

Session 4: Vapor Intrusion Issues at Petroleum Sites

The Significance of Hydrocarbon Biodegradation: Interpreting Observations of Hydrocarbon and Oxygen Behavior Above Shallow LNAPL Sources

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INTRODUCTION

Many field and laboratory studies indicate petroleum hydrocarbon vapors biodegrade readily in the vadose zone when sufficient oxygen is present. Roggemans et. al.¹, and Davis² present empirical databases which attribute hydrocarbon vapor attenuation with oxygen consumption and production of carbon dioxide. Abreu and Johnson^{3,4} created a three-dimensional multicomponent numerical model to simulate steady state vapor transport scenarios for aerobically biodegradable hydrocarbons which calibrates to Roggemans et. al. empirical data. Abreu and Johnson modeling indicates that when source concentrations are high and a relatively thin layer of clean soils separate source from building, hydrocarbon vapors can accumulate and an anoxic zone develop beneath the building slab or basement. Vadose zone hydrocarbon vapors may be absent at equivalent depths alongside the building where oxygen can diffuse downward through an open surface. Modeling illustrates sensitivity to source strength and depth to source for a given building type and size. Lower strength sources must be much closer to buildings (shallower) to generate the same hydrocarbon vapor accumulation and anoxic zone relationships as compared to higher strength sources. Abreu and Johnson modeling suggest a predictable relationship may be derived which combines source strength, source depth, and a type classification of building characteristics to predict where hydrocarbon vapor accumulation is possible. When validated through comparison to an expanded empirical database, these parameters may be incorporated into regulatory guidance as suitable screening criteria to determine where sub-slab investigation is warranted. Hydrocarbon vapor accumulations beneath buildings are only rarely observed at petroleum hydrocarbon release sites, since there is usually sufficient transport distance and/or sufficiently low source concentrations for biodegradation to attenuate vapors within the vadose zone. Examining sites where hydrocarbon vapor accumulation beneath buildings has been observed can help understand the high source strengths and short transport distances required for these conditions to occur.

CASE STUDY SUMMARY

Characteristics of three published sites where hydrocarbon vapor accumulations and associated anoxic zones are present beneath buildings are examined in the general context of Abreu and Johnson modeling boundary conditions. Published descriptions are cited from an engineered slab-on-grade building constructed at the former "Chatterton" petrochemical site in Delta, British Columbia (Hers et. al.⁵), a residential home with basement in Paulsboro NJ (Laubacher et. al.⁶), and a slab-on-grade shop building on the former Texaco refinery site in Casper WY (Luo et. al.⁷). Each site was underlain by generally sandy vadose zone soils, and each building had nested soil vapor probes installed through the slab or basement as well as alongside the building. Each site exhibited significant oxygen concentrations and low to non-detect hydrocarbon concentrations alongside the buildings at comparable depths to anoxic zones with significant hydrocarbon vapor accumulations measured

beneath the buildings. However, the aerobic/anoxic zone boundary was only depressed by a few feet, at most, alongside the buildings relative to the basement or slab. Significant hydrocarbon vapor attenuation was observed over transport distances of only a few feet where oxygen was present. Hydrocarbon sources were gasoline-range LNAPL in all cases. Source concentrations were not measured for the same constituents or in the same manner for all sites, but available data indicate source concentrations were generally within one order of magnitude of the 200 mg/l value assumed as a maximum by Abreu and Johnson. Clean soil thicknesses separating source zones and buildings varied at these sites, with the greatest thickness (approximately 12 ft) occurring at the Paulsboro NJ.

CONCLUSIONS

Published case studies where petroleum hydrocarbon vapor accumulations and associated anoxic zones are present beneath buildings have site characteristics that fall within the boundary conditions of the Abreu and Johnson numerical model simulations. Modeling and empirical data illustrate that where high strength sources are located short distances beneath buildings, a complete vapor intrusion pathway is possible. However, such conditions are easily identified, and are rarely encountered at UST release sites. An expanded empirical site database, supported by modeling, should allow derivation of combinations of source strength, source depth, and building characteristics that can be used as vapor intrusion screening criteria. If source characterization (strength and depth) were performed adjacent to a building as the first investigation step, screening criteria could be used to determine whether petroleum hydrocarbon vapor accumulation beneath the building is possible. Buildings that pass screening criteria could require no further investigation. Buildings that fail screening criteria might require more intrusive investigation, such as sub-slab and indoor air sampling, as the next investigation step.

REFERENCES

1. Roggemans, S.; Bruce, C.L.; Johnson, P.C.; Johnson, R.L. Vadose Zone Natural Attenuation of Hydrocarbon Vapor: An Empirical Assessment of Soil Gas Vertical Profile Data; American Petroleum Institute Bulletin: No. 15; Dec. 2001
2. Davis, R. Vapor Attenuation in the Subsurface from Petroleum Hydrocarbon Sources: An Update and Discussion on the Ramifications of the Vapor-Intrusion Pathway; LUSTline Bulletin 52, May 2006
3. Abreu, L.D.V., Johnson, P.C. Effect on Vapor Source – Building Separation and Building Construction on Soil Vapor Intrusion as Studied with a Three-Dimensional Numerical Model; Environmental Science and Technology, 2005, 39, 4550-4561
4. Abreu, L.D.V., Johnson, P.C. Simulating the Effect of Aerobic Biodegradation on Soil Vapor Intrusion into Buildings: Influence of Degradation Rate, Source Concentration, and Depth; Environmental Science and Technology, 2006, 40, 2304-2315
5. Hers, I., Atwater, J., Li, L., Zapf-Gilje, R. Evaluation of Vadose Zone Biodegradation of BTX Vapors; Journal of Contaminant Hydrology, 2000, 46, 233-264
6. Laubacher, R.C., Bartholomae, R., Reisenger, J.H. An Evaluation of the Vapor Profile in the Vadose Zone above a Gasoline Plume; In Proceeding of the Petroleum Hydrocarbons & Organic Chemicals in Ground Water. November 12-14, 1997. pp 396-409
7. Luo, H., Dahlen, P., Johnson, P.C., Creamer, T., Peargin, T., Lundegard, P., Hartman, B., Abreu, L., McAlary, T. Spatial and Temporal Variability and Oxygen Concentrations Beneath a Building Above

a Shallow LNAPL Source; In Remediation of Chlorinated and Recalcitrant Compounds: Fifth international Conference; May 22-25, 2006

