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Review of Best Practices, Knowledge and Data Gaps, and Research Opportunities for the U.S. Department of Navy Vapor Intrusion Focus Areas

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EXECUTIVE SUMMARY

Vapor intrusion (VI) refers to the movement of chemical vapors from contaminated soils or groundwater through the subsurface and into buildings (indoor air). This exposure pathway has attracted significant attention from regulatory agencies over the past decade in response to several well-publicized cases. Virtually all of the current regulatory documents generated are guidance and have not been promulgated as law, allowing for negotiation on the approach to follow in accordance to site-specific conditions. Nevertheless, experience indicates that this guidance also leads to higher costs in mitigation, public relations, and potential litigation. In response to the need for future research and development on reducing high costs and uncertainties of VI assessment strategies (Department of the Navy, DON, 2008), the objective of this report is to identify existing best practices, knowledge and data gaps, and future research into new strategies and techniques. This study was supported by the Navy Environmental Sustainability Development to Integration Program (NESDI) Program, as part of the study on Improved Strategies for Assessment of Vapor Intrusion, under direction by the Space and Naval Warfare (SPAWAR) Systems Center Pacific.

This report provides a review by a team of subject-matter experts of current best practices, opinions on the current state of knowledge and data gaps, and offers suggestions for research directions for the following three Navy-identified VI focus areas:

- Sub-surface sampling for complete determination of VI pathway, which minimizes the need for intrusive sub-slab sampling.
- Passive indoor air sampling methods to improve VI exposure estimates.
- Indoor air source separation to determine if indoor air contamination is from VI or indoor sources.

The report is a resource to Navy site managers on current assessment approaches on these focus areas, supporting improved VI assessment by following methodology accepted by the regulatory and scientific communities. Nevertheless, there are challenges that will impose uncertainties and complications to VI assessment, making it an expensive undertaking, particularly for responsible parties with large numbers of sites each with large numbers of buildings, such as the Navy. The ultimate goal is to develop a robust and streamlined screening and assessment strategy that will be applicable and efficient at most Navy sites.

Insight into the nature and scope of VI issues at naval facilities is provided by a recent review (Kim Brown, NAVFACHQ, personal communication). The review reflected input from 97 sites with potential VI issues from both Base Realignment and Closure (BRAC) and Environmental Restoration, Navy (ER,N) sites. For these sites, the identified contaminants of concern (COCs) included chlorinated solvents (76.3% of sites), petroleum constituents (14.4% of sites), and other or unspecified compounds (e.g., PCBs, methane; 16.5% of sites). The contaminated matrix driving the VI issue was identified as groundwater at 61.9% of the sites, soils at 48.5% of the sites, landfills at 2.1% of the sites, and was not specified at 15.5% of sites. Out of the sites that reported potential issues, 23.7% affirmed the need for remedial action, 17.5% reported no required action, and 40.2% did not yet know or did not specify a requirement for remediation. While project-related VI costs were only reported for <20% of the sites, the total cost identified for these 19 sites was in excess of $6.9 million.

Current best practices for sub-surface sampling include the three following components. However, site-specific conditions will dictate the optimal scope, methods, sequence, and frequency of sampling for each site.

1. Develop a Conceptual Site Model (CSM) by incorporating existing data into a framework based on the theory of vapor fate and transport. Follow a simple plan view and cross-section to depict nature, extent, fate and transport, source, pathways, and receptors. Use CSM to facilitate communication and identification of significant data needs.
2. Identify COCs, establish risk-based screening levels, and select adequate methods of analysis.
3. Select sampling strategy based on the CSM, with the objectives of identifying the vapor source and the pathway into the building.

Current uses for passive samplers for VI assessment in the U.S. were reviewed. Currently, these methods are mainly applied for qualitative assessment of volatile organic compounds in shallow soil gas. Quantitative use of passive samplers is more extensive in other countries. Both qualitative and quantitative passive samplers provide information on the presence and relative proportions of compounds in indoor air. This information may suffice to determine the completeness of the VI pathway and to impose pre-emptive mitigation.

Current practices for distinguishing between the relative contributions to indoor air by indoor, subsurface, and outdoor air sources are challenging and often ambiguous. This is due to low risk-based target indoor air concentrations, which often are within the range of variability of analytical reporting limits. Even though there may be locations where the effect of indoor or outdoor sources on indoor air measurements may be technically resolved, communicating this technical analysis to non-technical stakeholders is still a challenge. Therefore, improved methods for resolving indoor sources would be very valuable.

Assessing the existence of a complete VI pathway with subsurface information faces several knowledge and data gaps. These are associated with characterizing the extent and distribution of COCs in the subsurface, and the attenuation in concentration between subsurface and indoor air. This explains regulatory preference for indoor air data for making decisions about the potential for VI. Unfortunately, it also leads to significant challenges in resolving the relative contribution of chemicals from background sources. General knowledge gaps related to subsurface characterization include:

- Lack of consistent and uniform application of ***sampling methodologies***, adequate for the risk-based target concentrations.
- Lack of understanding of ***temporal and spatial*** concentration ***variability***.
- Lack of understanding of COCs and ***analytical methods*** adequate to risk-based target concentrations.
- Lack of ability for quantification of ***fate and transport processes*** and assessment approach for site-specific conditions.

For both qualitative and quantitative passive samplers, knowledge and data gaps are related to the need for characterization of their capabilities for measurement of vapors, and acceptance by the regulatory community. Some of the issues of concern are:

The relative merits of competing products with different designs.

Capabilities and limitations of ***thermal desorption and solvent extraction*** methods for the ***spectrum of chemicals***, range of concentrations, and combinations and permutations of mixtures of these chemicals. To reach reporting limits appropriate for risk-based screening levels.

Potential for ***starvation effect*** during soil gas sampling, which is a function of the physical characteristics of the geologic materials and the geometry and uptake rate of the sampler.

Limits on the ***maximum duration of deployment***, particularly in humid or high- concentration atmospheres where there may be saturation of adsorptive sites and desorption of lighter VOCs, or degradation of chemicals between adsorption and
analysis attributable to ground level ozone.

Regulatory acceptance.

Key knowledge gaps and data needs related to indoor source separation are related to temporal variability and building factors (i.e., pressure, ventilation, and mixing within the building). Normally, indoor air sampling is required by regulatory entities when subsurface concentrations are above VI screening levels. This sampling is done to resolve the relative contributions from indoor, outdoor, and subsurface sources, which is one of the common and difficult challenges of VI assessment. In almost all cases, indoor air samples will contain detectable concentrations of volatile organic compounds (VOCs) that originate from consumer products and building materials (interior sources). Indoor air samples will also include compounds that are common contaminants in soil and groundwater, originating from interior and outdoor (ambient or background) sources. Background concentrations for several of these compounds are within the range of risk-based target concentrations. Knowledge and data gaps relevant to the assessment of background contributions include:

- Limitations on applying literature values for indoor air concentrations in residential buildings not associated with contaminated soil or groundwater, especially for buildings with a history of VOC use, storage, or handling.
- Extent of removal of indoor sources and waiting period before collection of indoor air samples. Evaluation of factors affecting these, including building ventilation rates.
- Demonstration and validation of pressure-cycling strategies (sampling building under positive and negative pressure relative to the subsurface by either adjusting building pressure or sub-slab vacuum).
- Demonstration and validation of forensic methods for fingerprint chemical contributions from the subsurface versus indoor sources.
- Demonstration and validation of using buildings as flux chambers.

The research opportunities for the Navy Focus areas reflect the study team's collective experience and projections of the potential benefits and costs associated with conducting research in each topic area. Where applicable, the study team has also identified ongoing research programs for potential collaboration.

Current VI assessments use sub-surface concentration data and attenuation factor estimates, with the assumption that these are representative and applicable to the site of interest. First, research into sampling and analysis methods is needed to better understand how to deal with the spatial and temporal variability that have been reported using conventional sampling and analysis methods. Second, research is needed in understanding the differences in attenuation factors as a function of site-specific conditions and chemical types. Additional research on soil gas sampling is needed to demonstrate:

- The degree of agreement of different sampling methods for evaluation of diverse chemicals in assorted types of geologic materials.

- The limits of active soil gas sampling in low-permeability materials.
- The capabilities and limitations of quantitative passive soil gas sampling.
- The practical limitations of sampling for semi-volatile organic compounds.
- The comparative aspects of individual sampling protocols (purge rate, vacuum, volume, etc.).

Research opportunities for passive samplers involve their demonstration for several kinds of monitoring. Successful demonstration of their reliability, and publication in reputable scientific literature, will support their acceptance by the regulatory community. Current efforts on this area include research funded by the Environmental Security Technology Certification Program (ESTCP) to assess the relative performance of four quantitative passive samplers for indoor air, outdoor air, and soil gas monitoring (ESTCP-0830, Geosyntec Consultants, Inc., 2008). The research will include controlled laboratory experiments and field-testing to assess the capabilities and limitations of the samplers for quantification of a wide range of compounds of different physical and chemical properties. Testing will include methods designed to minimize the starvation effect during soil gas sampling. Navy could collaborate with this effort by allowing testing in one or more field sites. The potential cost savings with this research are very large, and there is ~$1 million in funding in place that makes the leverage on this opportunity very large.

Passive samplers have other potential applications and additional research may be appropriate in these areas as well. Passive samplers can be used to monitor long-term time-average concentrations in vent-pipes of sub-slab venting systems to assess performance over time and provide documentation for use when a petition for closure is ultimately prepared. Passive samplers may also be used in flux chambers of various designs, since they can provide a longer term average measure of flux, which will minimize variability imposed by short-term temporal variability. Qualitative passive samplers can also be used to assess relative concentrations of target compounds in several media (soil gas, sub-slab, and indoor air samples), which might be possible to analyze using compound ratios to assess whether VI is occurring, even without rigorously quantified concentrations.

Research opportunities for indoor source separation include improved sampling and analytical techniques to provide more representative long-term average concentration data. Experience has shown that there may be advantages to a few different forensic techniques of data collection and analysis to resolve relative contributions of vapors from indoor and subsurface sources. Pressure cycling and building mass balance strategies have been shown to provide a very clear indication of VI and resolution of background contributions, but more work is required to develop a protocol accepted by regulatory agencies. ESTCP Project ER-0707 will characterize building foundation permeability through induced depressurization, and the Navy could collaborate by allowing testing in some sites.

A summary of recommendations for future VI research opportunities for the Navy to consider is provided and the significance of each topic is ranked (high, medium, or low), opportunities for synergy with existing research programs are indicated, costs are ranked (high, medium, or low), and a general timeline for implementation for each research area is provided.

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ACRONYMS AND ABBREVIATIONS

1,1-DCE	1,1-dichloroethylene
1,1,1-TCA	1,1,1-trichloroethane
API	American Petroleum Institute
ASTM	American Society for Testing and Materials
ATD	Automated thermal desorption
BRAC	Base Realignment and Closure
CalDTSC	California Department of Toxic Substances Control
CH_4	methane
CSM	Conceptual site model
CSSIA	Compound-Specific Stable Isotope Analysis
cis 1,2-DCE	cis 1,2-dichloroethylene
CO_2	carbon dioxide
COC	compounds of concern
CWAs	Chemical Warfare Agents
DoD	Department of Defense
DON	Department of the Navy
DQO	Data quality objective
EPRI	Electrical Power Research Institute
ER,N	Environmental Restoration, Navy
ESTCP	Environmental Security Technology Certification Program
F	mass flux
FID	flame ionization detector
ft	feet
GC	Gas Chromatography
GC-MS	Gas Chromatograph-Mass Spectrometer
H	Henry's Law Constant
HPV	High purge volume
HVAC	heating, ventilating and air conditioning
IH	industrial hygiene
ISO	International Standards Organization
ITRC	Interstate Technology and Regulatory Council
K_{oc}	octanol partitioning coefficient
L	liters
LARWQCB	Los Angeles Regional Water Quality Control Board
L/min	liters per minute
LNAPL	light non-aqueous phase liquid
m	meter
MADEP	Massachusetts Department of Environmental Protection
MAGS	Modified Active Gas Sampling
mL	milliliters
MTBE	methyl tert-butyl ether
MWSRAS	Midwestern States Risk Assessment Symposium
NESDI	Navy Environmental Sustainability Development to Integration program
NIST	National Institute of Standards and Technology
NJDEP	New Jersey Department of Environmental Protection
NPL	National Priorities List

NYSDOH	New York State Department of Health
O_2	oxygen
ORNL	Oak Ridge National Laboratory
OSHA	Occupational Safety and Health Administration
OSWER	Office of Solid Waste and Emergency Response
Pa	Pascal
PCE	tetrachloroethylene
PEL	Permissible Exposure Limit
PIANO	paraffin, isoparaffin, aromatics, naphthenes, olefins
PID	photoionization detector
pCi/L	picoCuries per Liter
PDMS	Polydimethylsiloxane
ppbv	parts per billion by volume
ppmv	parts per million by volume
QA/QC	Quality Assurance/Quality Control
$Q_{building}$	building ventilation rate
Q_{soil}	volumetric flow rate of soil gas into a building
R&D	research and development
RTI	Research Triangle Institute
SF_6	Sulfur hexafluoride
SPAWAR	Space and Naval Warfare Systems Command
SVOCs	semi volatile organic compounds
TAGA	Trace Atmospheric Gas Analysis
TCE	trichloroethylene
TICs	Toxic Industrial Chemicals
US	United States
USEPA	United States Environmental Protection Agency
VI	vapor intrusion
VOCs	volatile organic compounds
α	Alpha or attenuation factor
$\mu g/m^3$	microgram per cubic meter
%	percentage

1. INTRODUCTION

The Department of the Navy (DON, 2008) has recently issued policy on assessment of vapor intrusion (VI) and has identified this pathway as an issue to be addressed in future research and development (R&D) to reduce the high costs and uncertainties of current VI assessment strategies. The Navy commissioned a study team of subject-matter experts to review current literature, summarize best practices, identify knowledge and data gaps, and identify opportunities for optimization of assessment approaches and tools. The ultimate goal was to develop a robust and streamlined screening and assessment strategy that will be applicable and efficient at most Navy sites. This report provides a review of best practices for three focus areas identified by the Navy for this work assignment and provides opinions on the current state of knowledge gaps and data needs and suggestions for research directions. The three focus areas identified by the Navy are as follows:

1. Best practices for sub-surface sampling that provide the best indication of a potentially complete VI pathway while minimizing the requirement for intrusive sub-slab sampling.
2. Best practices and potential advantages and disadvantages of passive indoor air sampling methods to determine if an indoor air exposure from a potential source exists, without assigning a concentration (risk level) before indoor sources can be eliminated as the cause.
3. Best practices for indoor source separation to improve complete pathway verification, including possible forensic and pressure cycling strategies.

This study was initiated under requirements of the Navy Environmental Sustainability Development to Integration Program (NESDI) Project on Improved Strategies for Assessment of Vapor Intrusion, through Performance Work Statement RO13 with the Space and Naval Warfare (SPAWAR) Systems Center Pacific to document these best practices and identify new approaches to optimize VI assessment.

1.1 REPORT ORGANIZATION AND SCOPE

Section 1 describes the purpose and organization of this report. Section 2 provides background information, including a summary of the typical approach for assessing VI and the challenges that often develop to justify the need for this review. Section 3 provides a review of best practices for each of the three Navy focus areas in succession. Section 4 identifies knowledge gaps and data needs, and Section 5 provides suggestions for research opportunities. Section 6 provides conclusions and a summary of the study team recommendations for future VI research opportunities for the Navy to consider.

2. BACKGROUND

Vapor intrusion (VI) refers to the movement of chemical vapors from contaminated soils or groundwater through the subsurface and into indoor air. This exposure pathway has attracted significant attention from regulatory agencies over the past decade, partly in response to several well-publicized cases involving indoor air quality impacts that were more extensive than had been anticipated. Regulatory guidance documents were subsequently developed to standardize the process of investigating, assessing, and managing risks associated with VI. Virtually all of these documents are guidance and have not been promulgated as law, which provides opportunities for negotiation of different approaches for various site-specific conditions. Practical experience over the past decade has shown that the current regulatory approaches do not always lead to resolution among the parties concerning the significance of VI and the necessary future actions. In addition, the current approaches could lead to higher than necessary costs of assessment, mitigation, public relations, and potential litigation. Improvements might be achieved by identifying best practices (existing strategies and methods that have been tested and demonstrated to minimize many of the common challenges), and through future research into new strategies and techniques.

