Evaluation of Vapor Intrusion from a Subsurface Diesel Plume Using Multiple Lines of Evidence

John A. Connor, Farrukh Ahmad, and Thomas E. McHugh Groundwater Services, Inc, 2211 Norfolk, Suite 1000, Houston, Texas, 77098-4054

Abstract

Vapor intrusion from affected soils and groundwater into overlying structures has been identified as a potential mechanism for human exposure to volatile organic chemicals (VOCs), including petroleum hydrocarbons. However, in many cases, background concentrations of organic vapors in indoor air, associated with household products, vehicles, or ambient air, can lead to incorrect conclusions regarding the occurrence of subsurface vapor intrusion impacts. To investigate alleged vapor intrusion impacts from a subsurface diesel plume, a series of investigations has been conducted near a railway facility in Mandan, North Dakota, where organic vapors had been detected in both the subsurface and in indoor air. The results of this investigation demonstrate how multiple lines of evidence, including statistical cluster analysis, can be employed to distinguish between background indoor air quality and organic vapors associated with actual subsurface vapor intrusion.

To distinguish vapor intrusion impacts from background indoor air sources, this paper describes data management procedures and statistical methodologies for: i) comparing the organic vapor composition of indoor air, ambient air, and subsurface vapors; ii) comparing indoor air concentrations to background indoor air data compiled nationally and locally; iii) measuring vertical vapor concentration profiles within vadose zone soils and between subslab and indoor air, and iv) evaluating the temporal effect of soil vapor extraction (SVE) system operations on organic vapors in the subsurface and in indoor air. For the Mandan site, this evaluation showed that the indoor air composition in target buildings overlying the diesel plume closely matched the composition in background buildings located away from the affected area and exhibited a moderate match to ambient outdoor air. In contrast, all subsurface vapor sources (sub-slab gas, SVE discharge, well headspace gas) formed a very distinct cluster from that of the indoor air and ambient air data sets, such that the subsurface vapors could not create the vapor composition observed in the indoor air. The multiple lines of evidence indicated that indoor vapor sources were the likely cause of the VOCs measured in indoor air, with no evidence of contribution from subsurface vapor intrusion.

Introduction

Vapor intrusion from affected soils and groundwater into overlying structures has been identified as a potential mechanism for human exposure to volatile organic chemicals (VOCs) in indoor air (USEPA 2002). While vapor intrusion has been found to have impacted indoor air quality at a number of sites where chlorinated VOCs were present in underlying groundwater (Case and Gorder 2006; DiGiulio et al. 2006), petroleum hydrocarbons in soils or groundwater are recognized to pose a lesser potential for such vapor intrusion impacts (DeVaull et al. 2002; NJDEP 2005; Hers et al. 2006) due to greater vapor attenuation within the subsurface. For many sites where vapor intrusion is a concern for either chlorinated VOCs or petroleum hydrocarbons, background concentrations of organic vapors in indoor air, associated with household products, vehicles, or ambient air, can lead to incorrect conclusions regarding the occurrence of subsurface vapor intrusion impacts. Specifically, the presence of a specific VOC in both indoor air and subsurface vapors can lead to the assumption that the indoor air concentrations resulted from subsurface vapor intrusion, even though other background sources may fully account for the indoor air condition. To investigate alleged vapor intrusion impacts from a subsurface diesel plume, a series of investigations has been conducted near a railway facility in Mandan, North Dakota, where organic vapors had been detected in both the subsurface and in indoor air. The results of this investigation demonstrate how multiple lines of evidence, including statistical cluster analysis, can be employed to distinguish between background indoor air quality and organic vapors associated with actual subsurface vapor intrusion.

Both chlorinated VOCs and petroleum hydrocarbon VOCs have been found to be present in indoor air due to household products such as cleaning solvents, paint, adhesives, and aerosols, product or gasoline fuel residuals on hands and clothing, and ambient air sources (e.g., vehicle exhaust) (OSHA 1999; Olsen and Corsi 2002; USEPA 2002; McHugh et al. 2004). To distinguish actual vapor intrusion impacts from background indoor air and ambient sources, the following 4 types of investigation can be performed:

- *i)* Compare Vapor Composition Among Various Media: Characterize organic composition of indoor, ambient, and subsurface vapors based on 10 to 20 principal VOCs present in each medium and compare statistically to identify similar and dissimilar media.
- *ii)* Compare Indoor Air Above Affected Area to Background Indoor Air: Compare composition and concentrations of organic vapors measured in structures located directly above the affected soil and groundwater zone(s) to conditions observed in prior published studies on indoor air quality and to conditions measured in local background buildings located away from the affected zone(s).
- *iii) Evaluate Vertical Vapor Concentration Profiles in Subsurface:* Measure vertical vapor concentrations within the unsaturated soil zone between the subsurface source (i.e., affected groundwater or soil) and the ground surface to quantify vapor attenuation rate and/or compare sub-slab and indoor air vapor composition and concentrations to evaluate potential for vapor intrusion to be occurring.
- *iv)* Evaluate Temporal Effect of Vapor Remediation System on Indoor and Subsurface Vapor Concentrations: Compare indoor and subsurface vapor concentrations before and after activation of remediation system designed to intercept and/or remove subsurface vapors (e.g., soil vapor extraction system or sub-slab vent) to determine relative effect of remedial actions. Significant reduction of vapor concentrations in indoor air upon activation of the remediation system indicates prior vapor intrusion. However, no significant change in indoor air quality following system activation, particularly if significant drop in subsurface vapor levels are observed, suggests that no such vapor intrusion had been occurring.

These methods of evaluation are generally applicable to sites where vapor intrusion effects are of concern, for either chlorinated or petroleum hydrocarbon VOCs. In combination, the multiple lines of evidence provided by these analyses provide a confident technical basis for distinguishing between the effects of background sources and subsurface vapor intrusion, as well as for identifying the specific source and nature of vapor intrusion effects when vapor intrusion is occurring.

These data evaluation methods have been applied to investigate concerns regarding vapor intrusion from a subsurface diesel plume detected beneath a portion of the downtown area of Mandan, North Dakota, in proximity to a railway fueling facility and other diesel sources. Although the source(s), quantity, and composition of the light non-aqueous phase liquid (LNAPL) underlying downtown Mandan have been the subject of disagreement (Hostettler and Kvenvolden 2002; Stout and Uhler 2006; Stout et al. 2006), some or all of the petroleum LNAPL is understood to have been present in the subsurface for over 20 years and to consist of predominantly middle distillates. In 2002, a soil-vapor extraction (SVE) system was installed and operated in the affected area to mitigate organic vapor concentrations in the subsurface. At present, a multi-phase extractions system is being installed to recover both free-phase diesel and diesel vapors from the subsurface. The site investigation followed a multiple line-of-evidence approach, with the overall objective of determining whether the subsurface-to-indoor-air pathway was complete or incomplete for structures overlying the LNAPL plume.

Methods for Characterization and Comparison of Vapor Composition

As part of this effort, specific laboratory analysis and data evaluation methods have been utilized to characterize and compare the chemical composition of vapors from different sources (i.e., indoor air, ambient air, sub-slab vapors, well head vapors, SVE discharge, etc.). Brief descriptions of the methodologies employed for this purpose are presented below.

Vapor Sampling Locations

At the Mandan, North Dakota, site, an extensive vapor sampling and testing effort was undertaken by various parties over the period of 2000 to 2004. Site conditions consisted of a LNAPL floating atop a shallow water table approximately 17 to 20 feet below ground surface and overlain by an unsaturated soil zone. Vapor samples were collected from ambient air, indoor air, sub-slab (i.e., sub-foundation) vapor, vadose zone soil gas, vapor headspace within monitoring wells completed in the LNAPL zone, and the untreated vapors produced by the SVE system. The resulting database included information from 17 indoor air monitoring locations, 8 ambient air monitoring locations, the SVE system, 12 wellhead vapor sampling points, 5 sub-slab vapor sampling points, and 6 vertical soil vapor profiles, with analytical results on a total of over 350 vapor samples. These data provide a detailed basis upon which to evaluate the presence or absence of subsurface vapor impacts on ambient or indoor air in the Mandan area.

Laboratory Analytical Methods and Procedure for Selecting Principal VOCs to Characterize Vapor Composition

Vapor samples were analyzed for VOC content principally using USEPA Method TO-15, which measured over 30 individual analytes. To support statistical comparison of vapors from different media, the chemical composition of vapors samples collected at the Mandan site was characterized on the basis of the 17 principal VOCs that were detected in subsurface vapor, ambient air, and indoor air samples. When evaluating potential vapor intrusion associated with volatile mixtures such as petroleum products, it is important to consider a broad range of VOCs and not to limit the analysis to the specific chemical(s) of concern with regard to human health (e.g., benzene). Specifically, while benzene could be present in both indoor air and subsurface vapors at a site, the presence or absence of other VOCs may serve to demonstrate that the two vapors are, in fact, associated with distinct sources. For example, in the absence of some of the other principal VOCs associated with the subsurface vapor source, it may be clear that the benzene measured in indoor air could not have come from the subsurface. Conversely, the presence of the same principal VOCs in both media may suggest that vapor intrusion is occurring, particularly if a number of these VOCs are absent from background indoor air locations.