The Use of Empirical Data to Evaluate the Impact of Biodegradation on Petroleum Hydrocarbon Vapor Intrusion

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INTRODUCTION

The USEPA and others have used databases of VOC concentration measurements to better understand vapor intrusion process and to support the development of screening concentrations for preliminary pathway evaluation. Typically, subsurface VOC concentration measurements (e.g., from groundwater or soil gas) are paired with shallower subsurface or above-ground VOC concentration measurements (e.g., from soil gas or indoor air). When such paired data are compiled for a large number of sites with diverse characteristics, the resulting database can be used to evaluate VOC attenuation along the vapor intrusion pathway. To date, the largest of these databases are composed primarily of chlorinated VOC measurements. As a result, these databases are not suitable for the evaluation petroleum hydrocarbon vapor intrusion because they do not reflect the differences in attenuation observed between petroleum and chlorinated VOCs due to difference in biodegradation and other factors.

PETROLEUM HYDROCARBON DATABASE

In order to evaluate the impact of biodegradation on petroleum hydrocarbon vapor intrusion, we have compiled the largest database of paired petroleum hydrocarbon measurements available to date. We have compiled measurements collected from over 100 sites in Colorado and more than 50 sites located elsewhere around the country. The sites cover a broad range of environmental characteristics with soil type ranging from predominantly clay to predominantly gravel and depth to groundwater ranging from 2.6 ft to 65 ft. The resulting database contains over 10,000 paired measurements of petroleum hydrocarbon concentrations.

In order to evaluate the key factors influencing petroleum hydrocarbon vapor intrusion, we have included a wide range of data on factors that may influence petroleum hydrocarbon attenuation. Most importantly, we have included oxygen concentration measurements, when available, in order to evaluate the relationship between oxygen concentration and petroleum hydrocarbon attenuation. In addition, we have included information on a variety of factors that may contribute to measurement uncertainty and variability. These factors include: sample point construction details, sample collection methods and analytical methods, lateral distance from the contaminant source to the measurement point, and lateral distance paired measurement points (i.e., lateral distance between paired groundwater and soil gas measurement points). By understanding the contribution of these factors to measurement uncertainty and variability in VOC concentration, we can more accurately assess the actual petroleum hydrocarbon attenuation. This evaluation will support the development of petroleum hydrocarbon screening concentrations for preliminary evaluation of the vapor intrusion pathway. In addition, we will be able to provide recommendations to improve the future quality of field measurements.

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A Model and Estimates for Subsurface Soil Vapor to Indoor Air Vapor Intrusion Including Oxygen Limited Biodegradation for a Multi-Component Gasoline Vapor Source

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Abstract

Development, parameters, results, and interpretation are presented for a subsurface soil to indoor air chemical vapor intrusion model that includes oxygen-limited biodegradation. The modeled scenario includes simple mixing within a building enclosure, diffusion-dominated soil vapor transport in a homogeneous subsurface soil layer, and a steady-state subsurface gasoline vapor source. The soil layer is divided into a shallow aerobic zone including biodegradation, and a deeper anaerobic zone in which biodegradation is neglected. Aerobic biodegradation of multiple chemical constituents is included in the model, with first-order kinetic rates estimated from measured biodegradation data for aromatic and aliphatic gasoline constituents. Oxygen demand is represented by the summed demand in aerobic biodegradation of the multiple source chemicals and an additional respiration term proportional to the organic carbon concentration in soil. Limited oxygen availability is specified, with oxygen supplied from the soil surface below the building foundation. Modeled results are calculated from the algebraic model with a range of representative parameters for the source vapor concentration, unsaturated soil characteristics, and building parameters. The results show both the effects of reaction kinetics and subsurface oxygen limits on chemical attenuation (as a ratio of indoor air to source vapor concentration). Comparison of model results to results that neglect biodegradation shows that the difference in estimates can be represented with two separate factors: (1) A factor accounting for chemical-specific aerobic reaction rate kinetics. This indicates an exponential decrease in attenuation factor (that is, lower indoor air concentrations) with increased source-to-building separation distance. Comparable model results that neglect biodegradation show a linear dependence. (2) A factor defined by the ratio of summed maximum oxygen demand to oxygen availability. This factor is approximately proportional to the aerobic soil depth divided by the building to source separation distance. Further, for applied site screening purposes, the model indicates that confidence in a minimum source to building separation distance is likely to be much greater than confidence in a specified attenuation factor, based on the indicated sensitivity to model input parameters.

Identifying the Source of Benzene in Indoor Air Using Different Compound Classes From TO-15 Data

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Extended Abstract

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INTRODUCTION

The presence of benzene in indoor air is frequently attributed to intrusion from soil gas, even though benzene concentrations in outdoor and indoor air are often very similar. All too frequently, outdoor air is ignored as a source of benzene to indoor air, and on-site samples are normally only taken for indoor and soil gas benzene, while outdoor air samples are not collected. Not considering outdoor air as a potential source of benzene to indoor air ignores the fact that outdoor air is the source of indoor air, especially considering that the typical design air exchange rate for commercial buildings and private residences is on the order of 1 complete exchange per hour [1], and considering that indoor and outdoor concentrations of benzene are often very similar.