2.1 TYPICAL APPROACH FOR ASSESSING VI

Every VI assessment is unique to some degree and regulatory guidance varies from jurisdiction to jurisdiction. Nevertheless, the evaluation of VI at a given site (which may include one or several buildings) tends to follow a phased approach, as shown in Figure 2-1.

Step 1: The impetus may be a regulatory request or requirement, property transaction, voluntary action based on historical records or data from previous compliance or cleanup activities, or an occupant complaint.

Step 2: If a State-specific guidance document exists, it will often be used as the default guidance for the local regulators. Alternatively, the Tri-Services Handbook (2008), the Interstate Technology and Regulatory Council (ITRC) VI guidance (2007), and the United States Environmental Protection Agency (USEPA) Office of Solid Waste and Emergency Response (OSWER) draft subsurface vapor intrusion guidance (USEPA, 2002) may be considered potentially applicable for Navy sites. While most guidance documents do not have the force of law, they are often followed strictly in practice.

Step 3: Preliminary screening typically involves comparing existing data regarding concentrations of chemicals in the subsurface to screening levels designed to be protective for the VI pathway. If, at any step of the process, it is confidently demonstrated that VI is not a current problem and that problems in the future are unlikely, then no further work should be needed beyond documenting the results of the evaluation. If the evaluation shows a potentially complete pathway (i.e., potentially unacceptable risks attributable to VI), further investigation or mitigation steps can be considered. There are two general approaches to data collection: (1) collecting subsurface data (sampling soil gas or groundwater, usually outside of the building footprint) to characterize the nature, extent, fate and transport of chemicals of concern in the subsurface to assess whether they are likely to pose a risk (i.e., assessing the source and pathway), and (2) collecting indoor air and sub-slab soil gas samples to assess concentrations near the building(s) of interest (i.e., assessing the "receptor," if the building can be considered the receptor in this context). There is considerable debate about these two approaches (beginning at the underground source and working up toward the receptor or beginning at the receptor site on top and working down toward the source, sometimes referred to as "bottom-up" versus "top-down" approaches), which is discussed in more detail in subsequent sections.

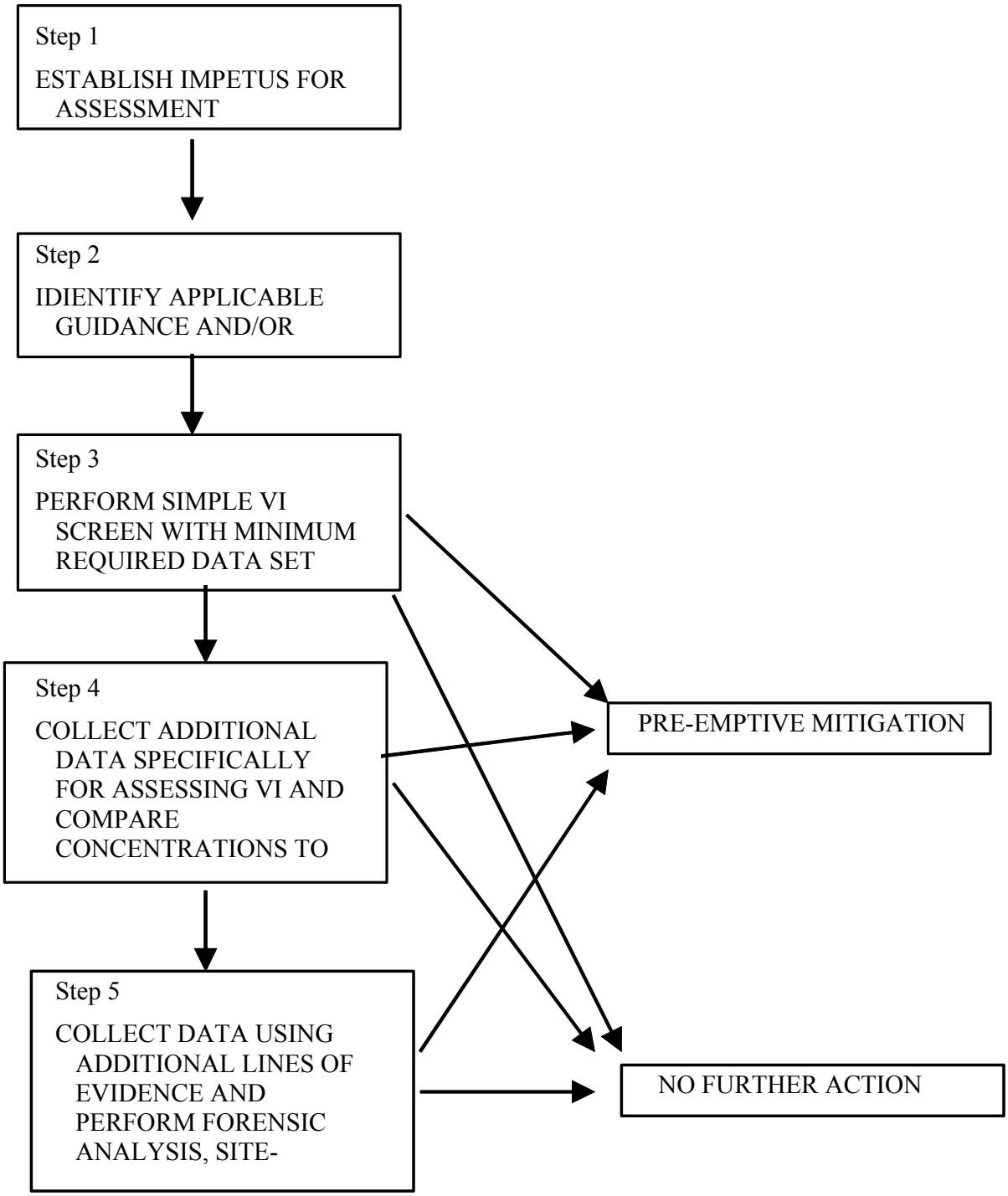

Figure 2-1. Typical progression for evaluating VI.

Step 4: Site-specific data collection for VI assessments typically focuses on collection of groundwater, soil gas, sub-slab soil gas, and/or indoor air and outdoor air samples to quantify concentrations of volatile organic compounds (VOCs) for comparison to screening levels for each media (e.g., USEPA, 2002; Oak Ridges National Laboratory, ORNL, 2008). By comparison to Step 3, this data collection focuses on specific locations more appropriate for the VI pathway, i.e.,

groundwater samples just below the water table and soil gas samples close to occupied buildings, etc. VI investigations may start with a large area with potential impacts and many buildings in the area. The initial site characterization efforts may be somewhat widely spaced and/or rely on semi-quantitative approaches to narrow the scope of the investigation to those buildings with the most potential for VI.

In many cases, porosity, moisture content and other data that affect the migration and fate of vapors are also collected to support mathematical modeling of subsurface vapor fate and transport. Indoor air and sub-slab soil vapor sampling and analysis is considered by some to provide the most direct evidence for assessing risks (breathing zone concentrations). However, several compounds in indoor air of residential buildings that are not associated with contaminated land are commonly present at concentrations at or above risk-based target concentrations (Dawson and McAlary, in press), so this step is often complicated and ambiguous. If concentrations exceed generic screening levels, additional assessment may be performed (Step 5) or risk-management measures may be implemented.

Step 5: There are many cases where the assessment in Step 4 is ambiguous because of spatial and temporal variability in the data, and because the health-based screening levels for many compounds are very low (in the range of typical background indoor air concentrations or difficult to resolve from laboratory reporting limits). In these cases, more detailed assessment may be conducted (including forensic analysis of the data, building pressure/ventilation assessment, site-specific mathematical modeling, assessment of geologic barriers or preferential pathways), followed by a risk assessment. Various alternative lines of evidence are also recognized (ITRC, 2007) such as flux chambers, building pressure/ventilation testing, characterization of barriers or preferential pathways, but these supporting lines of evidence are infrequently used at most sites.

In some cases, pre-emptive mitigation is considered less onerous and less costly than ongoing monitoring, especially when the data do not clearly show any VI impacts. This may or may not be the case, because although it is relatively inexpensive to install a sub-slab venting system (e.g., typical radon mitigation system), the ongoing operation and maintenance burden may be considerable over time, and there are few cases yet where long-term costs can be fully assessed. Long-term operation and maintenance of risk-mitigation systems also leads to issues of land use controls, impact to property values, risk communication, liability if the system fails, and questions regarding who is responsible if the building changes ownership. Some proponents are also hesitant to commit to this approach because they are concerned that installing a vapor recovery system might be used later as evidence of an admission of responsibility in litigation.

There is a spectrum of scenarios encountered in practice, bounded by the ones where (1) there is clearly no significant source or no occupied buildings, and there are no plans for future construction on the site, and the pathway is by definition incomplete, and (2) the potential for VI above levels of concern is obvious and justifies proactive mitigation with minimal investigative activity. Most of the sites, however, tend to fall between these extremes, and the typical investigative approach faces several challenges, described in Section 2.2.

2.2 CHALLENGES ASSOCIATED WITH VI ASSESSMENT

VI assessments conducted in accordance with most current guidance documents are often challenging for several reasons, including the following:

1. **Risk-based target concentrations are generally very low.** In preparing risk assessments and deriving risk-based screening levels, it is typically assumed that people drink about 2 L of water per day and inhale about 20,000 L of air per day (USEPA, 1989). As a result, the

calculated concentrations posing no significant risk are much lower for the inhalation route of exposure than the ingestion route. For many chemicals, the target breathing zone concentrations are so low (often in the $\mu g/m^3$ range) that sample collection and analysis require special care to maintain acceptable data quality.

2. **Background concentrations and indoor chemical sources may confound the results.** Typical indoor air concentrations in residential buildings that are not located near contaminated soil or groundwater can be similar to or greater than risk-based target concentrations for some common carcinogenic chemicals (especially benzene, tetrachloroethene [PCE], chloroform, carbon tetrachloride, and methyl tert-butyl ether [MTBE]). It can be very difficult to distinguish the relative proportion of contributions from the subsurface versus interior sources such as consumer products and building materials. Furthermore, compounds that are not present in the subsurface are often detected, and this can require time and effort to explain to stakeholders such as building owners and occupants. In many areas, outdoor air contains concentrations of chemicals above risk-based target concentrations, so indoor air sampling for comparison to screening levels will often result in a false-positive determination (falsely concluding VI poses an unacceptable risk). Navy policy (DON, 2008) outlines methods for assessing background contributions of chemicals to indoor air, including identification and, if possible, removal of consumer products that may be sources of VOCs prior to indoor air sampling, and concurrent sub-slab or soil gas sampling and indoor air sampling (comparison of which can sometimes indicate the origin of the compounds detected by a comparison of relative concentrations in both samples).

3. **Sampling within and directly beneath buildings is intrusive and requires well-planned risk communication with building occupants**. Verifying the presence or absence of a complete VI pathway without such invasive sampling is one of the focus areas discussed in more detail below.

4. **Site-specific conditions can have a significant effect on VI processes.** Factors such as geologic setting, climate, building design and condition, ventilation system design and operation, and building occupancy will affect VI significance. Therefore, it becomes difficult to specify a generic recipe for assessment that will be efficient and effective at most sites. Most guidance documents provide a flow-chart with decision logic to guide the assessment process; however, the decision logic needs to be more conceptual and rely heavily on use of professional judgment, or very prescriptive to accommodate all the combinations and permutations of possible site conditions, the wide range of expertise currently in the profession, and satisfy the regulatory goal of minimizing the risk of a false negative decision.

   One alternative recently suggested by Johnson (2008) is a taxonomic approach, where certain categories of sites are identified, and a default approach for site assessment is developed for each category. This may constrain the possibilities for each type of site sufficiently to allow a detailed and specific logic to be developed that is not overly complicated or restrictive. This approach for developing a site-specific assessment strategy is discussed further in Section 5.

5. **Temporal variability causes uncertainty.** Most risk models assume long-term exposures, while most sampling methods provide only point-in-time "snap-shots" of concentrations. Indoor air quality is subject to temporal variations imposed by variations in the emission rates of indoor sources as well as by weather conditions (wind, rain, barometric pressure) and other factors can also affect subsurface soil and groundwater concentrations (groundwater level changes, surface conditions, rainfall, etc.). For example, a regional drought can result in falling groundwater levels, which can expose chemicals in deeper intervals to a continuous

gas phase in the unsaturated zone, which can increase the potential for VI. Alternatively, in a wet season, fine-grained soil layers in the unsaturated zone may become so highly saturated that they act as a partial or significant barrier to upward vapor transport.

Risk assessments are typically based on 25-year (occupational) or 30-year (residential) exposures, so it would be preferable to have sampling methods that would provide data representative of long-term average concentrations. Currently, most indoor air samples for VI investigations are collected over 24 hours or less. In comparison, radon samples are typically collected over a minimum of 3 days, and often over approximately 1 week to minimize temporal variability. Kuehster, Folkes, and Wannamaker. (2004) and McAlary *et al*. (2002) showed temporal variability in indoor air concentrations measured over 24 hours of about one order of magnitude. With this level of temporal variability inherent in the current standard practices for indoor air quality monitoring, multiple rounds of sampling and analysis may be necessary or appropriate, which increases costs.

Short-term variability in soil vapor concentrations from properly sealed probes or temporary probes in high-permeability soils has been shown to be generally a factor of 2 or less (Hartman, Picker, and Villarreal, 2008; USEPA, 2006a; Luo *et al*., 2006; McAlary, 2008). Seasonal variability in soil vapor concentrations depends on seasonal variations in rainfall and groundwater levels, and has been shown to also vary with depth (McAlary *et al*., 2007; McAlary, 2008; personal communication with T. E. McHugh in 2008).

Generally, soil vapor concentrations tend to be more consistent over time near the source and more variable near the ground surface — provided that the source is not periodically exposed and submerged by changes in groundwater elevation or infiltration, such as an light non-aqueous phase liquid (LNAPL) smear zone. Sub-slab soil vapor samples have the potential for highly variable concentrations in response to soil-building pressure differential changes (Luo *et al*., 2006). Barometric pumping can also affect shallow soil vapor concentrations (Massmann and Ferrier, 1992).

6. **Spatial variability in subsurface concentrations likely exists at most sites.** There may be orders of magnitude of spatial variability in discrete soil gas and groundwater samples collected from beneath and around buildings as small as a single domestic residence. Spatial variability tends to be the dominant concern for gas-phase samples collected below the ground surface and temporal variability tends to be the dominant concern for air samples collected above the ground surface.

   Decision-makers often have difficulty incorporating spatial and temporal variability in the data into the decision-making, and if they err on the side of caution, the risk management approaches may be overly conservative by a large margin. In some cases, regulators will address spatial and temporal variability by asking for large amounts of data, assuming that more data will reduce the uncertainty or increase the confidence. This effort becomes very expensive and frequently does not significantly reduce the uncertainty because the influence of temporal and spatial variability is unavoidable using conventional monitoring approaches.

7. **VI compounds of potential concern are not yet fully understood.** About 115 compounds are considered to have the potential to pose a risk via VI (USEPA, 2002; American Society for Testing and Materials [ASTM], 2008; California Department of Toxic Substance Control [DTSC], 2005). However, this is based only on the volatility of these compounds, and not on considerations of mobility or attenuation in air concentrations resulting from the VI intrusion process.

8. **Methods of laboratory analysis impose some challenges and limitations.** Although there are analytical methods available for the determination of volatile compounds in air, some of the sampling and/or measurement techniques may not be applicable or practical for all constituents and applications in VI investigations. Current methods may be unable to achieve reporting limits lower than the risk-based target concentrations for many of the compounds mentioned above. Currently, USEPA Method TO-15 is the most commonly used analytical method. However, the TO-15 method applicability list does not include over half the compounds listed on the OSWER (USEPA, 2002) guidance list. Although current sample collection and analysis methods can be modified to meet the criteria for some VI investigations, the minimum performance standards must meet those specified in the Department of Defense (DoD) Quality Systems Manual for Environmental Laboratories (DoD, 2006). Some contaminants (e.g., petroleum fuels) may contain dozens of volatile compounds not found on the OSWER or other lists. Furthermore, some regulatory guidance documents specify the use of sampling and/or analytical methods that may not be appropriate for a particular site, and negotiation of a site-specific approach is often protracted because regulators and field sampling personnel are often less familiar with sampling and analytical options for air or soil gas than soil and groundwater samples. While, in general, site assessment should be streamlined to focus on the chemicals known or reasonably suspected to be present at concentrations of potential concern based on data from historical site information and/or historic soil and groundwater investigations, local regulatory requirements may supersede this practical approach. For example, New Jersey (New Jersey Department of Environmental Protection, NJDEP, 2005) requires analysis for all TO-15 analytes regardless of whether they are compounds of concern at a site.