For each of the media analyzed (indoor air, ambient air, well headspace, and the SVE system exhaust), "principal VOCs" were identified for each medium based on average concentrations, detection frequency, and having been analyzed in all media to be compared. The resulting list of 17 principal VOCs identified in this evaluation are listed in Table 1 below. In all cases, the principal VOCs for use in characterization and comparison of vapor compositions will be site-specific in nature, depending on the particular mix of organic compounds present in indoor, outdoor, and subsurface vapors.

No.	Principal VOC	CASRN	No.	Principal VOC	CASRN
1	Benzene	71-43-2	10	4-Ethyltoluene	622-96-8
2	Toluene	108-88-3	11	1,3,5-Trimethylbenzene	108-67-8
3	Ethylbenzene	100-41-4	12	1,2,4-Trimethylbenzene	95-63-6
4	m,p-Xylene	1330-20-7	13	Methylene Chloride	75-09-2
5	o-Xylene	106-42-3	14	Carbon Disulfide	75-15-0
6	n-Hexane	110-54-3	15	2-Butanone	78-93-3
7	Cyclohexane	110-82-7	16	Trichloroethene	79-01-6
8	n-Heptane	142-82-5	17	Tetrachloroethene	127-18-4
9	Styrene	100-42-5			

Table 1. Principal VOCs for Evaluation of Vapor IntrusionPathway at Mandan, North Dakota, Site.

Statistical Data Evaluation Methods

For the Mandan site, the composition of vapor samples collected from different media (indoor air, outdoor air, sub-slab vapors, wellhead vapors, etc,) were evaluated for their relative similarity or dissimilarity using a standard exploratory statistical method known as

agglomerative cluster analysis (Everitt et al. 2001). Agglomerative cluster analysis involves an iterative series of pair-wise evaluations to identify the two most similar datasets within a group of datasets, based on a defined set of characteristics (in this case, concentrations of individual VOCs). After each iterative step, the two most-similar datasets are then linked (or combined) and treated as a single dataset for the next round of pair-wise evaluations. This evaluation process is continued until all of the datasets have been linked together, with the first links indicating the greatest similarities and subsequent links indicating incrementally decreasing levels of similarity. Based on this linking process, the datasets are grouped into distinct clusters based on their relative similarity to each other, which can be then be plotted as hierarchical trees or "dendrograms." In mathematical terms, the "similarity" between datasets (in this case, datasets of vapor measurements from different media) is quantified as the Euclidean distance or some variation of this distance (e.g., absolute value or squared value), which can be viewed as the magnitude of a vector between two points (or dataset characteristics) in multi-dimensional (or multi-parametric) space. Predictably, Euclidean distances are influenced by scale effects (e.g., magnitude of concentration, in this case), and, therefore, datasets are often normalized by a common parameter (e.g., concentration of common chemical constituent) in order to assess other factors of similarity or difference.

For the Mandan site, cluster analysis was used to evaluate the similarity in the vapor composition among different media (e.g., ambient air, background indoor air, indoor air above plume, sub-slab vapors, SVE system vapors, and well headspace vapors), as characterized by the normalized average concentrations of the 17 principal VOCs measured within each medium. The absolute concentrations of the 17 principal VOCs varied widely between media (e.g., over 2 orders of magnitude). Therefore, in order to compare the various media in terms of *composition* rather than concentration, the mean concentration of each of the 17 principal VOCs within a medium was normalized by dividing each principal VOC concentration by the mean benzene concentration in that medium. This correction is appropriate as, if a subsurface vapor source were indeed causing indoor air impacts, VOC concentrations in indoor air would be expected to be significantly lower than concentrations in the subsurface vapor (e.g., by a factor of 100 - 10,000x); however, given the similar diffusivities of the various principal VOCs, the normalized vapor compositions (i.e., the relative concentrations of each of the principal VOCs) would be similar between the indoor air and the subsurface vapor (or any other source medium, such as outdoor air). Using the normalized data sets, similarity of the various datasets was analyzed based upon the squared Euclidean distance measures and average linkage method, as provided by MATLABTM Release 13.1 (Matlab, Inc., PA).

Cluster analysis was also used to determine whether the indoor air composition of *individual* buildings overlying the affected area exhibited differences from the local background monitoring locations (i.e., vapor levels observed in buildings not overlying the LNAPL plume). Again, the buildings were clustered using the squared Euclidean distance measures and average linkage method. However, absolute VOC concentrations were used in this analysis (i.e., the concentrations were not normalized) so that any buildings with elevated VOC concentrations due to vapor intrusion could be distinguished from background buildings. This approach thereby considered both the composition of the various indoor

vapor samples and the magnitude of measured concentrations as key variables in determining similarity.