The lack of ambient outdoor air benzene data can lead to the erroneous conclusion that soil gas is the source of indoor air benzene, when the actual source is outdoor air or specific indoor sources. In such cases, steps taken to mitigate intrusion of soil gas are wasted, since any reduction in indoor air benzene is insignificant compared to the influence of outdoor air or specific indoor sources.

Frequently, only the benzene data from the commonly-used TO-15 air method is considered, despite the fact that TO-15 reports data on more than 60 common organic air pollutants from a wide variety of sources, and include aliphatic and aromatic hydrocarbons typical of petroleum products and vehicle exhaust, ubiquitous halogenated organics (e.g., Freons), and oxygenates such as ethanol, isopropanol, and acetone that are emitted by common domestic activities. Many of these pollutants have the potential for providing source apportionment information to help determine the source of benzene in indoor air. In the present study, we are investigating the relationship between benzene and different classes (and different sources) of organic air pollutants at several sites thought to be impacted by soil gas from former manufactured gas plant (MGP) activities such as buried gas holders. Both a statistical (principal component analysis) approach and a more intuitive approach based on urban air chemistry are being pursued in order to develop tools that can differentiate sources of indoor air benzene at specific sites.

METHODS

TO-15 data was obtained from four sites thought to be impacted by proximity to former MGP activities. At each site, parallel indoor, outdoor, and soil gas air samples were obtained, and the results for all organics reported by TO-15 were obtained. For the majority of organics, non-detects in most

samples eliminated those compounds from the data set, resulting in ca. 15 to 20 organics being available for the source apportionment studies at each site.

Two different approaches are being used to determine if the different classes of organic compounds detected in the TO-15 analyses can be used to differentiate the impact of outdoor air and soil gas on indoor air benzene. Data are being analyzed using multivariate statistics in SAS® (SAS Institute, Cary, NC). Analytes dominated by data below the reporting limit (non-detect) are removed from the data set prior to analysis. In addition, samples containing non-detect values that exceeded the detected values are removed from the data set because the non-detect value contain no information about the analyte distribution in the air sample. Concentrations are transformed to rank values in SAS using mean values for ties. Principal components analysis (PCA) is done on the correlation matrix of the ranked TO-15 data to determine whether the variability in the data set can be accounted for by a substantially smaller number of principal components. PCA results are evaluated graphically to determine whether PCA can adequately discriminate indoor, outdoor and soil gas air samples. In addition to statistical analyses, the concentrations different classes of organic compounds that are characteristic of different sources of organic air pollutants are compared to benzene concentrations in an effort to identify the primary source of indoor air benzene.

RESULTS AND DISCUSSION

Examples of the compound classes which have the potential to differentiate various sources of air organics is shown in Figure 1. Generally speaking, urban air contains a mix of organics from all sources of human activity including petroleum products and their combustion residues, halogenated solvents and Freon refrigerants and propellants, oxygenates from fuels as well as some general oxygenated solvents. Indoor air typically contains the same organic mix as nearby outdoor air, with the addition of organics emitted by personal activities such as ethanol, isopropyl alcohol, and acetone. The presence (as well as absence) of different compound classes can be used to help determine the likelihood of different sources to benzene in an air sample. For example, if petroleum is the ultimate source of benzene in an air sample, the air sample should contain other major petroleum organics including some of the other volatile aromatic organics (e.g., alkyl benzenes) as well as petroleum alkanes such as isooctane. In contrast, if MGP products are responsible for benzene in an air sample, even though the distribution of benzene and other alkyl benzenes may look similar to a petroleum source, the *lack* of alkanes would indicate an MGP, and not a petroleum source. Halogenated organics such as Freons are neither MGP nor petroleum hydrocarbons, but are ubiquitous in urban air. Therefore, the proportion of benzene to Freons in indoor air should be similar to that in outdoor air, if outdoor air is the source of the indoor benzene. In contrast, if the indoor benzene is from soil gas (e.g., contaminated with petroleum or MGP products), then the relative proportion of benzene to Freons should be much higher, since neither petroleum nor MGP contaminants should contribute Freons to the air.

The concept of using ratios of different organics to differentiate sources of benzene is shown in Figure 2 for data samples collected in (and outside of) several businesses located in a strip mall. At this site, two soil gas samples had benzene concentrations ca. 10-fold higher than indoor air and, therefore, soil gas contaminated with gasoline was thought to be the source of indoor air benzene (even though outdoor and indoor air concentrations of benzene were virtually the same). However, when benzene is ratioed to Freon 11 (as a tracer of urban air) and to isooctane (as a tracer of petroleum products), it is clear that indoor and outdoor air (and the uncontaminated soil gas) are remarkably similar, while the

contaminated soil gas is substantially different in composition. Thus, given the facts that (1) indoor and outdoor air benzene concentrations were very similar, and (2) the ratio plot with the tracer organics clearly shows that soil gas is not related to indoor air, we conclude that the major source of benzene in indoor air is outdoor air, and can further conclude that any attempts to reduce indoor air benzene by reducing soil gas intrusion will be fruitless.

The application of principal component analysis to differentiate the air samples from the same strip mall as shown in Figure 2, is illustrated in Figure 3. Note that, while there is some discrimination between indoor and outdoor air, the discrimination is much larger between indoor air (and outdoor air) and soil gas. These results, taken along with the similar concentrations of benzene in indoor and outdoor air at this site, lead to the same conclusions as the tracer ratio plot (Figure 2), that the indoor air benzene at this site is contributed by outdoor air, not soil gas.