9. **Compounds of concern (COCs) for VI may behave differently from one another in the subsurface.** For example, many volatile petroleum hydrocarbons degrade over short distances where oxygen is present, so their behavior will be significantly different than chlorinated solvents and other recalcitrant compounds in well-oxygenated subsurface environments. The optimal investigation approaches for hydrocarbons are probably much different than the optimal approach for chlorinated solvents or other recalcitrant compounds. This is a key element in the taxonomic screening approach suggested by Johnson (2008).

10. **Variability exists across guidance and regulations, from the national to state level, as well as between and within states.** This variability may be reflected in differences in target risk levels, default attenuation factors, consideration of background concentrations, preferred lines of evidence, protocols for data collection, or personal experiences of the regulators (Eklund, Folkes, Kubel, and Farnum, 2007). Some states are highly prescriptive while others allow more flexibility. Familiarity with the technical aspects of VI also varies within agencies and across the consulting profession, so guidance is not always consistently followed, assessment approaches may vary, and decision-making may also vary, depending on the type of site (i.e., service stations, National Priorities List [NPL] sites, etc.).

    The general assessment approach described in the Section 2.1 is not consistently applied in all jurisdictions now. Regulators in several states have expressed concerns with the reliability of estimating indoor air impacts using sub-surface sampling data. For example, state regulatory guidance documents for New Jersey (NJDEP, 2005) and New York (New York State Department of Health, NYSDOH, 2006), following a top-down approach, indicate a strong preference for collection of sub-slab and indoor air samples as the primary lines of evidence for assessing VI. This approach places the emphasis on collecting data only at and in the immediate proximity of the receptor (the building), and generally results in little or no

data being collected to characterize the source and verify a complete or incomplete VI pathway, or the nature, extent, fate, and transport of chemicals of interest in the vadose zone and shallow groundwater. This emphasis can often make it difficult to clearly distinguish VI from background, or develop sufficient understanding of the site to make appropriate risk management decisions.

11. **VI for occupational settings is an unresolved issue.** For occupational settings, determining when Occupational Safety and Health Administration (OSHA) applies and when risk-based VI guidance applies is an important decision point that is not always clearly delineated. Navy policy (DON, 2008) states: "When applicable, OSHA standards and workplace requirements will be considered and incorporated into the Conceptual Site Model (CSM) when evaluating potential exposures related to VI pathway for industrial settings." This issue has been argued extensively for almost a decade, with no clear and universally applicable resolution, so it should be discussed with the lead regulatory agency where appropriate. In circumstances where the building occupants are employees and their work involves use of chemicals, and they have had appropriate health and safety training, exposure monitoring, and access to appropriate personal protective equipment, then OSHA Permissible Exposure Limits (PELs) are applicable for the chemicals used as part of the normal employee activities. PEL application may or may not extend to legacy chemicals in the subsurface that are no longer in use, chemicals that originated from another site, chemicals that are breakdown products of the chemicals used by the employees, or workers who do not meet the criteria listed above (i.e., office workers as co-occupants in an industrial building).

    Even when risk-based VI guidance applies, consideration of OSHA rules and procedures may still be useful. In some cases, buildings may include both occupational and non-occupational uses. It can be especially challenging to assess VI at industrial sites because the concentrations present in industrial settings can be a reasonable margin below OSHA PELs and be orders of magnitude higher than risk-based target concentrations. So, acceptable concentrations in an occupational setting may cause elevated reporting limits or otherwise obscure resolution required to reliably assess the contribution from VI.

12. **Stakeholder concerns are often more significant than for other pathways.** Occupants of affected or potentially affected buildings have concerns over health, property value, communication, uncertainty, etc. It is more common to have significant stakeholder involvement with VI than other pathways because avoidance is difficult (building occupants can find substitutes for contaminated drinking water but not for contaminated breathing air), and the other challenges described above often make it difficult to provide a clear determination of whether or to what extent VI may be occurring. Litigation for health-related damages, medical monitoring, property devaluation, or nuisance has also been associated with VI sites.

2.3 RECENT REVIEW OF VI AT NAVAL FACILITIES

The nature and scope of the VI issue at naval facilities was recently reviewed (Kim Brown, NAVFACHQ, personal communication). The review was fairly comprehensive, but not all-inclusive, reflecting input from both Base Realignment and Closure (BRAC) sites, and Environmental Restoration, Navy (ER,N) sites. The BRAC sites span Northeast, Southeastm and West, while the ER,N sites included Hawaii, Midlant, Northwest, Southeast, Southwest and Washington. A total of 97 sites were reported where VI was a potential issue of concern. Of the 97 sites with potential VI issues, identified COCs included chlorinated solvents (76.3% of sites), petroleum constituents (14.4% of sites), and other or unspecified compounds (e.g. PCBs, methane; 16.5% of sites). The

contaminated matrix driving the VI issue was identified as groundwater at 61.9% of the sites, soils at 48.5% of the sites, landfills at 2.1% of the sites, and was not specified at 15.5% of sites. Out of the sites that reported potential issues, 23.7% affirmed the need for remedial action, 17.5% reported no required action, and 40.2% did not yet know or did not specify a requirement for remediation. There are at least four installations with one or more buildings with VI mitigation systems installed. While project-related VI costs were only reported for <20% of the sites, the total cost identified for these 19 sites was in excess of $6.9M. While limited, this review provides insight into the nature and scope of the VI issue at naval facilities.

3. REVIEW OF BEST PRACTICES FOR NAVY FOCUS AREAS

The Navy commissioned this study to review and document best practices, identify technology and knowledge gaps, and recommend investment areas to improve assessment of the VI pathway at Navy sites with particular emphasis on three main focus areas:

1. Sub-surface sampling methodologies that provide a technically defensible evaluation of the VI pathway while minimizing the requirement for intrusive sub-slab sampling.
2. Passive indoor air sampling methods to determine if there is an indoor air exposure from a potential source, without assigning a concentration (risk level) before indoor sources can be eliminated as the cause.
3. Approaches to distinguish the contribution of indoor sources on indoor air quality to improve complete pathway verification, including possible forensic and pressure cycling strategies.

This section describes the current best practices, and the following subsections identify the technology and knowledge gaps and recommended areas for future research and development.

3.1 FOCUS AREA 1 - BEST PRACTICES FOR SUB-SURFACE SAMPLING TO ASSESS VAPOR INTRUSION

Sub-surface sampling data (typically soil gas and/or groundwater samples collected outside the building) can be used to assess the source and pathway, and may provide necessary and sufficient data to support risk management decisions without "intrusive" data (i.e., data that are collected from inside the building, such as sub-slab and indoor air samples). Collecting sub-slab and/or indoor air samples is typically disruptive to building occupants, and the results can be confounded by background concentrations and indoor sources. Therefore, it is logical to follow a "bottom-up" phased investigation approach, progressing from the source to the pathway (much of which can be assessed without intrusive sampling) and then the receptor (sub-slab and/or indoor air sampling), rather than the opposite "top-down" sequence. If the subsurface vapors can be characterized with reasonable confidence, the more intrusive building sampling can be focused on locations where unacceptable impacts are suspected, and avoided otherwise.

Assessing the potential forVI using subsurface data collected outside the building usually involves measuring concentrations of compounds of interest in soil gas or groundwater, and multiplying these by a factor that accounts for the reduction in concentration between the location of the soil gas or groundwater sample and air inside the building (the "attenuation factor," alpha factor, or simply "α"). The reliability of the estimate of indoor air concentrations depends on the representativeness of the subsurface concentration measurement and the attenuation factor. A summary of the current best practices is provided in the subsections below.

3.1.1 Regulatory Preferences

The confidence in VI pathway assessment depends on the representativeness of the sub-surface data and the attenuation factor. Some regulatory agencies have an expressed preference for relying on one type of sub-surface data more than others. For example, the NJDEP generally prefers to use groundwater data to map the subsurface distribution of chemicals, followed by indoor air data for assessing risks, with sub-slab data as a supporting line of evidence for assessing background contributions. They rely less on external soil gas data, which may be because the water table is relatively shallow throughout most of the state, so the vadose zone is often of limited thickness. Furthermore, soils in the northeastern U.S. are often fine-grained, with relatively low permeability, which makes soil gas sampling more difficult, and current experiences with soil vapor sampling have

resulted in skepticism about the reliability of soil gas data. This skepticism is shared by New York state regulators. It may be possible to alleviate this concern over time with improved sampling methods or alternative characterization strategies that are discussed further in Section 5.

Bulk soil sampling and chemical analysis faces a high risk of negative bias via volatilization losses (USEPA, 1993). Therefore, a high soil VOC concentration may be sufficient to conclude there is potential VI risk, but low concentrations may be attributable to a negative bias, and therefore may not be sufficiently reliable to support conclusions regarding the absence of potential VI risks. Many (but not all) regulatory documents caution against the use of bulk soil analyses for assessing VI.

Regulators have expressed concern over the ability to predict an attenuation factor. Johnson (2005) discusses the sensitivity of calculated attenuation factors to model inputs and how to minimize the potential for flawed and inaccurate calculations. For reasonable ranges of inputs, the variability is not as large as perceived, and the full range of reasonable inputs matches well with the full range of empirical data available. Still, the current lack of confidence by regulators in the ability to predict an attenuation factor may impose limitations on the extent to which sub-surface data are permitted for VI assessments or require the use of a conservative estimate, which may be overly conservative in many cases.

In light of the current uncertainties associated with VI assessment, regulators have expressed a preference for a "multiple lines-of-evidence" approach, which involves collecting a combination of sub-surface and internal (sub-slab and indoor air) data, collecting large numbers of samples or risk management decisions that err on the side of caution by a margin of safety sufficient to accommodate uncertainty. However, there is little or no current regulatory guidance on the number of samples needed for various scenarios or on the margin of safety for VI assessments.

3.1.2 Sampling Strategy

Sub-surface sampling can be used to quantify the vapor source concentration, and if the source concentration is too low to pose an unacceptable risk via VI, even with conservative assumptions, then a strong argument can be made for no further action. If the source concentrations are higher than *de minimus* levels, data also can be collected to better characterize the factors that most impact the overall attenuation, including soil properties that affect vapor transport, as well as the potential presence of barriers or preferential pathways.

If the sources are far from the buildings, focusing data collection on the pathway may be sufficient. If it can be demonstrated that the transport of chemicals does not extend to any occupied buildings, characterizing the source may be unnecessary. For example, if VOCs are present in groundwater, but the water table is very deep, collecting soil gas data may be sufficient to assess the vertical profile of vapor concentrations and avoid the higher-cost groundwater data. Similarly, if samples collected along a property boundary are clean and no other lines of evidence exist to indicate off-site impacts, the VI investigation can be potentially limited to the property where the suspected release occurred.

For petroleum hydrocarbons and well-oxygenated sub-foundation regions, aerobic biodegradation can considerably reduce concentration over short distances. In this case, the source concentrations alone, multiplied by a conservative attenuation factor, would provide an overly conservative screening, and it is often appropriate to consider vertical profiles of hydrocarbon vapor and oxygen data, with screening based on samples shallower than the source depth. Furthermore, attenuation factors for some simple scenarios incorporating biodegradation have been investigated with mathematical modeling (Abreu, Ettinger, and McAlary, 2007), and considerable research is being conducted to provide field data to demonstrate the degree of bioattenuation that can occur to

regulatory agencies (Luo *et al*, 2006, 2009; McAlary *et al*., 2007; Lundegard, Johnson, and Dahlen, 2008).

If concentrations are neither negligible nor high enough to justify pre-emptive mitigation, sub-surface data alone may not provide sufficient information for risk-management decision-making. The data from the sub-surface investigation can focus interior investigations on those buildings having a reasonable potential for adverse VI impacts, and this information alone is a very valuable screening step. Sub-surface soil vapor sampling together with soil sampling for physical properties can provide sufficient information to support conceptual and mathematical models of the fate and transport properties and provide a reasonably good estimate of whether indoor air concentrations are likely to be acceptable or not.

3.1.3 Soil Gas Sampling Methods

Many different methods are available for soil gas sampling (ASTM, 1992; California Environmental Protection Agency, CalEPA, 2003; and other state guidance documents), most of which were developed several years to decades ago. Screening levels for assessing human health risk (often less than 1 ppbv) are orders of magnitude more stringent than screening levels for other soil gas monitoring purposes, which include, for example:

- Assessing methane migration around landfills (about 50,000,000 ppbv).
- Determining presence/absence of VOCs in soil near underground storage tanks (about 100,000 ppbv).
- Assessing progress of soil vapor extraction systems for protection of groundwater (about 1,000 ppbv).
- Mapping subsurface plumes based on relative concentrations (variable).

As a result, many historic soil gas sampling methods were not designed for and may not be capable of meeting the data quality objectives (DQOs) of VI assessments, including detection limits, precision, accuracy, and reproducibility. A set of suggested quality control procedures for improving on the data obtained for soil gas sampling is provided in Appendix A.

The current empirical data collected and compiled by the USEPA (Dawson, 2008) show that soil gas sample data in that data set have the poorest of all correlations with indoor air concentrations, worse than both sub-slab and groundwater concentrations. However, in carefully controlled studies (Luo *et al*., 2006; McAlary, 2008; Ririe, Sweeney, Daugherty, 2002), properly collected soil gas samples show much less short-term temporal variability than sub-slab data, especially as the soil gas sampling point approaches the soil gas source (e.g., deeper soil gas samples near the water table). These conflicting results suggest high variability may exist in the many soil gas survey sampling strategies and deployment.

3.1.4 Attenuation Factors

Concentrations measured in sub-surface samples do not represent exposure point concentrations for the building occupants, and as such cannot be used to assess risks directly. To assess risks, one must estimate indoor air concentrations, which is typically done by multiplying groundwater and/or soil gas concentrations by an attenuation factor ("alpha factor" or α). The attenuation factor can be selected using one of four main options:

1. Empirical Data: The USEPA has commissioned Research Triangle Institute (RTI) to compile a database of information from VI sites, and recently performed a detailed analysis of attenuation factors for groundwater to indoor air, soil gas to indoor air, and sub-slab soil gas

to indoor air (Dawson, 2008). They presented summary statistics with which to select an attenuation factor. Default values listed in the OSWER draft subsurface VI guidance (USEPA, 2002) were 95th percentiles of the empirical attenuation factors. The 95th percentile values tend to be an order of magnitude higher than the average values, which adds a degree of conservatism. If the 95th percentile attenuation factor is used with an upper estimate of concentration (maximum or 95th percentile), the calculated indoor air concentration is likely to be significantly higher than the actual value because of compounded conservatism.

2. Mathematical Modeling: Several models are available for calculating the attenuation factor. The most commonly used and recognized in regulatory guidance is the screening-level model of Johnson and Ettinger (1991). Generally, VI models predict the emission rate from a source beneath the building into the building and the dilution of those emissions by the exchange of air between indoor and outdoor air. Various models can address many additional processes, but a detailed description is beyond the scope of this document. The utility and reliability of a model depends on how well the site conditions match the model assumptions and the representativeness of the input parameters.
3. Combination of Empirical Data and Mathematical Modeling: The mathematical model predictions can be calibrated using an empirical data set. For example, if there is confidence in empirical knowledge of sub-slab attenuation factors, these can be used to select some of the lesser-known model inputs and ensure that model projections and empirical data match at that point. The model is then used to extrapolate to conditions not discernible from empirical data (i.e., effect of distance and soil type), or is used to guide how empirical data are categorized and used.
4. Tracers: These are compounds that originate from the subsurface at elevated concentrations and are present in an overlying building at concentrations that can be clearly resolved against outdoor air concentrations and typical indoor air background levels. Examples of chemicals used as tracers in VI analyses include radon, 1,1-dichloroethylene, and potentially other daughter products of degradation of compounds of concern in the subsurface (cis-1,2-dichloroethylene).