Evaluation of Multiple Lines of Evidence for Vapor Intrusion at Mandan, North Dakota, Site

The available database of air and vapor samples has been evaluated to determine whether diesel fuel underlying the downtown Mandan area was impacting indoor air quality in overlying buildings based on 4 principal lines of investigation: i) comparison of vapor composition among different media, ii) comparison of indoor air within buildings above the affected zone to indoor air measurements from national studies and local background buildings, iii) analysis of vertical concentration profiles in the unsaturated soil zone above the groundwater plume and between sub-slab vapors and indoor air, and iv) evaluation of the temporal effects of the SVE system operation on both subsurface and indoor air vapor concentrations. The procedures and results of these evaluations are described below.

1) Comparison of Organic Vapor Composition Among Various Media

In order to determine the likely origin of VOCs detected in indoor air above the affected groundwater zone, for each of the different media for which vapor samples had been collected (i.e., indoor air in buildings overlying the LNAPL plume, local background indoor air, ambient air, headspace vapors in monitoring wells in the LNAPL plume, vapor recovered by the SVE system, and sub-slab vapors), the distribution of the 17 principal VOCs in each medium, characterized as the normalized average concentrations, were analyzed using 2 principal statistical analysis tools: a) cluster analysis of the vapor composition and b) frequency of detection of principal VOCs.

- a) <u>Cluster Analysis of Vapor Composition</u>: Cluster analysis was used to determine the similarity in average normalized concentrations of the principal VOCs within ambient air, background indoor air, indoor air above the LNAPL plume, sub-slab vapors, SVE system vapors, and well headspace vapors. Results showed that indoor air in buildings located above the LNAPL plume was most similar to background indoor air, followed by ambient air. Well headspace vapors were most similar to SVE system vapors followed by sub-slab vapors. Finally, the air samples (indoor air above plume, ambient, and background indoor air) and vapor samples (well headspace, sub-slab, and SVE) clustered into two distinct groups with low similarity (see Figure 1A). Given the dissimilar composition of indoor vs. subsurface vapors and the close relationship between indoor air above the plume and at background locations, these findings indicate that vapor intrusion is not the source of organic vapors measured in indoor air above the plume.
- b) <u>Relative Frequency of Detection of Principal VOCs</u>: Examination of the frequency of detection for BTEX (benzene, ethylbenzene, toluene, and xylenes) and non-BTEX petroleum VOCs (hexane, cyclohexane, styrene, 4-ethyltoluene, and trimethylbenzenes) in indoor air and subsurface samples exhibited a sharp contrast between the different media. BTEX was found to be prevalent in all media analyzed, being detected in 69% to 72% of subsurface samples (i.e., well headspace and SVE system), in 85% of indoor air

samples for buildings overlying the LNAPL plume, and in 95% of background indoor air samples. In contrast, non-BTEX petroleum VOCs were frequently detected in subsurface vapor samples (i.e., present in 59% to 61% of the samples analyzed), but were relatively rarely detected in indoor air (i.e., in only 9% of indoor air samples in buildings overlying the LNAPL plume and in only 16% of background indoor air samples). If VOCs were migrating from the subsurface to indoor air, then, given the very similar air diffusivities of the 17 principal VOCs, the detection frequency for BTEX and non-BTEX petroleum VOCs should be very similar in subsurface vapor samples and in indoor air samples for buildings overlying the LNAPL plume. Furthermore, the detection frequency for BTEX and non-BTEX petroleum VOCs should be much lower in background indoor air samples in comparison to indoor air for buildings located over the LNAPL plume. However, the observed detection frequency for non-BTEX petroleum VOCs was much lower than the detection frequency for BTEX in all indoor air samples, and the detection frequency for both groups of VOCs is higher in background indoor air compared to indoor air for buildings overlying the LNAPL plume. These results indicate that the BTEX and other VOCs detected indoor air do not originate from subsurface diesel fuel.

2) Comparison of Indoor Air Above the Affected Groundwater Area to Background Indoor Air

In order to better understand the origin of VOCs detected in indoor air in buildings overlying the LNAPL zone, the average VOC concentrations (non-normalized) measured in these buildings were compared to background indoor air concentrations as had been determined in prior national surveys conducted by USEPA and others (USEPA 2002) Results of this analysis showed that the principal VOCs identified in indoor air at the Mandan site were widely detected in indoor air in buildings across the country not known to be affected by vapor intrusion. In addition, the average concentrations of these principal VOCs were consistent with the range of background VOC concentrations reported in these indoor air background studies, as compiled by McHugh et al. 2004 (Shah and Singh 1988; Stolwijk 1990; Fitzpatrick and Fitzgerald 1996; Foster et al. 2002; USEPA 2002; Sexton et al. 2004). It is therefore reasonable to expect that these same VOCs could be detected in indoor air in buildings in Mandan, North Dakota, as they had been in background studies throughout the U.S.