CONCLUSIONS

The contribution of outdoor air to indoor air benzene is frequently ignored, even though indoor and outdoor benzene concentrations are often very similar, and even though buildings typically exchange their air with outdoor air at least one time per hour. Based on our studies to date, the use of organic compounds that are indicative of different sources of benzene should be useful for determining the relative contributions of outdoor air and soil gas to indoor air benzene. Caution will be needed as this approach is applied, since many potential tracer compounds are likely to have spurious concentrations at some locations (e.g., xylenes are good indicators of petroleum contamination, but are also used in spray paints). The use of compound ratios and principal component analysis to determine the source of benzene in indoor air is currently being applied to different sites, and these studies should help to evaluate the general value of these approaches.

REFERENCES

[1] American Society of Heating, Refrigeration, and Air Conditioning Engineers, ASHRAE Fundamentals Handbook, 1981.

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Figure 1: Classes of Organics in Urban Air (from TO-15)

Halogenated (and Freons): Some are ubiquitous, and some are from local sources. None are petroleum or MGP hydrocarbons.

BTEX and volatile PAHs come from MGP, petroleum, and solvents (paints, etc)

Alkanes and cyclic alkanes are mostly from petroleum products and vehicle exhaust, but not MGP

Some oxygenates (e.g., ethanol, acetone) are indicative of personal activities

Figure 2: Ratio plots for indoor air, outdoor air, contaminated soil gas, and uncontaminated soil gas at a strip mall.

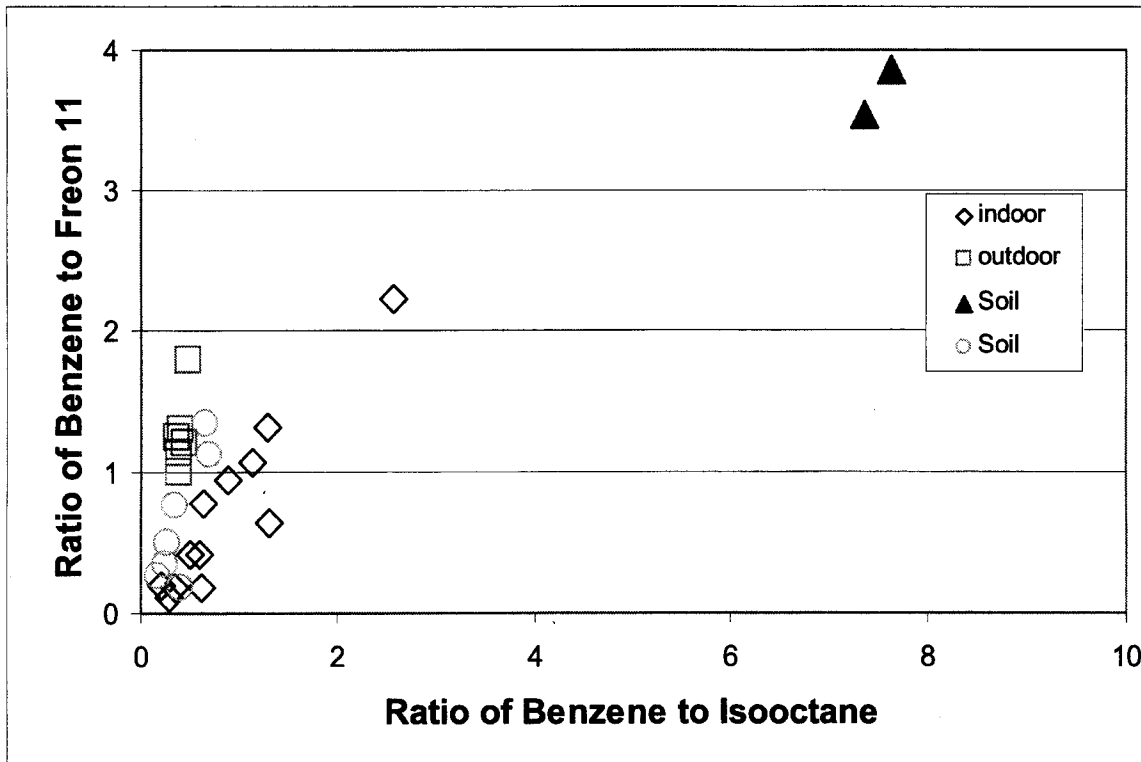
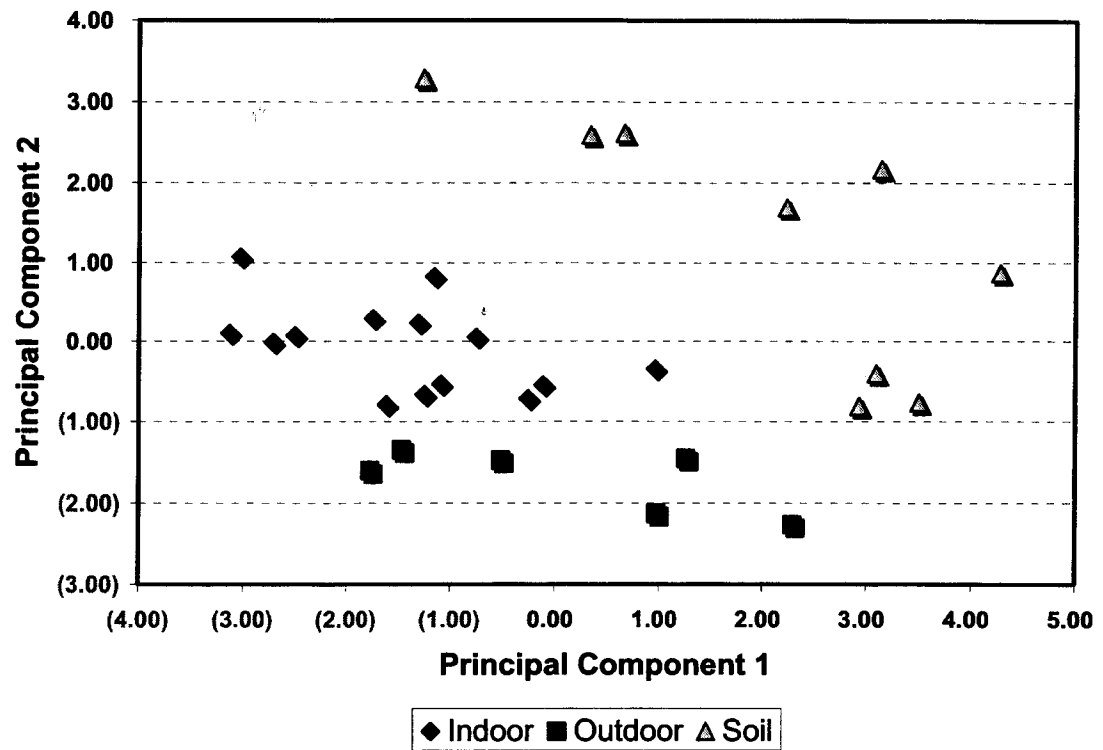