The uncertainty in predicting indoor air concentrations from sub-surface sampling and analysis generally increases as the distance between the building and the subsurface samples increases. Therefore, it is generally preferable to collect data in reasonably close proximity to buildings for assessing VI.

3.1.5 Mathematical Modeling

The accuracy with which one can calculate indoor air concentrations based on sub-surface data depends on several factors, including the quality and quantity of data, the comparison between the site conditions and assumptions inherent in the mathematical model, and complexities such as geologic heterogeneity, spatial/temporal variability, building foundation permeability and ventilation rate. The models and/or the default input values are designed to be somewhat conservative, i.e., to over-predict impacts. Using sufficiently good quality data and an appropriate mathematical model, however, it is reasonable to expect the calculated indoor air concentrations to agree within about one order of magnitude with measured indoor air concentrations (Johnson *et al*., 2002; Hers, Zapf-Gilje, Johnson, and Li, 2003). One order of magnitude uncertainty in the modeled attenuation factor is often a manageable level of uncertainty in the context of other sources of uncertainty in a VI assessment. Three of these sources of uncertainty are as follows:

1. The maximum concentration of vapors close to a source can be hundreds of millions of $\mu g/m^3$. For example, the maximum possible vapor phase concentration of trichloroethylene (TCE) is about 400,000,000 $\mu g/m^3$ (or 80,000,000 ppbv). Soil vapor screening levels for TCE vary between guidance documents, within the range of 0.1 to 1,000 $\mu g/m^3$ (0.02 to 200 ppbv). Therefore, in the process of mapping the distribution of sub-surface concentrations, using order of magnitude ranges (10,000, 1,000, 100, 10, etc.) is usually sufficient. This process often allows easy categorization of buildings into groups that do or do not warrant internal data collection, even with a margin of one order of magnitude uncertainty in sub-surface concentrations.
2. Concentration distributions in the subsurface often change over distances that are small relative to the distance between buildings. For example, at the lateral margins of a groundwater plume, concentrations often decrease by two or more orders of magnitude over distances similar to the distances between two residential buildings (~50 ft). Therefore, even if the subsurface concentrations are mapped to the nearest order of magnitude, identifying which buildings are within the region of potentially unacceptable soil vapor concentrations, and which buildings are not, is possible.
3. Measured sub-slab and indoor air concentrations are themselves variable in time and space. Having these data may reduce the margin of uncertainty in estimating a 30-year average exposure point concentration (which is ultimately the information required for risk assessment in most cases), but uncertainty may still exist in extrapolating from sub-slab and indoor air samples to a 30-year average indoor air concentrations that is not much less than an order of magnitude. Therefore, the uncertainty in estimating long-term average indoor air concentrations from sub-surface data and an attenuation factor may not be much greater than the estimate based on intrusive (sub-slab and indoor air) sampling.

There are several potential criticisms of the use of sub-surface data and mathematical modeling to calculate indoor air concentrations. These criticisms should be anticipated and managed appropriately. Sub-surface soil gas samples at depths comparable to the depth of the building foundation may have lower concentrations than soil gas immediately beneath the building, especially for petroleum hydrocarbons. This is a function of the total transport distance and has been shown in model simulations (Abreu, Johnson, and McAlary, 2006; Abreu and Johnson, 2005; Bozkurt, Pennell and Suuberg, 2009). This criticism can be overcome by collecting deeper soil vapor samples and/or vertical profiles of soil vapor concentration data. Mathematical modeling is not accepted by some regulatory agencies, and is viewed with suspicion by others. This can be addressed by selecting reasonably conservative model input values and taking care to demonstrate that the model assumptions are applicable to the site-specific conditions, following various rules of thumb (e.g., Johnson, 2005). It can also be addressed by using conservative default values for the attenuation factor, which may be overly conservative, but if the added conservatism does not have a significant impact on risk management decisions, it may facilitate regulatory approval and risk communication. If risks are below target levels by a reasonable margin of safety using a conservative modeling approach, it should be acceptable to petition the regulatory agency for no further action.

3.1.6 Building-Specific Factors

Sub-surface investigations may not be suitable for all types of site conditions. If there is a large building, with a source directly beneath the building (e.g., a former vapor degreaser inside a large building), groundwater or soil gas samples collected directly adjacent to the building may be far enough away to miss the region of elevated concentrations. Angled borings are possible, but they generally are much more expensive, and are seldom an attractive option for large buildings. Installing

probes in vertical boreholes is conventional, and many practitioners are inexperienced in the challenges of installing probes and setting good seals in angled borings, so there is a real risk the probes will not be installed to the intended location or not properly sealed.

Conversely, if the source of chemicals is not beneath the building(s) of interest, it should be possible to collect sub-surface samples along the side of the building closest to the source, and obtain a conservative estimate of the concentrations beneath the building. Modeling results suggest that soil gas samples should generally be collected at least 1 m below the building footings to avoid underestimating vapor concentrations beneath the building (Abreu, Johnson, and McAlary, 2006). The optimal depth to represent concentrations beneath the building(s) of interest will vary depending on site-specific conditions.

Buildings are not all equally susceptible to VI, but the variability is not easily predicted in advance. Two factors are especially important: building leakage and pressure differential. Most buildings have floor openings that provide a pathway for gas flow between the soil and the building (floor drains, cracks, sumps, utility penetrations, etc.). The extent of the leakage depends on the design, build quality, and age of the building. However, it is reasonable to assume that all buildings leak to some degree, and considering that most floor slabs are underlain by highly permeable gravel, even a small opening can act to funnel soil gas flow from beneath the building if the pressure gradient is sufficient. Most residential and many commercial/ industrial building have a pressure differential that fluctuates between negative and positive (i.e., at times, the building pressure is higher than the soil gas pressure, and vice versa). Therefore, it is reasonable in many cases to consider buildings overlying elevated soil vapor concentrations as candidates for internal investigations. In tall buildings in cold climates, the heated air inside the building rises, causing a pressure gradient that can sustain a vacuum in the lower floors that exceeds the range of typical fluctuations. Conversely, tall buildings in hot climates may have air conditioners that maintain indoor air at a colder temperature than outdoor air, which reverses the stack effect, and causes pressure in the lower floors.

Avoiding intrusive investigations may also be possible if the heating, ventilating, and air conditioning (HVAC) system(s) for a particular building are designed and operated to supply a continuous positive pressure in the building. Assessment can sometimes be made by contacting facilities engineers and reviewing test and balance reports. The air exchange rates vary considerably according to the building use. Heat sources and washrooms are typically serviced with exhaust fans and may be under negative pressure. If there is sufficient make-up air, the remainder of the building may be neutral or positive, and in large buildings, the distribution of negatively and positively pressurized conditions may be reasonably well known and controlled. Alternatively, measuring the pressure differential across the building envelope using a micromanometer with data-logging capabilities is relatively simple, and although this involves entry to the building(s), it may be less disruptive to occupants than sampling and analysis. The operation of any HVAC system is adjustable, so even if a particular building is positively pressurized to a degree that limits or prevents VI, administrative controls and possibly monitoring to verify the pressure differentials may be required if this system is to be relied upon as a risk mitigation measure.

For undeveloped land where no buildings exist, indoor and sub-slab data are not available for assessing the potential for VI, and the assessment typically must reply on soil gas and groundwater data. In some cases, areas covered with asphalt pavement have been considered for shallow soil gas sampling (just beneath the asphalt layer) as a surrogate for a sub-slab sample; however, asphalt is typically much more permeable than concrete, and much more likely to have significant gas-transfer across the pavement. Therefore, shallow soil gas samples beneath asphalt are often very similar to atmospheric air. Additionally, off gassing of chemicals from the asphalt may contribute to

background concentrations in the subsurface. Concrete roadways or parking lots may provide a more reasonable surrogate for sub-slab sampling, depending on the condition of the concrete, which can be very highly variable. More competent surface covers could be constructed to simulate a floor slab, but the experience from soil vacuum extraction technology demonstrations, where such covers were used to try to enhance the radius of influence, indicates that affordable temporary covers are not very effective barriers to atmospheric air.

3.1.7 Summary of Current Best Practices for Sub-Surface Investigation

No two sites are identical, so the optimal scope, methods, sequence, and frequency of data collection will vary from site to site. The strategy should be guided by the site-specific conditions. A subsurface sampling program using current best practices will probably consist of many or all of the following components:

1. Develop a Conceptual Site Model: Incorporate existing data into a framework based on the theory of vapor fate and transport and judgment based on experiences at similar sites. Develop a simple plan view and cross-section to depict nature, extent, fate and transport, source, pathways, and receptors to facilitate communication. Use the Conceptual Site Model to help identify significant unknowns or data needs.
2. Identify COCs, establish risk-based screening levels, and select methods of analysis that achieve reporting limits lower than the risk-based screening levels, including close communication with the analytical laboratory regarding fittings, flow controllers, canister certification, and turn-around time, etc.
3. Select number, locations, depths, and frequency of sample collection based on a conceptual site model of the source, pathway, and receptors. If the results are to be used for a human health risk assessment, it is recommended that a risk assessor be involved in this planning stage. There should be a specific focus on supporting the selection of an appropriate attenuation factor by collecting data that can be used specifically for mathematical modeling:
    a. Source: Depending on the location of the vapor source, collected data may include samples of groundwater just below the water table and/or soil gas just above the water table or at depths and locations corresponding to the highest concentrations that could have a complete pathway to an occupied building. Data collection will depend strongly on whether the source is under the building or not. If the source is not under the building, the source concentrations may be characterized by samples collected upgradient but near to the building. If the vapor source is beneath the building (e.g., leaks from a former vapor degreaser inside an industrial building), it may be more difficult or overly expensive to avoid intrusive investigations. In certain cases, direct collection of indoor air may be the best initial step.

    b. Pathway: Soil coring and visual inspection for texture and moisture is good practice at a minimum. In some cases, a natural geologic barrier to vapor migration may be present (e.g., a laterally continuous layer of fine-textured material with a persistently high moisture content between the source and the building), and characterizing the barrier is more valuable than characterizing the source or receptor. Low permeability alone is not necessarily a barrier to vapor transport because vapor transport is generally dominated by diffusion; however, if there is appreciable recharge via rainfall, irrigation, utility leakage or stormwater runoff, a low-permeability layer in the unsaturated zone may also retain high water content, which can significantly impede upward diffusion from underlying vapor sources. For petroleum hydrocarbons, vertical profiles of vapor concentrations and

oxygen (O_2), carbon dioxide (CO_2), and methane (CH_4) are especially valuable to assess biodegradation along the pathway, which can be sufficient to mitigate risks. It is also important in some cases to consider the possibility of preferential pathways resulting from man-made conduits or fractures or other higher permeability areas in main geological units.

c. Data collection: Table D4 of the ITRC guideline (2007) provides a good reference for selecting the investigative methods that would most likely be used as primary, secondary, and supporting lines of evidence as a function of the site-specific conditions. Table D5 of the ITRC guideline (2007) provides information on the pros and cons of various investigative strategies. These tables provide a very up-to-date, comprehensive, and easily accessible summary that will help guide the selection of a site-specific approach for VI assessment, and as such, are reproduced in Appendix B. Three other non-regulatory guidance documents by the American Petroleum Institute (API, 2005), Electrical Power Research Institute (EPRI, 2005) and GeoProbe (2006) provide useful advice for sub-surface investigation programs. Collectively, these documents provide a good summary of the current best practices for sub-surface sampling for VI assessment, although there are some inconsistencies that are discussed in Section 4.

   Many attempts have been made to develop rules-of-thumb for spacing between sample locations and depths, as well as sample frequency; however, this effort depends on site-specific conditions, and cannot be generalized without risking a false negative outcome or inefficiency, neither of which is desirable. Vapors diffuse at appreciable rates in unsaturated soils, and in many cases, the COCs have been present in the subsurface for a long time (several decades), attributable to historic handling practices. In this case, lateral diffusion results in a certain degree of spreading of concentrations, and it is common to see vapor concentrations form concentric rings around release areas with concentrations falling by an order of magnitude every 3 to 10 m, depending on soil porosity and moisture content (Mendoza, 1995; Abreu and Johnson, 2005; Lowell and Eklund, 2004). This may assist in selecting lateral sample spacing. Vertical sample spacing is equally important, and many guidance documents suggest that vertical profiles of soil vapor concentrations should be collected (ITRC, 2007), particularly for assessing aerobically degradable compounds in conjunction with O_2 and CO_2 measurements (API, 2005). However, the selection of the number and spacing of samples vertically depends strongly on the thickness and geologic layering within the unsaturated zone, depth of the building foundation, and whether the compounds of interest are aerobically degradable or not.

d. Analysis: Check for state-specific guidance, certifications, and methods. Sampling and analyses are typically by evacuated stainless-steel canister and USEPA Method TO-15. Also, perform data validation/verification and resolve any data quality issues or concerns prior to interpretation. Appendix C provides detailed information on the best practices for the laboratory analytical aspects of VI assessments.

e. Interpretation: Compare measured source concentrations to generic screening levels as an initial step. If no exceedances exist, further interpretation may not be necessary. Alternatively, perform site-specific model calculations using soil property data as inputs. Model calculations should be supported by site-specific data, conservative inputs (tending to overestimate risks), or a sensitivity analysis and judgment of an experienced practitioner. To the extent that the analysis identified potentially unacceptable risks, the

interpretation should also identify areas of interest based on the concentration distribution to prioritize any subsequent investigations, including internal investigations.

Sub-surface investigations must be customized to site-specific conditions. The range of possible conditions is too wide to allow a simple "one size fits all" recipe approach to selecting the scope, locations, depths, frequencies, protocols, analytical methods, modeling techniques, and data interpretation tools. Using a conceptual site model to guide the assessment and a toolbox approach to provide a range of options is currently the best practice. Options for new techniques that may provide a simpler screening with less customization are discussed in Section 4.

3.2 FOCUS AREA 2 - BEST PRACTICES FOR PASSIVE SAMPLING METHODS

Passive sampling has several potential advantages compared to methods currently considered standard practice for VI assessments. Standard methods typically include (1) whole-gas sampling in passivated (e.g., Summa) stainless steel canisters, glass bulbs, or Tedlar bags with analysis by USEPA Methods TO-15, TO-14A, TO-3 or others, or (2) active adsorptive sampling (drawing air or gas through a tube filled with adsorbent media at a fixed flow rate for a measured time) and analysis by USEPA Methods TO-17, TO-10A, TO-13 or others. The standard methods are described in detail in several existing guidance documents (ITRC, 2007; Massachusetts Department of Environmental Protection, MADEP, 2002). Passive sampler applications are less commonly used in VI assessments, so there are more research opportunities.

Generally, two types of passive samplers exist: qualitative and quantitative. Both samplers use adsorbent media to sequester VOCs over time by passive uptake, and the mass of each chemical adsorbed is measured by laboratory analysis. In the quantitative samplers, the geometry is controlled so the uptake rate is known, and the average concentration to which the sampler is exposed over the duration of the sampling event can be calculated for certain conditions using equations based on Fick's Law. In the qualitative samplers, the geometry and rate of uptake are not controlled, so the mass adsorbed can only be related to concentration using empirical relationships.

Both quantitative and qualitative passive samplers have several potential advantages over the current industry standard (USEPA TO-series) sampling and analysis methods, including the following:

- Lower cost in most cases (for deployment, shipping and analysis)
- Consistent application by different operators with minimal training
- Longer sample interval (up to 14 days, and potentially more), which minimizes temporal variability inherent in shorter term samples (samples for TO-15 analysis are typically collected over a period of 24 hours or less) and provides concentration data more representative of long-term average exposures
- Small size and discrete appearance, which is less disruptive to occupants of buildings being monitored

Currently, the best practices for passive sampling are relatively well established for VOCs in indoor air and outdoor air, but are less well established for semi-VOCs (SVOC) and soil vapor monitoring.

3.2.1 Qualitative Passive Samplers

Several qualitative samplers have been developed, including the GORE™ Module (formerly known as the GORE-SORBER®) patented by W. L. Gore and Associates, and the EMFLUX® and BSure Kit™ samplers licensed by Beacon Environmental. Each of these samplers has subtle differences in

the deployment design, but they are all based on adsorption onto a sorbent cartridge followed by extraction, using thermal desorption techniques for analysis. This approach provides excellent sensitivity as well as information about VOCs and SVOCs in the subsurface. Deployment is typically several days, which provides time-integrated data.