Cluster analysis was again employed to determine whether *individual* buildings above the LNAPL plume exhibited strong similarities or differences compared to local background indoor air monitoring locations (see Figure 1B). This analysis found that 9 of the 12 indoor air sampling locations located above the LNAPL plume (representing 8 of 11 buildings) were very similar to the local background indoor air locations, both in terms of vapor composition and concentrations of the principal VOCs. Two buildings (AS-28 and AS-31) showed modest dissimilarity due to elevated concentrations of chlorinated solvents clearly not associated with diesel. In addition, 1 of the indoor air sampling locations (AS-48) was found to exhibit petroleum hydrocarbons vapors that were clearly distinct from local background indoor air quality, as well as from the other indoor air sampling locations above the LNAPL plume. However, the composition of the hydrocarbon vapors detected in this building are not consistent with the underlying diesel LNAPL source. Rather, this building exhibits types and concentrations of VOCs not typically associated with diesel fuels (e.g., n-hexane, cyclohexane, n-heptane, toluene, and MTBE). The presence of highly elevated concentrations of MTBE (i.e., 5840 ppbv), a chemical used exclusively as a gasoline oxygenate, shows that the indoor air impacts at this location were associated with a gasoline fuel source, not a diesel fuel source. In addition, no MTBE was detected in the well headspace vapors of monitoring wells containing free-phase diesel fuel in this area, which, in combination with the results of sub-slab sampling at this location (see sub-slab section), indicates that the indoor air impacts at this building were likely associated with an indoor source rather than a subsurface source.

3) Evaluation of Vertical Vapor Concentration Profiles in the Subsurface

Two types of vertical vapor concentration profiles were evaluated in this study: a) vertical profiles to measure attenuation of organic vapors in the vadose zone above the affected LNAPL plume and b) comparison of sub-slab vapor concentrations with indoor air in the building space immediately above the sub-slab sampling point. Results of these analyses are summarized below.

- a) <u>Attenuation of Organic Vapor Concentrations in the Unsaturated Soil Column</u>: In order to understand the vertical distribution of VOCs within the subsurface, multi-point depth profile sampling was conducted at two locations overlying the LNAPL plume, one in an unpaved area (PLSB-17), and the other in a paved area (DSSB-51). At both locations, the concentrations of principal VOCs were highest directly above the soil gas-LNAPL interface, directly above the water table. However, VOC concentrations decreased rapidly with decreasing depth and were generally non-detectable at all sampling depths within 10 ft of ground surface. These results indicate that VOCs originating from subsurface diesel impacts are most likely undergoing biodegradation within the vadose zone soils and are not causing impacts to ambient air.
- b) <u>Evaluation of Sub-Slab Vapor Data</u>: Under diffusive transport conditions, VOCs always move from areas of higher concentration to areas of lower concentration. Therefore, for buildings where subsurface vapor intrusion is occurring, VOC concentrations in sub-slab vapor samples must be higher than VOC concentrations in indoor air. Conversely, VOCs at higher concentrations in indoor air compared to sub-slab vapors (i.e., sub-slab/indoor air concentration ratio < 1) cannot be the result of VOC migration from the sub-slab zone to the indoor air. Even for VOCs with an sub-slab/indoor air concentration ratio between 1 and 10 (i.e., moderately higher vapor levels in sub-slab zone than in indoor air), it is highly unlikely that vapor intrusion could be the primary source of the measured indoor air concentrations in sub-slab zone would be expected to reduce by a minimum factor of 50 to 100x in comparison with indoor air (USEPA 2002; Hers et al. 2005).</p>

Sub-slab vapor samples were collected from four buildings located in downtown Mandan above the LNAPL plume for comparison to indoor air samples collected from immediately above the sub-slab sampling point at the same time. Ratios of sub-slab vapor to indoor air concentrations were calculated for these four locations (results not shown). At 3 sampling locations, the ratio of sub-slab to indoor air concentration was less than 1 for at least 7 of the 17 principal VOCs and less than 10 for at least 16 of the

17 principal VOCs. These results indicate that sub-slab vapors were not the source of the observed indoor air impacts in these buildings.

Elevated sub-slab VOC concentrations were detected at one building (a local bakery), where 11 of 17 principal VOCs had sub-slab to indoor air ratios of greater than 10. However, indoor air VOC concentrations in this building were comparable to background indoor air locations, indicating that the elevated sub-slab vapors are not causing an indoor air impact (See Figures 2 A and B).