Figure 3: Principal component analysis of TO-15 data from indoor, outdoor, and soil gas air at a strip mall.



The Importance of Background VOC Concentrations on VI Decision Making at Petroleum Hydrocarbon Sites

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Introduction

In the evaluation of the vapor intrusion (VI) pathway, the regulatory decision-making process often funnels investigations toward indoor air measurements. Some regulatory guidance expresses a preference for indoor air measurements while others move toward it when soil vapor evaluations do not conclusively show that vapor intrusion is insignificant. The problem is that the use indoor air concentrations can be the most difficult method from which to reach a conclusive decision. This is because for VI evaluations, it is the incremental increase in indoor air concentration due to VI that is the issue, not the absolute concentration itself. Since typical background levels of volatile organic compounds (VOCs) in houses, offices, and other buildings are relatively high compared to acceptable concentrations for many compounds, it is difficult or impossible to measure vapor intrusion directly using only indoor air measurements. This paper examines the use of indoor air data alone as a means of evaluating the pathway; and discusses data analysis methods that have been suggested to supplement the indoor air data and to provide a means of evaluating the data.

Evaluation of Indoor Air Data

Consider the example of benzene in a single-family house. The vapor concentration for a 10^{-6} incremental risk level for continuous exposure to benzene is typically quoted to be 0.098 ppbv (US EPA, 2002) with a range of 0.04 to 0.14 ppbv (0.13 to 0.45 $\mu\text{g}/\text{m}^3$) (EPA IRIS Database, <http://www.epa.gov/iris/subst/0276.htm>). If there were no other sources of benzene in houses, an indoor air measurement approach to evaluate the VI pathway might work if the analytical technique is sensitive enough. But, there are other background sources. One source is ambient air entering the building either through the HVAC system air intake [if any] or by in-leakage through doors, windows, and floors. A second, and more likely the greatest contributor, are indoor emission sources, such as cleaning products, paints, building materials, or stored fuels.

The median concentrations for benzene are roughly 0.87 ppbv in residential indoor air and 0.34 ppbv in outside air (see Table 1). So, the acceptable incremental increase allowable for vapor intrusion of 0.098 ppbv is ~11% of the typical indoor air value. Such a small incremental increase cannot be observed in a measurement study because it will be obscured by the total variability that is present. The total variability is the sum of the measurement variability (i.e., sampling & analytical), temporal variability (i.e., how will a measurement made now differ from a measurement made at another time?), and spatial variability (i.e., how will a measurement made at one location differ from a measurement made at another location?). For indoor air measurements, the temporal variability is believed to be the most important component of the total variability. Kuehster, et al. (2004) showed that concentrations of 1,1 DCE varied by about an order of magnitude over 6 yr in indoor air.

There are three general approaches to take into account background VOC concentrations:

1. Compare measured indoor air values to published values;

2. Compare measured indoor air values to experimental controls; or
3. Perform data analysis to extract vapor intrusion information from a set of site-specific measurement data.

Each of these three general approaches is briefly described below, followed by an example illustrating one specific type of data analysis method to evaluate vapor intrusion.

Approach #1 - Compare Measured Indoor Air Values to Published Values

Background concentrations should be considered when developing an experimental design for a given site. Comparing measured indoor air values to published values also can be a useful first step in data analysis. Published values cannot, however, be used to systematically correct measured data, for the reasons explained below.

Typical Background Concentrations

Table 1 summarizes the measurement data from several large databases for indoor air in existing residences, indoor air in office buildings, and ambient air. Median and maximum data are given for selected hydrocarbons often encountered at petroleum hydrocarbon sites. For comparison purposes, data also are given for selected chlorinated solvents. The table includes EPA's acceptable indoor air concentration based on a risk level of 10^{-5} or $HQ = 1$. The median value in ambient air or indoor air is greater than or nearly equal to the EPA target concentration for certain compounds (e.g., benzene, TCE). For such compounds, the comparison of measured indoor air concentrations to regulatory guidelines will lead to many false positive results for vapor intrusion.

Using Typical Background Concentrations To Evaluate Indoor Site Data

If background sources are not an issue, indoor air measurements may be an excellent approach for a given site. To make an initial determination of whether background sources are likely to be an issue, either during development of the experimental design or after indoor air data have been collected, the following steps are recommended:

1. Determine the acceptable indoor air concentration (i.e., risk endpoint) for the VOCs of greatest interest;
2. Identify and review the relevant data from the site (if available) or from the national databases summarized in Table 1.
3. Select an acceptable concentration to screen for false positive results. A recommended default screening concentration is the 95th percentile value for the compound chosen in step #2 (see Table 1).
4. Compare the risk endpoint to the selected percentile value for the compound from step #2. If the risk endpoint is higher than the selected percentile value, indoor air measurements should be considered. If the risk endpoint is lower than the selected percentile value, indoor air measurements are likely to result in an unacceptable level of false positive results.