Qualitative passive samplers have been used historically to map the distribution of VOCs and SVOCs in the shallow subsurface across a site and identify areas of concern. Qualitative results may also be used for VI studies to identify relative proportions of various chemicals and provide information regarding presence or absence in different media included in the investigation (i.e., groundwater, soil gas or indoor/outdoor air. The degree of consistency in the relative proportions of various chemicals in passive samples of these different media may assist the investigator in interpreting whether chemicals detected in indoor air samples are a result of subsurface intrusion or attributable to background contributions.

The primary limitation of qualitative passive samplers has been the inability to consistently correlate the mass on the sampler to a concentration in the soil gas. Therefore, qualitative passive sampling usually needs to be verified by parallel quantitative sampling and analysis. Otherwise, the results may be limited to assessment of presence/absence and relative magnitudes of detected compounds.

In some cases, the lack of a quantified concentration results may be an advantage. For example, qualitative passive samplers may be used for a preliminary assessment to identify chemicals present and their relative proportions, which may assist in selecting analytical methods for subsequent monitoring events. If the relative proportion of chemicals in soil gas samples is similar to the relative proportion of the same chemicals in indoor air, this may be considered sufficient indication of a VI condition to support decisions for pre-emptive mitigation in lieu of an expensive characterization.

The analytical sensitivity must be considered in this application to ensure that a concentration of concern will not result in a reported value below the limit of detection. Methods that employ thermal desorption prior to analysis have a much better sensitivity than methods that employ solvent extraction because a small portion of the total extract is actually analyzed using the solvent extraction method. This can also be managed by leaving the samplers exposed for a longer period. Selection of the appropriate method and exposure time is part of the design of a passive sampling program.

3.2.2 Quantitative Passive Samplers

Quantitative passive samplers are generally classified by their geometry and are categorized as axial, radial, membrane or badge types. The geometry of each sampler provides different adsorption rates as determined by the sampler's diffusion path and cross-sectional area. The detection limit for each passive sampler is a function of sampling rate, sampling time, the sensitivity of the analytical method, and the background concentrations on the unexposed samplers. Quantitative passive sampling has been used for industrial hygiene (IH) monitoring since the 1970s, so there is extensive experience with this technology. However, it should be noted that IH target concentrations are typically much higher than those for VI assessment, so the reporting limits for quantitative passive samplers have historically been much higher than required to meet the data quality objectives for VI assessments. Recently, the badge-style samplers have been demonstrated to provide quantitative concentration measurements to the low ppbv range, which meets the data quality objectives for risk-based indoor air target levels for many compounds (Oury, Lhuillier, Protois, and Mor´ele, 2006; Hendricks, 2003), and new designs are becoming available. Therefore, quantitative passive sampling is now starting to be considered as option for indoor air monitoring during VI intrusion assessments.

Several types of quantitative passive samplers are currently available, including the following:

- Automated thermal desorption (ATD) tube-style passive samplers (Brown and Crump, 1998), which have been in use for over 20 years in Europe. Sampling rates for specific sampling durations and applications have been validated for various compounds and sorbent tubes (International Standards Organization, ISO, 2003).
- Several badge-type samplers (i.e., SKC 575, SKC Ultra II, 3M OVM 3500/3520, and GABIE), which are commercially available and have been used for decades for industrial hygiene monitoring.
- The Radiello passive sampler, which is composed of a sorbent cartridge inserted into a cylindrical diffusive body. The sorbent and diffusive body can be customized for the specific application.
- Polydimethylsiloxane (PDMS) membrane samplers (Zabiegala, Partyka, Górecki. and Namieśnik, 2006; Górecki and Namieśnik, 2002), which utilize a membrane as a permeation barrier and a sorbent within the sampler to trap the VOCs.

Analysis of the adsorbent media quantifies the mass adsorbed, and this information along with the sampling time and compound-specific uptake rate can be used to calculate the average concentration to which the sampler was exposed. One of the key advantages is that the low reporting limits needed to reach risk-based target indoor air concentrations can be achieved simply by extending the exposure duration. Examples of the reporting limits as a function of exposure time for a select number of compounds are presented in Table 3-1.

For indoor air sampling, the risk-based target concentrations can be very low (depending on the individual compound toxicity and target risk level), so exposure periods longer than 1 week may be required in some cases. The selection of the sampler, adsorbent type, analytical method and exposure duration are all part of the design of a passive monitoring program.

Quantitative passive samplers typically take up VOC vapors at rates that are equivalent to sampling at flow rates ranging from a few milliliters per minute to a few tens of millimeters per minute. This can result in localized depletion of VOC concentrations near the sampler unless there is a certain minimum flow rate of air or gas past the sampler (referred to as the “face-velocity”). If the sampler causes localized depletion of vapor concentrations, the concentrations calculated will be lower (i.e., negative bias), which is referred to as the “starvation effect.” The starvation effect is usually negligible for monitoring indoor and outdoor air, where the face velocity is typically sufficient to avoid the starvation effect. However, the starvation effect may be significant when using quantitative passive samplers for soil gas assessment.

Table 3-1. Comparison of reporting limits after 24-hour and 7-day exposures for three different quantitative passive samplers (modified after Geosyntec, 2008).

Compound	ATD Tube Sampler		Radiello Sampler		PDMS Sampler	
	Reporting Limit ($\mu g/m^3$)		Reporting Limit ($\mu g/m^3$)		Reporting Limit ($\mu g/m^3$)	
	24-Hour Exposure	7-Day Exposure	24-Hour Exposure	7-Day Exposure	24-Hour Exposure	7-Day Exposure
1,1,1-Trichloroethane	97	14	7.8	1.2	29	4.1
1,2,4-Trimethylbenzene	45	6.4	2.1	0.31	2.9	0.42
1,2-Dichloroethane	69	10	4.5	0.68	14	2.0
2-Butanone (MEK)	42	6.0	2.6	0.40	19	2.7
Benzene	20	2.8	0.87	0.13	170	24
Carbon Tetrachloride	140	20	10	1.6	24	3.5
n-Hexane	14	2.0	1.6	0.24	35	5.0
Naphthalene	14	2.0	28	4.2	1.4	0.20
Tetrachloroethene	34	4.8	8.2	1.2	6.8	0.98
Trichloroethene	69	10	7.0	1.1	11	1.6

3.2.3 Summary of Current Best Practice for Passive Samplers

Currently, the primary application of passive samplers in VI assessment in the United States (US) has been for qualitative assessment of the distribution and relative magnitudes of VOCs in shallow soil gas. Quantitative passive samplers have rarely been used in the US for indoor air measurements to support VI investigations, although they have been extensively used in Europe, Canada, and Australia. Therefore, there are significant limitations on the familiarity of US regulators and practitioners with these technologies.

Both qualitative and quantitative passive samplers will provide useful information regarding the presence and relative proportions of compounds, which may be sufficient for assessing whether the VI pathway is complete or not. For example, if PCE, TCE, and cis 1,2-dichloroethylene (cis 1,2-DCE) are present in the subsurface soil gas in ratios of 1:10:100, but are present at in indoor air samples at ratios of 100:1:1, then the significantly different ratios are evidence of an interior or ambient background air source for one or more of the chemicals.

Alternatively, if similar concentration ratios are observed in both subsurface and indoor air samples and subsurface concentrations are significantly (greater than tenfold) higher, VI cannot be excluded as the cause of the indoor air concentrations of those chemicals. This information may be sufficient to make a management decision for pre-emptive mitigation, regardless of whether the concentrations exceed screening levels or even if no concentrations measurements are available.

The compound ratio method of interpretation can be hindered if one or more compounds are not detected in any samples. Passive samplers can help to minimize the truncation of the data sets if they are deployed for longer periods because this results in lower detection limits with no increase in the cost of analysis. In any event, the semi-quantitative results can provide direction for subsequent steps to take, with or without providing concentrations. This can help to avoid the scenario where concentrations are reported at levels above risk-based targets in advance of a determination of

whether they are attributable to background or subsurface sources, which can often result in an increased level of stakeholder interest and regulatory scrutiny.

3.3 FOCUS AREA 3 - BEST PRACTICES FOR IDENTIFYING CONTRIBUTIONS FROM INDOOR SOURCES

For all sampling programs that include indoor air samples, careful evaluation of the data will be necessary to evaluate whether and to what extent the chemicals detected in indoor air are attributable to outdoor air, subsurface vapors, or sources inside the building (consumer products and building materials). Outdoor air samples should be collected concurrent with indoor air samples to assess the contribution of vapors from ambient air. Indoor air concentrations above the outdoor concentrations may be attributable to either interior or sub-surface sources. Several lines of evidence may help to distinguish among the different sources, as described in the sub-sections below.

3.3.1 Comparison to Literature Values

Dozens of indoor air quality studies have been conducted in the past few decades at buildings that are not associated with contaminated land (Hodgson and Levin, 2003; Dawson and McAlary, in press). Where indoor air samples collected for a VI assessment have concentrations similar to the range of concentrations commonly detected in buildings that are not associated with subsurface vapors, there is a reasonable probability that the source of these compounds may be consumer products or building materials inside the building or outdoor air. Indoor air sources vary from building to building in response to consumer preferences, and in response to occupant activities, so this comparison alone does not constitute definitive proof of the source. However, this comparison can quickly identify whether background sources are worthy of further assessment.

In residences that are not affected by VI, several compounds (benzene, PCE, carbon tetrachloride, chloroform, and MTBE) have been commonly detected in indoor air samples at concentrations similar to risk-based target levels (Dawson and McAlary, in press). The detection frequency for these compounds is substantial, so there is a significant probability that background sources will be present at concentrations of potential concern, even when VI is not occurring. In other words, a false-positive determination of VI can occur if background source contributions are not identified.

3.3.2 Comparison of Compound Ratios in Soil Gas Samples

If the relative proportions of chemicals detected in soil gas samples and indoor air samples are similar, this often indicates that VI is the source of the chemicals in indoor air. Conversely, if there is an interior source of one or more chemicals, the relative proportions of chemicals in indoor air samples will be different from soil gas samples. Comparison of compound ratios is recommended as a forensic technique for VI assessment in several guidance documents (API, 2005; ITRC, 2007; NJDEP, 2005; NYSDOH, 2006).

Most petroleum hydrocarbons are readily biodegradable in the presence of oxygen, so their compound ratios may not be comparable to recalcitrant compounds such as chlorinated compounds. Furthermore, different classes of petroleum hydrocarbons degrade at different rates (DeVaull, 2007). Therefore, the compound ratio analysis is generally more difficult to apply with hydrocarbons.

Sub-slab samples are often used for compound ratio analysis, but this can provide misleading results. The pressure differential between the building and the soil gas beneath the floor slab is not constant, and vapor transport goes in both directions: from the soil into buildings and from buildings into the backfill material beneath the building (i.e., buildings “breathe” both ways; McHugh, de Blanc and Pokluda, 2006; Berry-Spark, McAlary, Bice, and DeFlaun, 2004; Luo *et al*., 2006). As a result, the sub-slab soil gas samples collected at a time when the building pressure is greater than the pressure beneath the floor slab may contain compounds that are attributable to indoor sources and not

sub-surface sources. In this circumstance, the compound ratio analysis may show similar conditions for sub-slab and indoor air samples (attributable to vapor extrusion), which could cause a false positive determination of VI (falsely concluding that VI poses an unacceptable risk). It is also important to look at the relative concentrations from the subsurface to indoor air. If VI from a subsurface source is occurring, the sub-slab concentrations will generally be higher than the indoor air concentrations by a factor of 100 to 10,000 for residential buildings, and usually even more for commercial/industrial buildings because of higher ventilation rates, thicker floor slabs, and HVAC systems that result in a net flow of outdoor air into the building with a commensurate positive pressure.

3.3.3 Forensic Analysis

Some laboratories (Alpha Woods Hole and Test America) are offering a forensic TO-15 analysis where they slow the run-time and get better separation of VOCs, which can help discern the source of hydrocarbons in a particular sample. Alpha Woods Hole laboratory also provides a report of relative proportions of paraffins, isoparaffins, aromatics, naphthenes, and olefins (PIANO), which is essentially a hydrocarbon fingerprinting method, similar to visual inspection or graphical analysis of the chromatograms, but with additional compilation of chemicals into categories and post-processing of the data using multi-linear plots of the five families of compounds. Indoor air samples often have a very high percentage of analytes with non-detect results, which hampers the data interpretation relative to soil gas samples where concentrations are often more readily detectable.

3.3.4 Tracer Compounds

Compounds originating from the sub-surface that are rarely detected in indoor air from background sources or are present at much higher than background levels may be used to establish a building-specific attenuation factor by measuring indoor air and subsurface concentrations of the tracer compound. This attenuation factor may then be multiplied by soil vapor concentrations of other chemicals to estimate their concentration in indoor air attributable to VI. McAlary *et al*. (2002) used hexachlorobutadiene for this purpose and demonstrated strong positive correlation between predicted and measured indoor air concentrations of other VOCs. Several others have used 1,1-dichloroethylene (1,1-DCE), which is a degradation product of 1,1,1-trichloroethane (1,1,1-TCA) by hydrolysis.

While 1,1,1-TCA is present in some consumer products (historically as a propellant or solvent in aerosols), the hydrolysis reaction is unlikely to be significant for indoor sources. In research applications, compounds such as helium or sulfur hexafluoride (SF_6) have also been used as emplaced tracer. Emplaced tracers are probably impractical in most VI assessments because there are challenges when emplacing tracers in the subsurface without disturbing natural conditions. In areas where radon concentrations are above background levels, radon has also been used as a naturally occurring tracer (USEPA, 2006b). Radon has a different source than VOCs, so this must be considered before using radon as a tracer. For a particular soil that produces radon gas, it is likely that radon will be produced at similar concentrations below a basement and beside it, whereas a VOC source may be only below the building and at some distance from the foundation. Therefore, radon and VOC concentration measurements from sub-slab samples may be more appropriate than those from deep soil gas samples for comparison with indoor air measurements.

3.3.5 Limited Target Analyte Lists

Where acceptable to the local regulatory agency, the interpretation of indoor air quality data may be simplified by limiting the target analyte list for indoor air samples to those compounds identified in subsurface samples at concentrations of potential concern for VI and/or to those compounds identified from historical site information as being potentially present in the subsurface. In practice,

this is not always possible and in some instances, the opposite is required. For example, NJDEP has clearly stated and strongly defended their recommendation to analyze all samples for the full list of chemicals in their specified version of the USEPA Method TO-15 analysis (NJDEP, 2005), at least until a VI assessment moves from initial sampling to periodic monitoring. This recommendation can add to the challenges of explaining background contributions to building owners, occupants, and other stakeholders. Forensics is also simplified by conducting a building survey in advance of indoor sampling and removing products containing VOCs to the extent practicable. If the removal results in contributions from interior sources that are lower than risk-based target concentrations, the interpretation of indoor air quality is generally simplified. In some cases, vapors from internal sources adsorb to building fabrics and slowly desorbs after the source is removed. Therefore, removal alone does not guarantee that background contributions will be below risk-based target concentrations. Therefore, an inventory of the chemicals present and additional lines of evidence such as compound ratio analysis may still be required.

3.3.6 Pressure Cycling

VI can be assessed by collecting indoor air samples twice, once with the building under an induced positive pressure relative to the subsurface and again with the building under negative pressure (or vacuum) relative to the sub-surface. Under consistent positive building pressure, VI is likely to be insignificant, and the indoor air concentrations are influenced only by indoor and outdoor vapor sources. Under an induced negative pressure, air will flow into the building from all discontinuities in the building envelope, including the subsurface. By collecting and analyzing indoor samples under prolonged control of both conditions, the relative contribution from the subsurface can be determined from the difference between the indoor air concentrations measured under positive and negative building pressure (McHugh, Nickles, and Brock, 2007; Berry-Spark, McAlary, Bice, and Zeeb, 2005). The analysis is somewhat simplified if the building air exchange rate is similar during both sampling events.

VI can also be curtailed by inducing a consistent vacuum beneath the foundation, instead of a pressure inside the building. Indoor air concentrations attributable to sub-surface VI drop very quickly after a sub-slab venting system is employed for mitigation. Figure 3-1 (Folkes, 2000) shows approximately 2 orders of magnitude decrease in indoor air concentrations of 1,1-DCE after installation of a sub-slab venting system. Perhaps the most interesting observation from Figure 3-1 is that the concentrations of VOC compounds originating from background sources were not affected. If VI is occurring, the difference in concentrations before and after cutting off the pathway will clearly distinguish the concentrations that are attributable to VI from those that are attributable to interior sources. This information can be used in resolving background contributions.