4) Evaluation of the Temporal Effect of Vapor Remediation System Operation on Indoor and Subsurface Vapor Concentrations

For sites where vapor intrusion has impacted indoor air quality, SVE systems (most commonly consisting of sub-slab ventilation systems) have been shown to be effective at mitigating indoor air impacts (Wertz and McDonald 2004; Brown Group 2006; Case and Gorder 2006). As a result, the effect of the SVE system operation on indoor air quality can be used as a check on the presence or absence of subsurface-to-indoor-air vapor intrusion. To evaluate the effect of the SVE system on indoor air quality in buildings overlying the LNAPL plume at the Mandan site, average indoor air concentrations were compared for the periods before and after activation of the SVE system in early 2002. As shown on Figure 3A, the average indoor air concentrations are similar before and after activation of the SVE system (actually increasing moderately for some VOCs), indicating that the SVE system has not resulted in a reduction of indoor air VOC concentrations. Similar results were observed for individual buildings, with no building showing a notable change in indoor air quality following activation of the SVE system regardless of proximity to the SVE system (results not shown). However, subsurface vapor concentrations, as measured in the SVE system effluent prior to treatment, have decreased by a factor of approximately 10x for BTEX and other petroleum related compounds, on average, since activation of the SVE system (see Figure 3B). If subsurface vapors had been causing a measurable effect on indoor air quality, the VOC concentrations in the indoor air would have decreased proportionately to the observed reduction in the subsurface vapor concentrations. The absence of a comparable change in VOC concentrations in indoor air in buildings in close proximity to the SVE system is another indication that no vapor intrusion was occurring at this site and that the VOCs detected in indoor air are associated with a source other than subsurface vapors (i.e., most likely common indoor sources of organic vapors).

Recommendations Regarding Methods for Evaluation of Multiple Lines of Evidence at Vapor Intrusion Sites

The data analysis described above clearly demonstrated that subsurface diesel was not causing impacts to ambient air or indoor air in the study area. Based on these results, the subsurface-to-indoor-air pathway and subsurface-to-ambient-air pathways were found to be incomplete at this site. This case study demonstrated that the following data evaluations methods are useful for characterizing and comparing vapor compositions as needed for sitespecific investigation of possible vapor intrusion impacts:

- Characterization of Vapor Composition Based on Principal VOCs: To support statistical comparison of vapors samples from different media, vapor composition may be characterized in terms of the principal VOCs consistently analyzed among each of the various media (e.g., indoor air, subsurface vapor, ambient air, background indoor air). Analysis of a broad list of VOCS (e.g., the 10 to 20 VOCs detected at the highest concentrations in over 50% of samples) and not simply those associated with health concerns (e.g., benzene) is important in order to be able to distinguish between different organic vapor sources. Concentrations within each data set can be normalized based on one common constituent (e.g., benzene) to support comparison of vapor composition and not simply concentrations.
- Statistical Comparison of Vapor Composition Among Various Media: Two types of statistical analyses of the vapor sample results were found to be useful for comparison of subsurface and indoor vapor compositions: i) cluster analysis of normalized average concentrations of principal VOCS, and ii) detection frequency of principal VOCS. Cluster analysis was highly effective in defining similar and dissimilar data sets, showing the indoor air above the LNAPL plume to be a close match to background indoor air and to be quite distinct from the composition of subsurface vapors.
- *Vertical Profiles of Soil Vapor Concentrations:* Two types of vertical vapor concentration profiles can be useful for assessing the occurrence of vapor intrusion: a) vertical profiles within the vadose zone soils above the affected groundwater zone and ii) comparison of sub-slab vapor concentrations with overlying indoor air. Discrete-depth soil vapor probes can be used to compile a vertical profile of soil vapor concentration for principal VOCS extending from the underlying affected soil or groundwater zone and indicate whether any vapors are migrating to ground surface so as to impinge on building foundations. Given the expected attenuation factor of 50 to 100x for subsurface vapors entering an indoor air space, sub-slab to indoor concentrations ratios of less than 10x or higher also show that indoor air concentrations cannot be explained by vapor intrusion.
- *Temporal Effects of Vapor Remediation System on Indoor Air and Subsurface Vapors:* If a remediation system has been installed to reduce subsurface or indoor vapor concentrations, evaluation of principal VOC concentrations in indoor air before and after activation of the remediation system can indicate whether a complete pathway for vapor migration into the building existed.



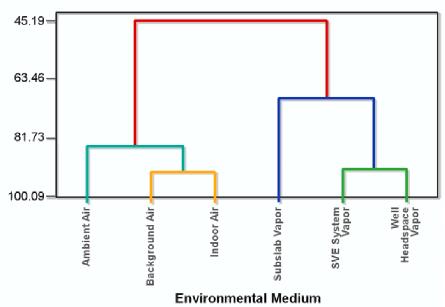


Figure 1A. Dendrogram showing similarity in distribution of principal VOCs in vapor samples from various media.