Correcting Indoor Air Data for Background Concentrations

Unfortunately, it is not useful to attempt to correct measured concentration data for generic background concentrations. There are 2 issues: the relative magnitude of the indoor air VOC concentrations compared to the concentration we are trying to measure and the range of typical indoor background concentrations (about a factor of 10 between the 5th and 95th percentile concentrations).

First, the difference between two (relatively) large numbers often is not very meaningful. In our benzene example above, suppose we make indoor air measurements and get results in the 0.8 to 1.0 ppbv range. Correcting for a typical indoor air concentration of ~0.9 ppbv will result in values ranging from -0.1 to 0.1 ppbv, all of which are close to the acceptable incremental concentration at 10⁻⁶ incremental risk. Some of the corrected values might be above the guideline and some might be below, so we don't know if any of these concentrations reflect a contribution from vapor intrusion. If we consider multiple houses, the same problem exists. Measurements made at an adjacent house might be in the 0.5 to 0.7 ppbv range and measurements made at another nearby house might be in the 1.5 to 2 ppbv range. Both of these sets of measurements are within the normal range of indoor air values, but may yield opposite results when corrected and compared with the risk endpoint.

Second, what correction to apply depends on how conservative one wants to be. If the median value is used, the correction will over-predict for one-half of the cases and under-predict for the other one-half. If the 10th or 25th percentile is used to be more conservative, the correction may no longer be very useful in excluding sites with only background concentration levels.

Third, any data correction will still result in some false positives. Even if a regulatory agency agreed to allow data correction using the 90th percentile value (an extremely unlikely scenario), measurements made in a 20-house neighborhood would still be expected to yield one or two houses that have positive non-zero values after the correction is applied, even if no vapor intrusion is occurring. If the risk endpoint is low enough, these non-zero corrected values can exceed the guideline and falsely indicate that unacceptable rates of vapor intrusion are occurring.

Approach #2 - Compare Measured Indoor Air Values to Controls

In some cases, site-specific correction factors can be developed from indoor air measurements made at near-by buildings where vapor intrusion is not occurring. These near-by buildings serve as experimental controls. Ideally, these are very similar to the buildings to be evaluated in terms of both mass flow of contaminants from outside air and emissions of contaminants from indoor sources.

Two types of experimental controls can be considered. One type are buildings in the area of suspected subsurface contamination that have VI control systems in place, such as sub-slab depressurization systems. The second type are buildings in a similar setting that are not in the area of suspected subsurface contamination. For example, if there are 10 houses to be evaluated near an industrial facility, the controls might be 10 other houses in a similar socio-economic neighborhood that is not near the industrial facility.

The measured concentrations in indoor air at the sites to be evaluated for vapor intrusion are compared to the data from the controls to see if there is a difference and, if there is, to see if this difference is statistically significant. First, the mean of each data set is compared: the mean for the data set of

buildings where vapor intrusion is suspected (X_{VI}) and the mean for the data set of buildings that serve as controls ($X_{Control}$). If $X_{VI} > X_{Control}$, vapor intrusion might be occurring. Second, the standard errors for the two data sets are calculated. The standard error is the standard deviation (σ) divided by the square root of the sample size ($n^{1/2}$). Three, the two data sets are compared at a selected confidence interval. For example, the 95% confidence interval is approximately equal to $X \pm 2\sigma$ for large values of n . If the confidence intervals overlap, the difference between the two mean values is not statistically significant.

The data set should be evaluated to see if it exhibits a normal (Gaussian) distribution or a log-normal distribution. Most indoor air VOC data will exhibit a log-normal distribution and data transformations may be appropriate before applying statistical tests.

Comparison of measured data to controls is only meaningful if the standard errors are known and are reasonably small. Comparison of data to a single control can be suggestive, but cannot be definitive. There is too much variability from building to building in indoor emission sources (and in air exchange rates) to rely upon a single point of comparison. If enough data were available, one could consider using multi-variable analysis techniques in order to consider several different factors.

Approach #3 – Perform Data Analysis

If measured concentrations of VOCs in indoor air exceed risk targets, vapor intrusion may or may not be occurring. It is possible in some cases to determine the contribution from vapor intrusion through data analysis. Numerous data analysis methods are possible and under development with examples provided by several individuals (McHugh, 2005; McAlary and Dawson, 2005; Kurtz, et al, 2004; Hawthorne, 2004, Trusedale, 2004). The authors have written a document titled, "Recommended Practices Manual for Decision Making in Vapor Intrusion Evaluation." The manual is expected to be helpful to responsible parties and their consultants, as well as regulators.

Some are suitable for the types of small data sets often encountered in VI studies, while others require relatively large data sets (e.g., log-probability plots, temporal plots). The methods suitable for small data sets are outlined below.

The data analysis methods outlined below can be used to determine whether or not various compounds exhibit similar behavior to one another. This information can be used to ascertain whether the measured concentrations in indoor air for a given VOC are the result solely of vapor intrusion, solely of background sources, or a combination of vapor intrusion and background sources.

The types of data analysis that can be employed will depend on the type of data that has been or can be collected. For example, if no soil-gas data are available, no attenuation factors can be calculated. If no radon data are available, it cannot be used as a tracer. Therefore, the data analysis options that might prove useful should be considered when designing the study.

When examining data sets to determine the impact of background sources on measured indoor air concentrations, the following data analysis methods should be considered:

Comparison of Measured Concentrations to Guidelines – If the measured indoor air values are below the relevant standards or guidelines, the effect of any background sources is not significant. No further data analysis may be necessary.