In large buildings, it is often possible to manipulate the Air Handling Units and mechanical fans to achieve positive or negative pressure (Berry-Spark, McAlary, Bice, and DeFlaun, 2004), although this will typically require cooperation of the facilities engineer and may result in short-term temperature or humidity changes that are undesirable for occupants. Commercial/industrial buildings commonly have air exchange rates of about one per hour, so manipulating air pressure manifests itself in changes in indoor air quality very quickly relative to conventional sampling durations (e.g., 24 hours or more). In smaller buildings, this can be accomplished using door-fans or window-fans. Wind gusts and other factors commonly contribute to pressure fluctuations of about ±3 to 5 Pascal (Pa), so the building pressure or vacuum should be designed to exceed this level to reduce the risk of ambiguous results.

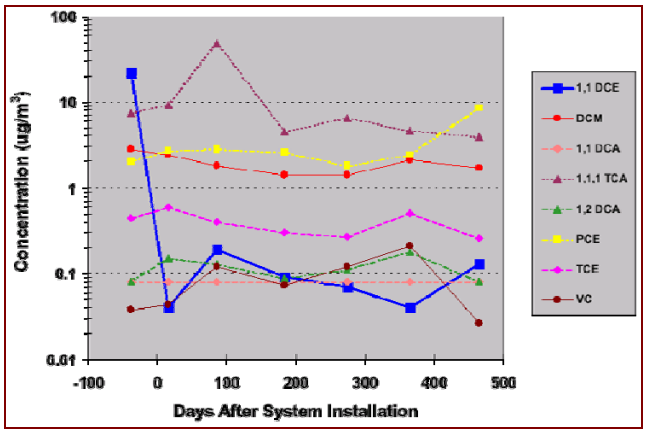

Figure 3-1. Chlorinated solvent vapors before and after sub-slab depressurization (Folkes, 2000).

3.3.7 Real-Time Analysis

The USEPA Trace Atmospheric Gas Analysis (TAGA) unit is a mobile laboratory with a dual quadrupole mass spectrometer that is capable of quantifying concentrations of selected compounds to low part-per-trillion levels several times each minute. This unit is outfitted with a long Teflon® hose and vacuum pump that allows the operators to survey a building in real time and identifies interior sources of chemicals. However, the cost of this system is about $10,000 per day, and the availability of the TAGA unit is limited.

Other mobile laboratories are currently offering analysis by gas chromatograph/mass spectrometer (GC-MS) using Method TO-15 with selective ion monitoring to achieve indoor air reporting limits low enough to meet risk-based target indoor air concentrations (Hartman, Picker, and Villarreal, 2008). However, they cannot perform continuous readings and cost and availability vary on a case-by-case basis.

3.3.8 Summary of Best Practices for Indoor Source Separation

Currently, distinguishing the relative contributions of indoor, subsurface, and outdoor air sources to the concentrations of vapors measured in an indoor air sample is challenging and often ambiguous because data variability and risk-based target indoor air concentrations for several compounds are so low, they are often within the range of variability of analytical reporting limits or typical indoor air concentrations. In some cases, an interior source imposes concentrations that are high enough to be easily identified or contribute chemicals that are not found in the subsurface. Even though there may be locations where the effect of indoor or outdoor sources on indoor air measurements may be technically resolved, communicating this technical analysis to non-technical stakeholders is still a challenge. Therefore, improved methods for resolving indoor sources would be very valuable.

4. KNOWLEDGE GAPS AND DATA NEEDS

The goal of this section is to provide an overview of knowledge gaps and data needs for the assessment of VI in the context of the Navy focus areas identified in Section 1. Approximately 25 regulatory guidance documents on VI exist now, and there are significant differences between them, which shows that there is still much to be learned about VI. Most guidance documents recommend screening sites by a multiple lines-of-evidence approach involving comparison of groundwater, deep soil gas, sub-slab soil gas, and/or indoor air sampling and analysis data to risk-based target concentrations derived using conservative assumptions. Target concentrations vary by orders of magnitude between guidance documents (Eklund, Folkes, Kubel, and Farnum, 2007), which is not typical of screening levels for other pathways (ingestion, dermal contact, etc.). Considerable spatial and/or temporal variability has been reported for data collected during VI assessments and the amount of data required to understand the variability can be very expensive to collect. Furthermore, indoor air results are often ambiguous, particularly because the risk-based indoor air target concentrations of several common chemicals are similar to background concentrations or practical analytical reporting limits. In many cases, responsible parties have selected pre-emptive mitigation in lieu of assessing VI because it may be perceived as less expensive. However, this may be more expensive in the long term and may be considered an admission of liability by some stakeholders. Currently, environmental scientists are actively debating opposing assessment strategies: starting with indoor air, and collecting sub-surface samples after as needed ("top-down" approach), or collecting sub-surface samples first and proceeding to indoor air sampling after as needed ("bottom-up" approach).

Much of the pure and applied research on subsurface VI over the past few decades has been related to radon. Indoor air samples for radon are typically collected using passive diffusive sampling devices (e.g., electrets) that are very easy to use, inexpensive to analyze, and collect a time-integrated sample over a minimum of 72 hours and often longer. If the concentration exceeds 4 picoCuries per liter (pCi/L)[1], a sub-slab venting system is typically installed at a relatively modest price of about $1,500 and operated for an annual electricity cost of about $100. However, this target concentration is easily resolved from background levels and analytical reporting limits. VI assessment and mitigation for VOCs is typically much more challenging than radon because there are usually multiple compounds and the risk-based target concentrations for many common compounds are not easily resolved above typical background levels or laboratory reporting limits. Therefore, additional information that is usually not collected during radon assessment is often required during VOC VI assessments and risk management decision-making.

Many regulatory agencies rely upon indoor air sampling and analysis as the ultimate test for assessing VI, and several public interest groups have also expressed a strong preference for indoor air sampling and analysis. This preference is based in part on concerns that external data (soil gas and/or groundwater concentrations measured outside the building footprint) may not provide a representative estimate of indoor air concentrations because of potential bias and variability in the subsurface concentration distribution and measurement methods as well as uncertainty in the attenuation factor from the subsurface to indoor air. However, there is a high probability that VOCs originating from consumer products or building materials or even outdoor air will be detected in

[1] USEPA reports that the risk of lung cancer for a non-smoker exposed to this level over a lifetime is 7×10^{-3} and the risk of lung cancer for a smoker exposed to this level over a lifetime is 6.2×10^{-2}.

indoor air samples. In some cases, background concentrations may be above health-based target levels, and if indoor air sampling and analysis is used as the sole line of evidence for assessing VI, there is a high risk of false-positive outcomes (falsely concluding that VI poses unacceptable risks). Therefore, some combination of assessment data is often preferred, which is described in some regulatory guidance documents as a "multiple lines of evidence" approach (e.g., USEPA, 2002; ITRC, 2007; NJDEP, 2005). Unfortunately, there are widely divergent opinions about which lines of evidence are the most reliable, how many lines of evidence are needed for a confident decision, the sequence in which data should be collected, and many technical details on investigative methods.

The remainder of this section discusses the knowledge gaps and data needs in each of the three Navy Focus Areas in detail. Future directions for research are discussed in Section 5.

4.1 FOCUS AREA 1 – KNOWLEDGE AND DATA GAPS FOR SUBSURFACE SAMPLING TO ASSESS VI

Assessing the potential for VI using subsurface data collected outside the building usually involves measuring concentrations of compounds of interest in soil gas or groundwater, and multiplying by a factor that accounts for the reduction (or "attenuation") in concentration between the location of the soil gas or groundwater sample and air inside the building. The reliability of the estimate of indoor air concentrations depends on the representativeness of both the subsurface concentration measurement and the attenuation factor. Knowledge and data gaps for both of these components are discussed in the Subsections 4.1.1 and 4.1.2.

4.1.1 Knowledge and Data Gaps for Subsurface Characterization

General knowledge gaps related to subsurface characterization include the following:

- Lack of consistent and uniform application of ***sampling methodologies***, which is particularly challenging for VI assessment because the risk-based target concentrations are very low.
- Lack of understanding of the site-specific factors that lead to significant ***temporal and spatial variability*** in measured concentrations and implications for the design of assessment programs.
- Lack of understanding of the range of chemicals that may require assessment and availability of ***analytical methods*** with sufficient sensitivity to meet risk-based target concentrations for some chemicals.
- Lack of ability to adequately quantify important ***fate and transport processes*** and the classification of which assessment approaches and methodologies may be most appropriate under different conditions and settings (i.e., there is no "one size fits all" approach for data collection).

Each of these areas is discussed in additional detail in the subsections below.

4.1.1.1 Sampling Methodology

Groundwater sampling has been the subject of a large body of research, and most practitioners have considerable training in the collection of groundwater samples to meet DQOs for site investigations to protect groundwater resources. Indoor air sampling using canisters and flow controllers is also standardized to the point where it is applied relatively consistently. In contrast, a wide variety of protocols for soil gas sampling is in common use today (ASTM, 1992; API, 2005; EPRI, 2005; CalEPA, 2003; CalDTSC, 2005; Geoprobe, 2006). Some were initially designed for less stringent data quality needs (i.e., landfill gas monitoring, soil vapor extraction system operational

monitoring, screening for leaking underground storage tanks, etc.). Furthermore, few guidance documents provide sufficiently detailed sampling protocols to prevent some of the common factors that can contribute to data bias and variability (leaks, sorption/desorption biases, incomplete purging prior to sample collection, etc.).

Some suggestions for quality control procedures for soil gas sampling are provided in Appendix A. Additionally, geologic material properties vary considerably from site to site, and some sampling methods are better suited to some geologic materials than others. However, there is relatively little basic research or regulatory guidance on which soil gas sampling methods provide reliable data for different geologic conditions (especially low permeability soils and fractured rock), complex chemical mixtures (including up to about 115 potential COCs), and a potential range of several orders of magnitude in concentrations.

Environmental scientists have concerns about data quality when risk-based target concentrations are very low. For example, soil gas screening levels for VI are as low as about 0.001 µg/L, compared to groundwater target concentrations typically at or above 1 µg/L. With very low reporting limits, there is an increased likelihood of false-positive biases attributable to equipment contamination and cross-contamination. Therefore, sampling protocols for soil gas in VI assessments must be very stringent.

Empirical soil gas data show high levels of variability, but it is unclear to what degree the variability is natural or the extent to which sampling biases or practitioner proficiency contribute to the variability. A recent review of soil gas data from sites with petroleum hydrocarbon vapors (McHugh, personal communication, 2008) identified a relatively high percentage of samples with high concentrations of both hydrocarbons and oxygen. These conditions are not expected because microorganisms degrade hydrocarbons in the presence of oxygen and an inverse relationship between hydrocarbon and oxygen concentrations is commonly seen. However, if there is a leak during sampling, anaerobic soil gas with hydrocarbons can mix with atmospheric air and result in a sample with high concentrations of both hydrocarbons and oxygen. A large database of sites was included in this review, so the concern over soil gas data quality is not isolated to individual practitioners.

The knowledge gap is that no single, widely accepted, and adequately detailed soil gas sampling protocol specifically designed to achieve the DQOs for VI assessments currently exists. Limited data support the selection of appropriate sampling methods for the wide range of soil types, chemicals of potential concern and concentrations that may be encountered during VI investigations. For example, temporary driven probes have been shown to provide representative soil gas samples in sandy soils, but there is a risk of deflection in soils with cobbles or rubble, which may cause leakage around the outer wall of the drive-pipe or casing. The risk of bias attributable to leakage increases in soils with low gas permeability (gas flows from the path of least resistance, and low-permeability soils impose more resistance to advective sampling than high permeability soils). If a seal or tracers are only applied near ground surface or above, there may be no way to detect or prevent cross-communication between intervals above the tip of a temporary probe. The risk of leaks is reduced by using probes installed by coring and placement of slurry seals throughout the borehole annulus (Geoprobe, 2006), but, there is limited data to demonstrate the conditions under which the additional effort of installing such probes is justified, and this is a subject of considerable debate among practitioners. There is also the need to identify acceptable sampling vacuum and flow rate, as well as purge volume and purging conditions (flow, total volume, time), which currently span a very broad spectrum, from much less than a liter (Schumacher *et al*., in press) to many thousands of liters (Lewis, Folsom, and Moore, 2005).

The design of sample locations, depths, frequencies, sampling techniques, and analytes is site-specific, and little guidance is available to help practitioners and regulators in this area. Deeper samples located closer to the vapor source typically exhibit less short-term temporal variability than shallower samples, but the extrapolation of these data to indoor air often involves using a conservative attenuation factor or mathematical model that does not account for the bioattenuation that occurs with some petroleum hydrocarbons. Soil gas sampling at various distances from buildings or beneath surfaces intended to mimic building floor slabs (i.e., "near-slab" sampling) is also discussed in many guidance documents, but the correlation between near-slab samples and sub-slab samples has not yet been researched in detail.

4.1.1.2 Temporal and Spatial Variability

Currently, knowledge of factors contributing to temporal variability is limited. Certain weather conditions can potentially affect soil vapor and shallow groundwater concentrations (e.g., rainfall events, barometric pressure changes, wind, seasonal temperature changes, and water table fluctuations). However, the magnitude of the temporal variability for one site to the next in response to different geologic materials, vadose zone thickness, chemical type, and concentration ranges has not been documented.

Knowledge of spatial variability and the contributing factors is also limited. Mathematical model simulations (e.g., Abreu and Johnson, 2006) show that under certain conditions higher concentrations may be present beneath a building than at comparable depths outside the building (Figure 4.1). Spatial variability around a building may be attributable to (1) advection imposed by building pressure differentials, (2) lower soil moisture content in soils beneath the building (rain shadow), (3) impediment to upward transport of vapors imposed by the foundation, or (4) impediment to downward transport of oxygen at sites with hydrocarbon vapors.

Note that on Figure 4.1, simulated concentrations immediately beneath the building are higher than concentrations at the same depth outside the building footprint, although at depths of few meters deeper than the foundation there is relatively little difference between simulated concentrations beneath and besides the building. To address concerns over spatial variability, some state regulatory agencies are requesting that soil gas samples be collected on all four sides of a typical residential building. This approach becomes impractical for sites where VOC plumes are present under residential communities of large numbers of houses. It may be preferable to specify the depth at which exterior soil gas samples are collected, but the information available to support a definitive position is insufficient.

Knowledge gaps regarding spatial and temporal variability impose challenges in designing an investigative program to assess VI. NJDEP regulatory guidance (NJDEP, 2005) recommends that soil gas samples collected outside a building footprint should be collected from within 10 ft of the wall of the building (i.e., "near-slab" soil gas samples). Knowledge gaps regarding the relationship between near-slab and sub-slab concentrations has led some practitioners to install angled borings to collect soil gas samples from beneath a building to minimize concerns whether near-slab sampling is representative of sub-slab conditions. However, other regulatory programs permit the collection of soil gas samples at greater distances from the building, which can significantly facilitate the process of acquiring access agreements (e.g., delineating the extent of COCs in soil gas and/or shallow groundwater in public rights-of-way instead of multiple private properties).

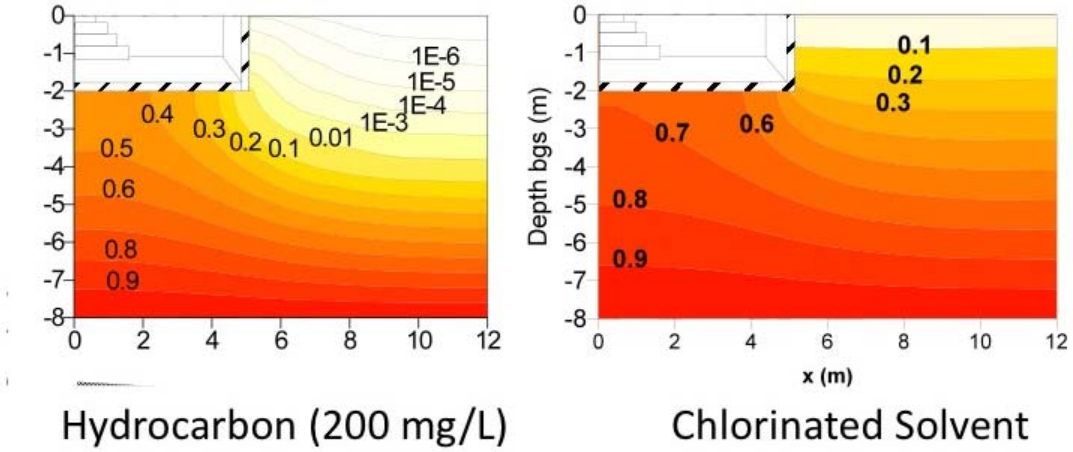

Figure 4.1**.** Simulated relative VOC concentrations in the subsurface near a residence with a basement, showing spatial variability of (a) hydrocarbon vapors (mg/L) from high concentration source and (b) chlorinated hydrocarbons. Contours are labeled to show VOC concentrations as a fraction of the source concentration.