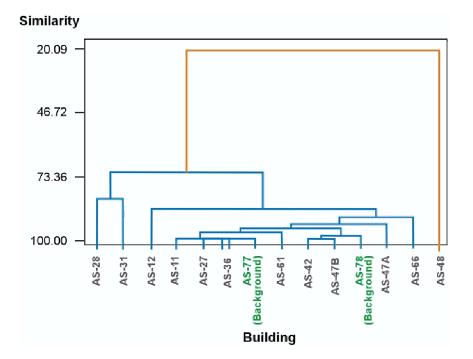


Figure 1B. Dendrogram showing similarity in distribution of principal VOCs in indoor air between individual buildings.

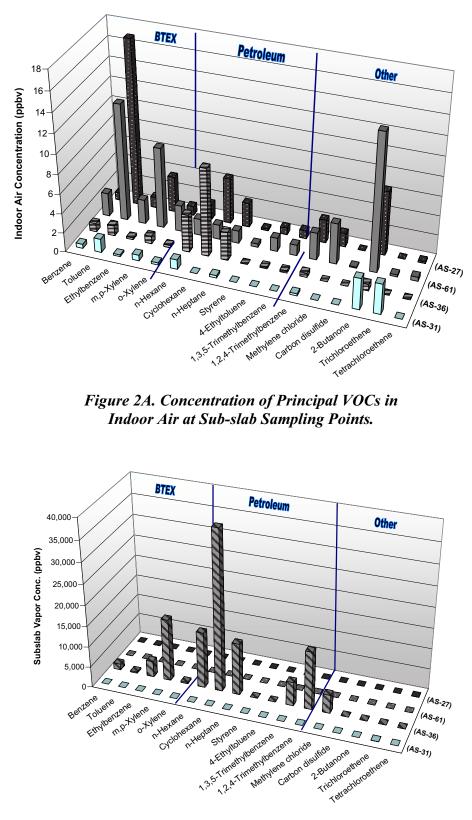


Figure 2B. Concentration of Principal VOCs in Sub-slab Vapor Samples.

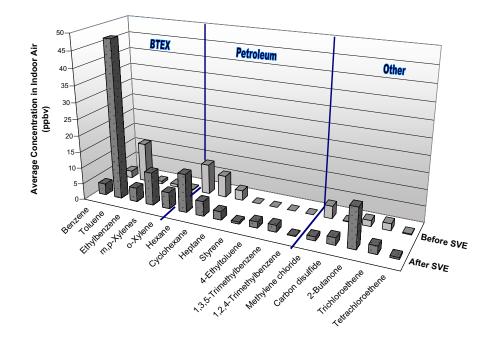


Figure 3A: Concentration of Principal VOCs in Indoor Air Above LNAPL Plume Before and After Activation of SVE System in Early 2002

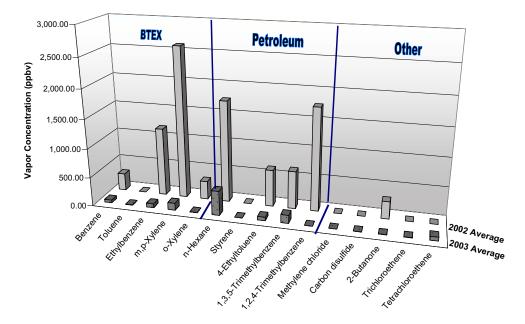


Figure 3B: Average Annual Concentrations of Principal VOCs in SVE System Discharge Gas During System Operation