Comparison Across Multiple Media or Sample Types – Evaluate the data to see if the compounds detected in indoor air are consistent with the compounds detected in soil-gas, ambient air, groundwater, and soil. If vapor intrusion is occurring, the same general mix of compounds typically will be seen in the various sub-surface samples and in the indoor air. In general, the measured concentrations should diminish with distance from the source, both vertically and laterally.

Comparison of Measured Concentrations to Typical Composition Data for Potential Sources – Evaluate the data to see what compounds are detected. Do the samples exhibit a typical “fingerprint” for gasoline, fuel oil, etc. If the release is aged, the lighter molecular weight compounds may be absent or present in diminished amounts.

Evaluation of Spatial Variability – Evaluate the data to see the relationship between samples collected in different locations, either within a single building or within multiple buildings. For example, compare data collected at the basement level to data collected on the first floor of the same house. If the measured VOCs are due to vapor intrusion, higher concentrations would be expected in the basement samples.

Evaluation of Temporal Variability – Evaluate the data to see the relationship between samples collected at different times.

Evaluation of Concentration Ratios – This evaluation method may take several forms. One, attenuation factors (α) can be calculated from the ratio of indoor air concentrations to soil-gas or sub-slab soil-gas concentrations. Determine if the α values are consistent from VOC to VOC. Two, the ratio of various compounds in a single media can be compared. For example, the ratio of toluene to benzene will be in the 1:1 to 3:1 range for most combustion-related sources. Three, evaluate the data set to see if any VOCs can be used as an indicator compound. An indicator compound is a compound that is not affected by background sources. Non-VOCs, such as radon, may also serve this purpose. In some cases, the experimental design may include the release of tracer compounds, such as SF₆, that serve as an indicator compound.

Evaluation of Mass Flow – As an alternative method to comparing compounds and their concentrations, it may be useful to think in terms of emission rates (mass flow). Concentration measurements alone do not provide any information about mass flow. Both concentration and volumetric flow must be measured or estimated, not just concentration. The building ventilation rate (Q_{Bldg}) can be measured using tracer gases or volumetric flow measurements. For office buildings and some commercial buildings, Q_{Bldg} can be estimated with a fair degree of accuracy based on the total airflow capacity of the HVAC system and the design spec for percent make-up air. Typical air exchange rates for houses and office buildings are shown in Table 2.

As a very gross 1st level check of mass flow, compare concentration levels in different media. For example, if the indoor air concentration is higher than the sub-slab soil-gas concentration for a given VOC, vapor intrusion of that compound probably is not significant (McHugh, et al., 2006). A 2nd level

check is to use pressure differential test results. For vapor intrusion to occur at significant rates, there must be a negative pressure differential between the building and the soil to induce advective flow. For a 3rd level check, use estimated ventilation rates and measured concentrations to calculate mass flow. For a 4th level check, use tracer gas or indicator compound results.

Example – Evaluating Benzene Using an Indicator Compound

A facility owner is asked to determine if vapor intrusion of benzene is significant at a neighboring single-family residence. The acceptable indoor air (target) concentration for benzene is 0.98 ppbv (3.1 µg/m³). Vinyl chloride (VC) is present at the site due to past releases from a 2nd facility, which went bankrupt and no longer exists. The following average concentrations are measured in the field:

Data Type	Benzene		Vinyl Chloride	
	ppbv	µg/m ³	ppbv	µg/m ³
Indoor Air	3.0	9.6	0.25	0.65
Sub-Slab Soil-Gas	100	320	500	1,280
Ambient Air	0.5	1.6	<0.036	<0.19

A tracer gas, helium, was released within the house to determine the air exchange rate. A value of 0.8 ACH was measured, which is a reasonable value for an older house. The house is about 10m by 10m by 2.5m, so the internal volume is 250 m³ and the ventilation rate is 200 m³/hr.

The first data analysis steps do not rule out vapor intrusion. Benzene has been detected in the indoor air. It also was detected in the soil gas. Furthermore, the concentration of benzene in indoor air exceeds the target concentration. The next steps in the data analysis are to look at relative concentration levels and mass flow rates.

Indoor sources of VC are relatively rare and no VC was detected in the ambient air. Therefore, VC can be used as an indicator compound. For VC, $\alpha = 5.0E-04$. If there are no background sources, it can be demonstrated that $Q_{soil} = [Q_{Bldg}][\alpha]$, where α = attenuation coefficient = the ratio of the the indoor air and the soil-gas concentrations. Substituting the measured values in the example yields:

$$Q_{soil} = [200 \text{ m}^3/\text{hr}][5.0E-04] = 0.10 \text{ m}^3/\text{hr} \text{ (1.7 L/min)}$$

The rate of vapor intrusion (Q_{soil}) can then be used with the measured sub-slab concentration of benzene to calculate the mass flow due to vapor intrusion (E_{VI}):

$$E_{VI} = [0.10 \text{ m}^3/\text{hr}][320 \text{ µg/m}^3] = 32 \text{ µg/hr}$$

The contribution of VI to the indoor air concentration of benzene is this emission rate divided by Q_{Bldg} :

$$\text{Benzene}_{VI} = [32 \text{ µg/hr}] / [200 \text{ m}^3/\text{hr}] = 0.16 \text{ µg/m}^3 \text{ (0.05 ppbv)}$$

If there are any background sources of VC that contributed to the measured concentration in indoor air, this will result in an over-estimation of the contribution of vapor intrusion to the benzene concentration in indoor air.

