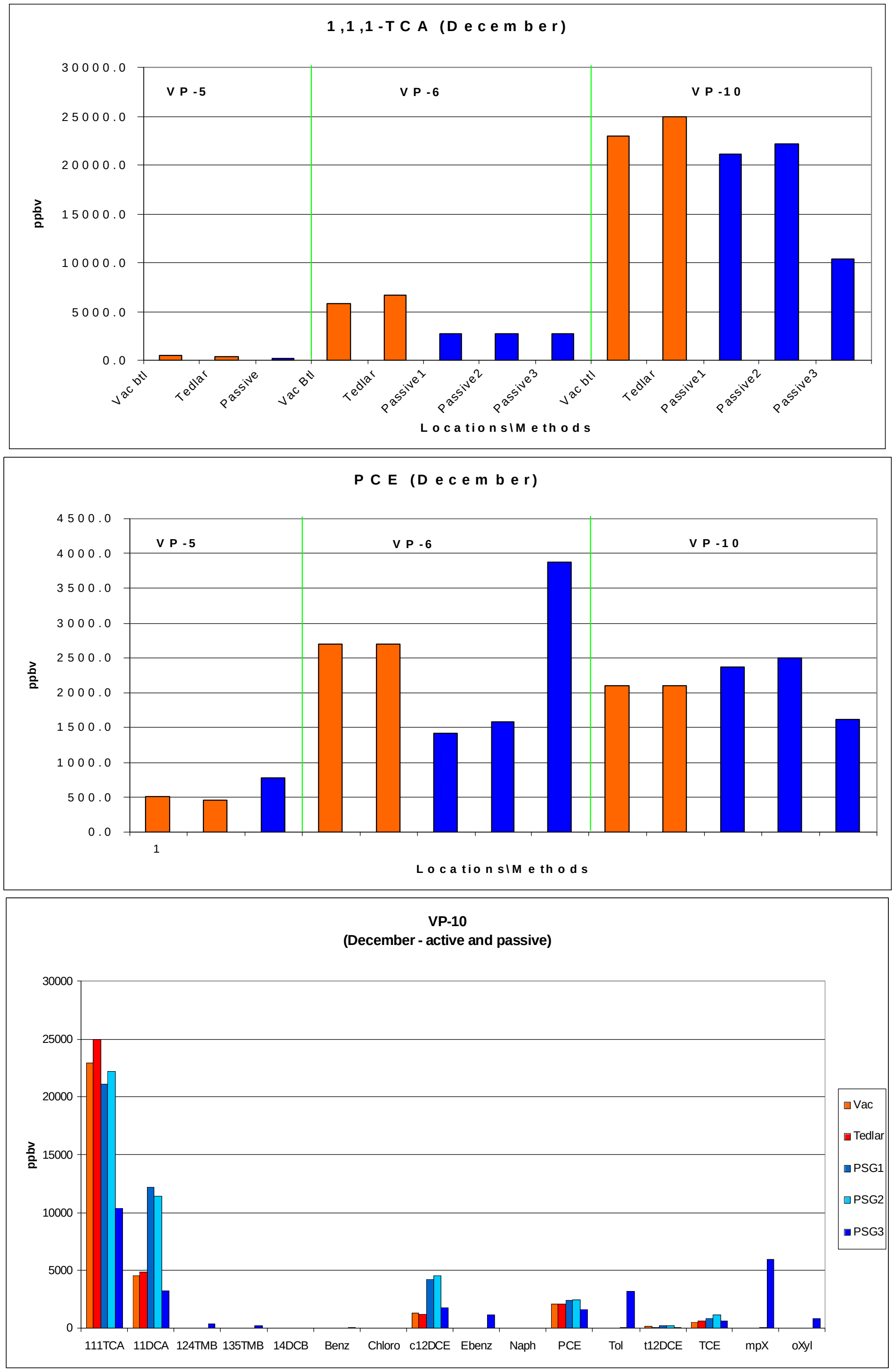
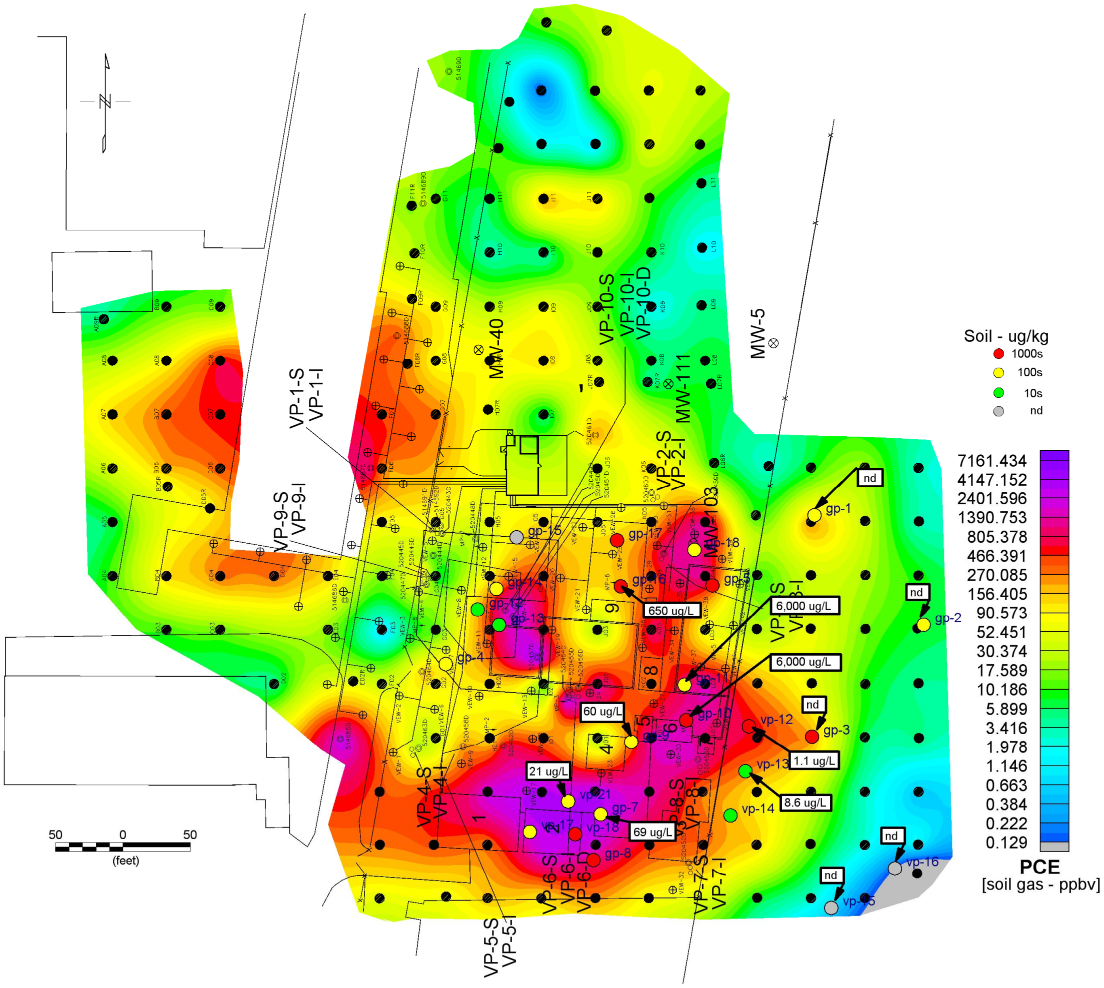


Figure 7. Site-wide passive soil gas survey, PCE, soil gas (ppbv, contours), soil (ug/kg, symbols), groundwater concentrations (ug/L, boxed)



The example also demonstrated the ability to report a quantified soil gas concentration from a passive sampler, and how the results compared to the active data. Despite the differences observed, there are positive comparative results between the active and passive datasets. In many cases, the comparability is strong. The results are encouraging in that soil gas concentrations reported using a passive approach are comparable to those reported with active techniques.

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KEYWORDS

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