Others have attempted to collect surrogate sub-slab samples by collecting shallow soil gas samples beneath sidewalks, driveways, parking lots, or other areas where the ground surface is covered with concrete or pavement. However, there has never been a rigorous assessment of whether the vapor concentrations under these surrogate surfaces are comparable to concentrations beneath floor slabs (building pressure differentials, utility penetrations, expansion joints, and sub-grade compaction may be sufficiently different to alter results). There is little research to support the selection of the most representative distances and depths for acceptable external soil gas sampling locations, and the number of samples required to provide necessary and sufficient data for screening and risk assessment in consideration of the spatial and temporal variability in soil vapor concentrations.

4.1.1.3 Analytical Methods and Target Analyte Lists

Knowledge is limited regarding appropriate analytical approaches for some of the chemicals listed in various VI publications (USEPA, 2002; CalDTSC, 2005; ASTM, 2008; US Air Force, US Navy, and US Army, 2009). There is uncertainty about whether all of the chemicals on these lists may pose a *bona fide* risk via the VI pathway, as opposed to a theoretical possibility of a VI risk. In contrast, NJDEP guidance limits assessment of VI to compounds that can be analyzed using USEPA Method TO-15, which eliminates about half the compounds on the USEPA, CalDTSC, ASTM, and DoD lists. To assess the rest of the compounds, several other analytical methods (TO-17, TO-10A, TO-13, etc.) must be used, which becomes very expensive, and there is very little practical experience with using these methods among the VI practitioners in North America. Currently, the vast majority of practical experience and research in the field of VI is limited to about 20 compounds or less (chlorinated ethenes, ethanes, and methanes, mono-aromatic hydrocarbons, MTBE, naphthalene, and radon).

4.1.1.4 Factors Affecting Vapor Fate and Transport

Assessment of the potential for VI depends on the factors affecting fate and transport of the compounds of concern in the subsurface and across the building foundation, which is typically

addressed through the development of a conceptual site model of the source, pathway, and receptor relationships at a given site. The conceptual model of one-dimensional vertical transport through uniform or layered geologic materials (Johnson and Ettinger, 1991) is often a good starting point, and generally provides an estimate of the attenuation factor that is within about one order of magnitude of measured values when site conditions match the model assumptions (Hers, Zapf-Gilje, Johnson, and Li, 2003; Johnson, 2005). However, there are conditions that can be significantly different from the simplified scenarios considered in the screening-level models, as discussed briefly below.

4.1.1.5 Preferential Pathways

Most guidance documents mention "preferential pathways" (leaky sewer pipes, granular fill around utility lines, etc.) as a consideration for spatial variability during VI assessment. However, preferential pathways such as these are present at most sites, and there is almost no research or case study examples that demonstrate whether pathways such as these will enhance VI relative to average or typical conditions. There are a few instances of explosions in buildings related to methane migration along preferential pathways, but this is typically driven by pressure gradients that result during methane production, and would not be relevant for chlorinated solvent sites, where this additional pressure gradient would not be expected. Therefore, the inclusion of preferential pathway concerns in VI guidance documents is poorly supported by the available knowledge and data. Additionally, knowledge and data are very limited regarding methods for the reliable and safe assessment of vapor transport along preferential pathways.

4.1.1.6 Geologic/Hydrogeologic Barriers

Geologic barriers can have a dramatic effect on subsurface concentration gradients. However, the texture, thickness, moisture, and other properties that would be adequate to comprise a substantial or complete barrier to VI have not been researched or documented in the literature. Neither is there sufficient data to be able to assess whether and to what extent the transport of vapors through a geologic/hydrogeologic barrier varies over time with seasonal and longer-term changes in weather.

4.1.1.7 Degradation

Biodegradation can cause dramatic decreases in concentrations over very short distances. Biodegradation rates have been extensively studied for petroleum hydrocarbons (DeVaull, 2007) and methane. But relatively little is known about factors affecting the oxygen supply and distribution, the degradation rates for vinyl chloride, and other chlorinated VOCs in the unsaturated zone and how to best design soil vapor sampling program to avoid false positive and false negative screening, considering the strong concentration gradients that can occur for biodegradable compounds (Figure 4-1).

4.1.2 Knowledge and Data Gaps for Attenuation Factors

Estimating indoor air concentrations from VI based on external data collection (Focus Area 1) requires both representative subsurface data and a representative estimate of the relationship between subsurface and indoor air concentrations (i.e., the attenuation factor). The preceding section discussed knowledge and data gaps related to the subsurface characterization, and this section discusses knowledge and data gaps related to the attenuation factor.

There are three options for estimating the attenuation factor between subsurface and indoor air concentrations (generic empirical data, mathematical models, and tracer compounds), and certain knowledge gaps exist for each, as described in the subsections below.

4.1.2.1 Generic Empirical Attenuation Factors

Research Triangle Institute (RTI) has compiled a database for USEPA of measured subsurface and indoor air concentrations, and the OSWER Guidance Expert Panel has performed n analysis to filter out less reliable data and develop order statistics (mean, and 5^{th}, 25^{th}, 75^{th}, and 95^{th} percentile values) of empirical attenuation factors for groundwater, soil gas, and sub-slab to indoor air (Dawson, 2008). This database is a large compilation of subsurface and indoor air VOC concentration measurements, so it is generic (i.e., not specific to any single site or building).

The generic data include variability attributable to natural spatial and temporal variability as well as potential biases from the sampling methods, quality assurance/quality control (QA/QC), and detection limits. As a result of variability in both the numerator and denominator, the range in calculated attenuation factors (the quotient) is likely to be higher than long-term average values. Some guidance documents use a conservative estimate of the attenuation factor (e.g., 90^{th} or 95^{th} percentile values); therefore, the screening levels derived from these upper estimates of the empirical attenuation factor may be more protective than intended for some sites and buildings, but the degree to which this is the case is unknown.

The database of empirical attenuation factors is dominated by data from chlorinated solvents and therefore does not provide information that is directly applicable to aerobically degradable petroleum hydrocarbons. Additional attenuation from biodegradation can be up to several orders of magnitude (DeVaull, 2007; Roggemans, Bruce, and Johnson, 2001; Abreu and Johnson, 2005). Applied research on attenuation factors for biodegradable petroleum hydrocarbons is being conducted by the API and petroleum companies (Luo *et al*., 2006; McAlary *et al*., 2007, Luo *et al*, 2009). These efforts are improving knowledge in this area, but additional research for a number of different field conditions is still needed to evaluate the frequency of false- negative and false-positive screening for VI impacts using various choices of the generic attenuation factors for groundwater, soil gas, and sub-slab soil gas.

The vast majority of data in the USEPA empirical database is for single-family residences, so there is a knowledge gap regarding to what extent large commercial/industrial buildings experience additional attenuation attributable to foundations that are more robust, additional ventilation, or additional dilution from larger building height. Building-to-building variability has been considered for years in the radon industry, but currently the amount of knowledge and information is insufficient for accurate predictions. Therefore, the most common regulatory approach with empirical attenuation factors is to use them for preliminary screening and select values that are near the upper end of the statistical distribution to minimize the risk of falsely concluding that VI does not pose a risk. While this is intentionally conservative, it is not known currently to what extent this may be overly conservative.

4.1.2.2 Modeled Attenuation Factors

Most of the mathematical models of VI are based on a certain conceptualization (e.g., upward diffusion from an underlying source, migration into the building and dilution in the building ventilation), and invoke a series of simplifying assumptions. For example, a steady-state model will provide a long-term average estimate of VI, but will not represent the range of conditions that may occur over short time periods. When the model formulation assumptions are not met, it is often unknown whether a new model is needed, whether a modification to an existing model is possible, or whether modeling is simply not a viable option. There have been a few comprehensive comparisons of field data collection and modeling to document the predictive ability of mathematical models (Johnson *et al*., 2002; Hers, Zapf-Gilje, Johnson, and Li, 2003). Comparison of model calculations

with real-world data can be challenging because the field data may be collected over periods that do not represent long-term average conditions.

Currently, some regulatory agencies do not accept mathematical modeling to estimate exposures via VI because of concern that the model results may not be sufficiently conservative. There has been little research, however, to assess how modeled results compare to measured concentrations and to identify how spatial and temporal variability, background contributions, or other factors affect interpretation of field data and the use of models. Where sufficient data are available for a rigorous comparison between the data and model calculations, the two approaches for assessing the attenuation factor typically agree within about an order of magnitude (Johnson *et al*., 2002). However, the difference is similar to the range of variability in a 24-hour sample of indoor air, and may therefore be a *de minimus* level of uncertainty until alternative, long-term assessment methods are developed to reduce data variability. Petroleum hydrocarbons degradation is not included in most common screening-level VI models. However, models are available that can simulate the effects of aerobic degradation on the VI pathway (Johnson, Mariush Kemblowski, and Johnson, 1999; Abreu and Johnson, 2005; DeVaull, 2007; and Davis, Patterson, and Trefry, 2009), although there is limited knowledge and data with which to assess which of these models provides the most practical and reliable simulations for various settings.

The Navy has many large buildings, and research is needed to evaluate using models for large buildings, particularly with respect to differences in model input parameters and data collection for model calibration. Factors such as the ventilation rate (which is typically dictated by building codes for high occupancy buildings), building pressure or vacuum (induced by ventilation systems or the stack effect), and the size of the building relative to the source area may all be different for large buildings. In general, large buildings could be considered any building with more than three stories, a footprint larger than about 2,500 ft^2, or a forced-air ventilation system that supplies air from outside the building.

4.1.2.3 Building-Specific Attenuation Factors Derived from Tracers or Marker Compounds

Tracers or marker compounds are chemicals that are detectable in the subsurface and indoor air at concentrations that can be resolved against analytical reporting limits and background levels to allow calculation of a building-specific attenuation factor (e.g., radon, 1,1-dichloroethene). The tracer should provide an attenuation factor that is building-specific and reduces or eliminates inter-building variability and uncertainty in estimating the attenuation factor. Since the attenuation factor for the tracer compound is calculated using site-specific measurements of sub-surface and indoor air samples, the issues of spatial and temporal variability and data bias that affect the empirical attenuation factors will also contribute to uncertainty in the tracer-based attenuation factor value. If the subsurface distribution of the tracer and the compounds of interest are not identical, the attenuation factors may actually be different for different compounds. The subsurface distributions, however, typically are not known, and the degree of associated uncertainty in the building-specific attenuation factor cannot be documented because of insufficient data.

Radon has a different source than the VOCs that are the focus of VI assessments, so the radon attenuation factor may be different, although the magnitude of the difference is unknown. McHugh, Nickles, and Brock (2007) noted in their recent Environmental Security Technology Certification Program (ESTCP) study:

"Radon is a useful tracer for the movement of soil gas because radon is emitted from all soils and is present in all soil gas. However, because VOCs in soil gas originate from specific sources while radon in soil gas originates from all soils, the distribution of radon and VOC may be different within

subsurface gas below a building. This difference could result in differences between the measured attenuation factors that are not attributable to indoor sources of VOCs."

"Radon data is [*sic*] likely to be most useful for the evaluation of VI when radon and VOC concentrations are measured at multiple sub-slab sample locations allowing for an evaluation of the differences in subsurface distribution of these chemicals."

In addition, radon may be present in outdoor air, potable water, and some building materials (gypsum drywall) at measurable levels, so this methodology can only be applied where indoor air concentrations are elevated above background. The USEPA and many states have compiled and posted information on websites with maps of the radon distribution, but knowledge is limited as to the representativeness of these large-scale maps for VI assessment (scale of a building), as well as what level of radon zone will typically result in radon concentrations that can be clearly resolved from background levels. Currently, there have been very few applications of radon as a tracer, so additional work would be valuable to facilitate acceptance of this tool for VI assessments.

In summary, Focus Area 1 (assessing VI using external data) faces several knowledge and data gaps associated with characterizing the extent and distribution of compounds of concern in the subsurface, and the fate and transport mechanisms that attenuate their concentrations between the subsurface source and indoor air. This explains why many regulatory agencies and public interest groups currently prefer indoor air sampling and analysis data for making decisions about the potential for VI. Unfortunately, this leads to significant challenges in resolving the relative contribution of chemicals from background sources, described further under Focus Area 3.

4.2 FOCUS AREA 2 – KNOWLEDGE AND DATA GAPS FOR PASSIVE SAMPLING METHODS

For both qualitative and quantitative passive samplers, there are knowledge and data gaps regarding:

- The relative merits of competing products with different designs.
- Capabilities and limitations of ***thermal desorption and solvent extraction*** methods for the ***spectrum of chemicals***, range of concentrations, and combinations and permutations of mixtures that may be encountered in order to reach reporting limits as low or lower than risk-based screening levels, which may be orders of magnitude different between soil gas and indoor air.
- Potential for ***starvation effect*** during soil gas sampling, as a function of the texture, moisture and porosity of the geologic materials and the geometry and uptake rate of the sampler.
- Limits on the ***maximum duration of deployment***, particularly in humid or high concentration atmospheres where there may be saturation of adsorptive sites and desorption of lighter VOCs, or degradation of chemicals between adsorption and analysis attributable to ground-level ozone.
- Regulatory acceptance.

Each of these knowledge and data gaps is described in the subsections below.

4.2.1 Relative Merits of Competing Products

There are at least two qualitative passive samplers (Gore Module and BSure Kit) and several quantitative passive samplers (Radiello, SKC Ultra II, 3M OVA3500, GABIE, PDMS membrane, ATD Tubes). Currently, several comparative studies between the passive samplers and active

sampling methods have been made, but very few studies comparing several passive samplers to each other (Oury, Lhuillier, Protois, and Mor'ele, 2006). This is the primary focus of ESTCP Project ER-0830 (Geosyntec Consultants, Inc., 2008).

4.2.2 Thermal Desorption vs. Solvent Extraction

Passive samplers can be configured with various sorbents, allowing for solvent extraction or thermal desorption to release the adsorbed VOCs for analysis. Carbon disulfide is used as solvent in extracting VOCs from samplers that use activated charcoal as the sorbent, such as the SKC 575, 3M OVM, Radiello, and PDMS samplers. Samplers that use the thermal desorption method for analysis include the SKC Ultra II, the Radiello Carbograph 4, and Perkin-Elmer tube style samplers.

Solvent extraction techniques are less sensitive than thermal desorption since only a fraction of the extract is injected into the GC for analysis, while the thermal desorption technique essentially transfers all of the adsorbed mass to the GC system. Despite the sensitivity gains using thermally desorbable media, target compounds do not sorb as strongly to these sorbents compared to the solvent desorbable media. Sorption efficiency in thermally desorbable media is lower to enable good recovery during analysis; however, this can lead to artifacts from competition for adsorptive sites and back-diffusion of less sorptive compounds in high concentration atmospheres or during extended sampling durations. Since detection limits decrease as a function of sampling time, the sensitivity gains using thermally desorbable sorbents may be offset by the shorter deployment periods typically used for passive samplers with thermally desorbable sorbents. Conversely, the lower sensitivity of the solvent extraction-based methods can be overcome using longer deployment periods, which has the added benefit of providing data that is less influenced by short-term temporal variability.

Comparison between thermally desorbable and solvent extraction samplers for long-term integrated sampling is limited and more research is required to determine their applicability for vapor phase measurements. In some cases, 24-hour samples are requested or required to comply with regulatory guidance, in which case, thermal desorption techniques may be the only ones capable of meeting the target reporting limits. For the range of chemicals that could potentially be a VI concern and the range of different risk-based target concentrations in various guidance documents, there is a lack of data to support the selection of the appropriate sampler and analytical method for a given set of site conditions.