The absolute concentration of benzene indoors is $9.6 \mu\text{g}/\text{m}^3$, which is well above the target level of $3.1 \mu\text{g}/\text{m}^3$. The contribution from vapor intrusion, however, of $0.16 \mu\text{g}/\text{m}^3$ is well below the target concentration. Vapor intrusion accounts for <2% of the measured concentration of benzene in the indoor air. Based on this evaluation, vapor intrusion of benzene is insignificant.

Summary

Typical background levels of volatile organic compounds in houses, offices, and other buildings are relatively high compared to the health derived acceptable concentrations resulting from VI. Thus, it is difficult or impossible to measure the potential impact of vapor intrusion directly using only indoor air measurements because it is the incremental increase in indoor air concentration due to VI that is the issue, not the absolute concentration itself.

This paper discussed the implications of background concentrations on decision making and reviewed and suggested techniques for making decisions. It is doubtful that one single technique is applicable to all sites and it is highly likely that different techniques or the same technique applied to different compounds will provide different answers. It is clear that decision making will require good professional judgment. To assist decision makers, a manual has been prepared with further information on the topics discussed in this paper; readers can request a copy for review from the authors.

References

Chan, W.R., W.W. Nazaroff, P.N. Price, M.D. Sohn, and A.J.Gadgil. Analyzing a Database of Residential Air Leakage in the US. *Atm. Env.*, Vol. 39, pp3445-3455. 2005.

Hawthorne, S. and Harju, J. Identifying the Source of Benzene in Indoor Air Using Different Compound Classes from TO-15 Data, proposal nto the American Petroleum Institute, Washington, D.C. November, 2004.

Hodgson, A.T. and H. Levin, Volatile Organic Compounds in Indoor Air: A Review of Concentrations Measured in North America Since 1990, LBNL- 51715, April 21, 2003

Kuehster, T. Folkes, D; and Wannamaker, E. "Seasonal Variation of Observed Indoor Air Concentrations Due to Vapor Intrusion" presented at Midwestern States Risk Assessment Symposium, Indianapolis, In, August 25-27, 2004.

Kurtz, J.P., Folkes, D., and Kuehster, T.E. "Approaches to Quantification of Background VOCs in Indoor Air" presented at the Midwestern States Risk Assessment Symposium, Indianapolis, IN, August 25-27, 2004.

McAlary, T. and Dawson, H. "How TO Determine, Interpret, and Resolve Background Contributions from Indoor Air Data" presented at AEHS Vapor Intrusion Workshop, San Diego, Ca, March 14, 2005.

McHugh, T. "Vapor Intrusion Investigation Methods", presented at API/NGWA Petroleum Vapor Intrusion Workshop, Costa Mesa, Ca, August 17, 2005.

McHugh, T.E., P.C. DeBlanc, and R.J. Pokuda. Indoor Air as a Source of VOC Contamination in Shallow Soils Below Buildings. *Soil & Sediment Contamination*, Vol. 15, pp103-122. 2006.

Persily, A. and J. Gorfain. Analysis of Ventilation Data from the US EPA Building Assessment Survey and Evaluation (BASE) Study. NISTIR 7145. December 2004.

Shah J.J. and Singh H.B., "Distribution of Volatile Organic Chemicals in Outdoor and Indoor Air" *Environ. Sci. & Tech.*, Vol. 22, No. 12, 1988

Truesdale, R. Final Report Describing VI Attenuation Workshop, Database, Analysis of Attenuation Factors, Precluding Factors, and Recommendations for VI Guidance Modifications; Subtasks 2.10 Deliverable, EPA Work Assignment 5, EPA Contract No. 68-W-98-215. RTI International Memorandum, May 17, 2004.

US Environmental Protection Agency. Exposure Factors Handbook, Volume III - Activity Factors, Chapter 17 - Residential Building Characteristics. U.S. EPA, ORD. EPA/600/P-95/002Fa. August 1997.

US EPA, Draft Guidance for Evaluating the VI to Indoor Air Pathway from Groundwater and Soils, November 2002.

US EPA, 2003 Urban Air Toxics Monitoring Program (UATMP) Final Report, EPA-454/R-04-003, July 2004.

Key Words:

Vapor intrusion, background, VOCs

Session 2: Modeling, Sampling and Analytical Considerations

Use of Predictive Models in Vapor Intrusion Investigations

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Predictive models can be of significant benefit for vapor intrusion investigations in helping identify sensitive parameters for site investigations, understand or quantify relevant transport processes, define unknowns, and bound uncertainties. In general, however, vapor intrusion modeling beyond simple conservative spreadsheet models is not performed and acceptance of more sophisticated models that can refine predictions is limited. Lack of regulatory acceptance stems, in part, from general unfamiliarity with relatively new models and concerns over the quality of data used to support their application. For petroleum hydrocarbon sites, the degree of conservatism is exaggerated with current simple spreadsheet models because the models do not account for biodegradation, which can be a critical attenuation mechanism, especially at dissolved-phase contamination sites. For these applications, a simple predictive transport model was developed to assess risk-based target levels in groundwater based on assuming conservation of mass, steady-state, one-dimensional transport in the unsaturated zone, and first-order biodegradation kinetics. The model is used to develop dimensionless type curves that can be applied to estimate risk-based target concentrations in ground water associated with vapor intrusion. The type curves are developed from knowledge of the mass flux across the building foundation, which can be determined from the risk-based screening level in indoor air, building size (area), and ventilation rate. Risk-based concentrations in ground water are extrapolated from the mass flux estimate on the basis of soil type (effective diffusion coefficient), depth to ground water, air-water partitioning (Henry's Law constant), and biodegradation rate. The model does not consider physical transport across the building foundation or gaseous-phase advection. Type-curve application indicates that current risk-based screening levels for benzene are far too conservative when applied to dissolved-phase contamination sites. Model assumptions were validated through an initial review of ground-water and soil-gas data collected at petroleum hydrocarbon sites.