References

- Brown Group (2006). Indoor Air Results and Mitigation, Status of Pre-Mitigation Indoor Air Test Map and Status of Post-Mitigation Indoor Air Test Map.
 - http://www.redfieldssite.org/indoorairresultsmitigation.php.
- Case, J. D. and K. A. Gorder (2006). The investigation of vapor intrusion at Hill AFB. Vapor Intrusion: The Next Great Environmental Challenge - An Update, Los Angeles, California, Air and Waste Management Association.
- DeVaull, G., R. Ettinger and J. Gustafson (2002). Chemical vapor intrusion from soil or groundwater to indoor air: Significance of unsaturated zone biodegradation of aromatic hydrocarbons. *Soil and Sediment Contamination* 11(4): 625-641.
- DiGiulio, D., C. Paul, et al. (2006). Assessment of Vapor Intrusion in Homes Near Raymark Superfund Site Using Basement and Sub-Slab Air Samples, U.S. EPA Office of Research and Development, EPA/600/R-05/147.
- Everitt, B. S., S. Landau and M. Leese (2001). Cluster Analysis. London, Arnold Publishers.
- Fitzpatrick, N. A. and J. J. Fitzgerald (1996). An Evaluation of Vapor Intrusion into Buildings Through a Study of Field Data. *11th Annual conference on Contaminated Soils*, University of Massachusetts at Amherst.
- Foster, S. J., J. P. Kurtz and A. K. Woodland (2002). Background indoor air risks at selected residences in Denver, Colorado.
- Hers, I., H. Dawson, et al. (2006). Review of empirical vapor attenuation factors from multiple sites Key data trends and results. *Vapor Intrusion: The Next Great Environmental Challenge - An Update*, Los Angeles, California, Air and Waste Management Association.
- Hers, I., H. Dawson and R. Truesdale (2005). Revising the empirical attenuation factors: Data analysis and preliminary results (Vapor Intrusion Workshop). 16th Annual West Coast Conference on Soil, Sediment, and Water. San Diego, California. http://iavi.rti.org/Resources.cfm?PageID=documentDetails&AttachID=170.
- Hostettler, F. D. and K. A. Kvenvolden (2002). Alkylcyclohexanes in environmental geochemistry. *Environmental Forensics* **3**: 293-301.
- McHugh, T. E., J. A. Connor and F. Ahmad (2004). An empirical analysis of the groundwater-to-indoor-air pathway: The role of background concentrations in indoor air. *Environmental Forensics* **5**: 33-44.
- NJDEP (2005). Vapor Intrusion Guidance, New Jersey Department of Environmental Protection. http://www.nj.gov/dep/srp/guidance/vaporintrusion/vig.htm.
- Olsen, D. A. and R. L. Corsi (2002). Fate and transport of contaminants in indoor air. *Soil and Sediment Contamination* **11**(4): 583-601.
- OSHA (1999). Technical Manual for Indoor Air Investigation, TED 1-0.15A.
- Sexton, K., J. L. Adgate, G. Ramachandran, G. C. Pratt, S. J. Mongin, T. H. Stock and M. T. Morandi (2004). Comparison of personal, indoor, and outdoor exposures to hazardous air pollutants in three urban communities. *Environmental Science and Technology* 38(2): 423-430.
- Shah, J. J. and H. B. Singh (1988). Distribution of volatile organic chemicals in outdoor and indoor air: A national VOCs data base. *Environmental Science and Technology* **22**(12): 1381-1388.
- Stolwijk, J. A. J. (1990). Assessment of population exposure and carcinogenic risk posed by volatile organic compounds in indoor air. *Risk Analysis* **10**(1).
- Stout, S. A. and A. D. Uhler (2006). Causation for variable n-alkylcyclohexane distributions in distillate nonaqueous phase liquids from Mandan, North Dakota. *Environmental Forensics* **7**: 283-287.
- Stout, S. A., A. D. Uhler and K. J. McCarthy (2006). Chemical characterization and sources of distillate fuels in the subsurface of Mandan, North Dakota. *Environmental Forensics* **7**: 267-282.
- USEPA (2002). Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance), United States Environmental Protection Agency.
- Wertz, B. and G. McDonald (2004). Evaluation of observed vapor intrusion in upstate New York. USEPA Workshop on Vapor Intrusion, San Diego, California. http://iavi.rti.org/Resources.cfm?PageID=documentDetails&AttachID=48.

Biographical Sketches

John A. Connor, P.E., P.G., D.E.E.: Mr. Connor is President of Groundwater Services, Inc. He received an M.S. degree in Civil Engineering from Stanford University and has over 26 years of experience in environmental engineering, with specialization in risk assessment, fate and transport modeling, and corrective action design. Address: GSI, 2211 Norfolk, Suite 1000, Houston, Texas, 77098-4054, Phone: 713-522-6300, Fax: 713-522-8010, Email: jaconnor@gsi-net.com.

Farrukh Ahmad, Ph.D., P.E.: Dr. Ahmad is an Environmental Engineer and Environmental Chemist with GSI with over 12 years of environmental project experience in environmental consulting. His project experience includes in situ remediation technology development, natural resource damage assessment, vapor intrusion assessment, and application of forensic and statistical techniques to environmental site investigations. Address: GSI, Phone: 713-522-6300, Fax: 713-522-8010, Email: fahmad@gsi-net.com.

Thomas E. McHugh, PhD., DABT: Dr. McHugh is a Vice President with GSI Environmental and has over 15 years of experience in consulting and research. He has worked on a number of projects related to vapor intrusion including field investigations and model development. He has contributed to U.S. EPA and state regulatory guidance on Vapor Intrusion and he is the Principal Investigator for a three-year DoD research project to study vapor intrusion processes at DoD facilities. Address: GSI, Phone: 713-522-6300, Fax: 713-522-8010, Email: temchugh@gsi-net.com.