4.2.3 Spectrum of Chemicals

While many VOCs have been evaluated using passive sampling methods, validation of the various passive samplers for SVOCs is limited. Sorbents potentially provide a significant advantage over traditional Summa canister sampling because the recovery of heavier and less volatile compounds is poor with Summa canisters. However, passive adsorptive samplers also face some challenges with a spectrum of target analytes that includes a wide range of adsorptive affinities. There are several types of adsorbent media (activated carbon, Tenax, polyurethane foam, and dozens of others). There is no "universal" applicable adsorbent media that can both efficiently adsorb a wide range of VOCs and SVOCs during sampling and release them efficiently during analysis by thermal desorption techniques.

To effectively target a wide volatility range, more than one passive sampler containing different types of adsorbent media may be required. Similarly, various passive sampler designs may be more or less appropriate for SVOC measurements. For example, the micro-porous diffusive body used for the Radiello sampler may not effectively allow for the adsorption of SVOC onto the sorbent as compared to other passive sampler designs because some SVOCs may adsorb to the body of the sampler instead of the adsorbent media inside. Use of a very strong adsorbent media such as

activated carbon facilitates capture of a wide range of compounds during sampling, but the temperatures required to thermally desorb some compounds can be so high that combustion or other reactions occur. Therefore, solvent extraction may be a preferable option. The optimal sorbent media and analysis type for all VI target compounds is not currently well known, and the complexities that can occur when there are mixtures of compounds is a further complicating factor.

4.2.4 Starvation Effect

The application of passive samplers for soil gas measurements presents several advantages and challenges. The deployment of the passive samplers directly into subsurface (sub-slab or deeper) is relatively simple with minimal opportunity for variability and bias attributable to protocols and inter-operator errors, which can occur during active soil gas sampling. However, passive samplers typically are employed at shallower depths than other soil gas sampling methods and therefore may be more prone to the effect of environmental variables such as rainfall events, changes in barometric pressure, and wind speed.

Quantitative passive samplers require a certain flow of gas past the sampler (face velocity) sufficient to replenish VOCs near the sampler at a rate greater than the rate at which the sampler removes vapors from the space being monitored. Otherwise, the sampler causes a decrease over time in the concentrations being monitored (referred to as the "starvation effect"), and results in a negative bias in the concentration data. Indoor and outdoor air velocities are typically high enough to avoid the starvation effect, but this may not be true for soil gas sampling. The extent of the starvation effect for different soil conditions and sampler designs is not well known.

4.2.5 Maximum Duration of Deployment

One of the key advantages of passive samplers is that they can be deployed for longer periods (several days or even weeks) compared to active samplers (usually <24 hours). This provides more time-integrated concentration data and minimizes artifacts attributable to short-term temporal variability. Furthermore, longer-term sampling increases the adsorbed mass of compounds of concern at the site relative to any blank contamination that may occur during storage, shipping and handling. Therefore, blank contamination becomes less significant as the samplers are deployed for longer periods.

However, in the presence of very high VOC concentrations, adsorptive sites may become filled and sampling rates may be negatively affected or less-adsorptive compounds may be displaced by more-adsorptive compounds. Uncertainty in the sampling rates translates to uncertainty in the analyte concentration. Additional tests are needed to identify which passive samplers perform better under these subsurface conditions.

In addition, as the duration of deployment increases, the mass of vapors adsorbed will also increase, and if the sampler is exposed to high concentrations, the adsorptive sites may become saturated, after which, the uptake rate may reduce, or competitive sorption may occur (highly adsorptive compounds displacing less adsorptive compounds). While this may affect analytical accuracy, it may not adversely affect risk-management decisions, particularly if saturation occurs because concentrations are orders of magnitude above screening levels, in which case, even data with a negative bias may be sufficiently reliable to justify invoking exposure controls.

4.2.6 Regulatory Acceptance

Regulatory acceptance of passive samplers for VI investigation has been hindered by lack of familiarity with the technique and lack of confidence in their performance over a wide range of environmental conditions and ability to meet very low target concentrations. Despite the many advantages that passive sampling offer, there is reluctance in adopting passive methods as a

quantitative tool for VI investigations, because there are few studies that compare results using conventional methods (i.e., TO-15 or TO-17) with passive sampling methods (Oury, Lhuillier, Protois, and Mor'ele,, 2006: Hendricks, 2003). However, data from passive samplers have been widely accepted for plume mapping purposes and to define the areas of a site requiring characterization that is more definitive. It may also be possible to use passive samplers for assessing compound ratios (i.e., ratio of TCE/PCE in subsurface and indoor air), which may be a useful screening technique to identify background contributions. However, no one has conducted a detailed study to demonstrate the effectiveness of this as an investigative technique. Further field and laboratory validation data are needed to assess the accuracy and precision of passive samplers under various environmental conditions.

4.3 FOCUS AREA 3 – KNOWLEDGE AND DATA GAPS FOR INDOOR SOURCE SEPARATION

If an external investigation identifies subsurface concentrations above VI screening levels or if indoor air sampling is otherwise required by the regulatory agency, the relative contributions from indoor, outdoor, and subsurface sources need to be resolved. Key knowledge gaps and data needs related to indoor source separation are described in the subsections below.

4.3.1 Temporal Variability

Resolving indoor source contributions is challenging enough without the added complexity of temporal variability in the data. The sample collection method can have a significant effect on the range of concentrations measured. For example, radon gas researchers adopted longer term, time-averaged passive indoor air sampling methods to meet analytical sensitivity requirements and found that these longer sampling periods minimize temporal variability. Radon sampling results for different sampling time intervals have shown that the temporal variability in the data decreases with increasing sample interval duration. Denman *et al*., (2007) found a factor of variability of 125× when comparing 1-hour samples collected at various times in the same general location, but only a factor of 2 to 3× variability in samples collected over 1-month time periods. Currently, most indoor air samples for VI investigations are collected over a period of 24 hours, except in commercial/industrial settings where 8-hour samples are sometimes used. The available data indicates a range of roughly one order of magnitude between minimum and maximum measured concentrations attributable to VI (Kuehster, Folkes, and Wannamaker, 2004). Long-term indoor air sampling for VOCs using current standard methods (TO-15 and TO-17) is possible, although rarely conducted. However, long-term sampling is well within the capabilities of quantitative passive samplers.

4.3.2 Building Factors

Several building-specific factors affect the potential for VI, as described in the subsections below.

4.3.2.1 Pressure and Ventilation

Vapor intrusion depends strongly on the volumetric flow rate of soil gas into the building (Q_{soil}), which is a function of the pressure difference between the building and sub-surface (Abreu and Johnson, 2005). The pressure difference can be caused by the stack effect (attributable to temperature differences between indoor and outdoor air), wind-driven suction (attributable to the Bernoulli effect), and mechanical ventilation systems (exhaust fans vs. air handling units). Currently, there have been only a few studies of the pressure differentials and causes in conducting VI investigations (Luo *et al*., 2006; Sundquist, Wertz, and Boyd, 2007). It is currently unknown to what extent the influence on VI attributable to building pressure and contributing factors can be extrapolated from one building to the next, or whether pressure differential monitoring and/or a ventilation assessment would be required for each building, particularly for large commercial and industrial buildings with HVAC systems.

In commercial/office buildings, it often may be possible to fill the data gaps regarding building pressure and ventilation with manageable effort. Mechanical engineers perform a routine test to assess building leakage called a Pressure/Ventilation Test, which in some cases is required as part of the contract for new building construction. Ventilation rates in commercial/industrial and multi-unit residential buildings are often specified in building codes, and monitored and recorded in a standard report called a Test and Balance Report. In other cases, pressure differentials between the building and subsurface can be monitored with relative ease and low cost by drilling a hole through the floor and connecting a micromanometer with data-logging capabilities. Information on building pressure and ventilation should be available from the facilities engineer, building custodian, or mechanical engineering subcontractor.

4.3.2.2 Mixing Within the Building

Convection and circulation of air inside a building will cause mixing to some degree, but the extent of mixing is not generally well known. Samples collected in the breathing zone (3 to 5 ft above ground) are typically well mixed within a single room in a single-family residence because of ventilation, but mixing between separate air spaces of larger buildings is a variable that depends on building-specific factors. This leads to questions regarding how many samples are required to assess the potential for VI and whether it is feasible or more appropriate to collect composite samples by moving samplers from room to room in proportion to occupancy duration.

Prior to mixing within the building, vapor concentrations would be expected to be higher in the immediate proximity of points of entry (sumps, floor drains, holes, and cracks in floors, etc.). It may be possible to gain valuable information for screening purposes by assessing concentrations at the points of entry. For example, elevated readings on portable meters such as a photoionization detector (PID) or flame ionization detector (FID) may be useful. However, more information is needed to assess whether the detection limits of these instruments are appropriate for this use. The analytical sensitivity of the portable analyzers is likely to be a limiting factor and the use of portable GCs or other tools may be needed.

Designnig a monitoring protocol that uses the building itself as a large flux-chamber may be possible, although research would be needed to assess whether and to what extent this would be practical. This may be achievable with activities similar to the pressure-cycling monitoring techniques (e.g., Berry-Spark, McAlary, Bice, DeFlaun, 2004; McHugh, Nickles, and Brock, 2007), and is described further in Section 5. Another approach along these lines is to measure the rate of air exchange (e.g., ASTM, 2006) and combine the ventilation air rate and average indoor air concentration to estimate the total emission flux. The mass flux of VOCs from the subsurface divided by the ventilation rate of the building provides a method of calculating the indoor air concentrations attributable to VI that may avoid some of the challenges associated with measuring concentrations and estimating an attenuation factor.

4.3.3 Summary of Knowledge and Data Gaps for Indoor Source Separation

In almost all cases, indoor air samples will contain detectable concentrations of VOCs that originate from consumer products and building materials (interior sources), and outdoor (ambient) air. Many compounds that are common contaminants in soil and groundwater are also commonly detected in indoor air from interior and ambient (background) sources, and background concentrations for several compounds are within the range of risk-based target concentrations. Resolving the relative contributions of VOCs from interior, ambient, and subsurface sources is one of the common and difficult challenges of VI assessment. There are several knowledge and data gaps relevant to the assessment of background contributions:

- What are the limitations of using literature values for indoor air concentrations in residential buildings not associated with contaminated soil or groundwater, especially for buildings with a history of VOC use, storage or handling?
- To what extent can containers of consumer products containing target compounds be removed prior to collecting indoor air samples? How long after these products are removed before can indoor air sampling be conducted? What factors affect the expected reduction in background concentrations in indoor air? This may vary as a function of the sorptive properties of the chemical(s) of interest (e.g., octanol partition coefficient, K_{oc}) and the ventilation rate of the building.
- To what extent can pressure-cycling strategies (sampling building under positive and negative pressure relative to the subsurface by either adjusting building pressure or sub-slab vacuum) be used as a cost-effective assessment tool?
- Can forensic methods of analysis be used to fingerprint chemical contributions from the subsurface versus indoor sources?
- To what extent does reversible flow (buildings breathing both ways) contribute to spatial and temporal variability in sub-slab sampling, and can this be understood, controlled, or prevented? Can sub-slab samples be collected in different ways to overcome this potential bias (i.e., sample only when building pressure is lower than sub-slab pressure, which may need to be manipulated)?

4.4 SUMMARY OF KNOWLEDGE AND DATA GAPS FOR VAPOR INTRUSION FOCUS AREAS

Considering all the complexities described above, it is challenging to select and implement a screening approach that quickly, inexpensively and unambiguously identifies buildings with a potential risk via VI. However, the Navy would benefit from having such tools or strategies because of the large number of building they may need to assess. The next section discusses research opportunities for developing these tools or strategies.

5. OPPORTUNITIES FOR FUTURE RESEARCH AND DEVELOPMENT

This section identifies research opportunities consistent with the discussion of best practices and identification of knowledge gaps and data needs for the Navy Focus areas. These reflect the study team's collective experience and projections of the potential benefits and costs associated with conducting research in each topic area. Where applicable, the study team has also identified ongoing research programs that the Navy should track and could potentially collaborate with to leverage its resources.

5.1 FOCUS AREA 1: RESEARCH INTO SUB-SURFACE SAMPLING TO ASSESS VAPOR INTRUSION

Current VI assessments use sub-surface concentration data and attenuation factor estimates, and the underlying assumption is that these are representative of, and applicable to, the site of interest. First, research into sampling and analysis methods is needed to better understand how to deal with the spatial and temporal variability that have been reported using conventional sampling and analysis methods. Promising opportunities are described in Subsection 5.1.1. Second, research to understand the differences in attenuation factors as a function of site-specific conditions and chemical types should be conducted. Typical site conditions that are likely to be encountered frequently and approaches for conducting applied research through detailed investigations at selected examples of each type of site are described in Subsection 5.1.2.

5.1.1 Alternative Methods for Sampling

Alternative sampling and analysis strategies that have the potential to yield more representative and/or less variable data for assessing the potential for VI risks are described below. However, research is needed before the capabilities and limitations of these alternative methods are known and sufficient field verification data have been collected to support scientific and regulatory review. Each of these alternatives can be assessed by a controlled program of field-testing trials at one or more sites where a VI assessment would already be performed, allowing for direct comparison of conventional sampling strategies to the alternative methods.

5.1.1.1 Soil Gas Sampling

Experience suggests that it is unlikely that a single soil gas protocol will be reliable and efficient in all geologic settings and for all chemicals. Therefore, a toolbox approach (e.g. API, 2005; EPRI, 2005; Geoprobe, 2006; ITRC, 2007) may be preferable, in which case, research is still needed to identify which sampling methods are appropriate for various combinations of geologic conditions, chemicals of interest and concentrations.

To put the need for soil gas sampling research in perspective, consider the development of groundwater sampling techniques. A significant effort was expended in the 1980s to develop groundwater-sampling methods. As a result, there are now demonstrated methods for low-flow sampling (Puls and Barcelona, 1996), passive diffusive bag samples (Vroblesky and Hyde, 1997), inertial pumps (e.g. Waterra™), piston pumps (e.g. Hammerhead™), submersible positive displacement pumps (e.g., Grundfos™), multi-channel systems (e.g., Westbay™, Solinst™), depth-discrete temporary probes (e.g. Hydropunch™, Waterloo profiler™), and other methods. By comparison, research into soil gas sampling has been limited to *ad hoc* testing by individual practitioners or vendors, a comparative demonstration at the Midwestern States Risk Assessment Symposium (MWSRAS) (Grosse, 2006), applied research by industry groups (API, 2005; EPRI, 2005) and three studies by USEPA labs (USEPA, 2006a,b; Schumacher *et al.*, in press), with a

collective budget that is a small fraction of the finances committed to groundwater sampling research.

Additional research on soil gas sampling is needed to demonstrate:

- The degree to which different sampling methods provide comparable results for different chemicals in different types of geologic materials.
- The limits of active soil gas sampling in low-permeability materials.
- The capabilities and limitations of quantitative passive soil gas sampling (see Section 5.2).
- The practical limitations of sampling for semi-volatile organic compounds.
- The comparative aspects of individual sampling protocols (purge rate, vacuum, volume, etc.).

It is preferable to conduct soil gas sampling research in the field rather than a laboratory because geologic heterogeneity, weather conditions, spatial and temporal variability, and other factors cannot be effectively replicated in a laboratory. The research can be conducted at sites where VI assessments are already planned by adding replicate and duplicate sampling by multiple methods and comparing the results.

The CalDTSC and Los Angeles Regional Water Quality Control Board (LARWQCB) are completing and update of their joint advisory for active soil gas sampling and held a series of meetings to accept opinions from interested parties. This is one of the more recent efforts toward establishing soil gas sampling protocols for VI investigations. It would be of benefit to the Navy to assess CalDTSC's progress. In addition, the Navy may choose to participate in the ASTM-led effort to prepare a series of standards on soil gas sampling involving both active and passive approaches.

5.1.1.2 Groundwater Samples

As noted above, groundwater sampling protocols are better established than soil gas sampling protocols (extensively researched, well-documented, and individual practitioners are comparably and adequately trained in most cases). Groundwater samples should be collected just below the water table if the data are to be used in VI investigation, which is not difficult in highly permeable geologic materials, although fluctuating groundwater tables may necessitate the installation of discrete multi-level well clusters or the use of temporary probes if these samples are to be collected over time. The collection of groundwater samples for VOC analysis is more challenging in low-permeability geologic materials where well yields are low.

There may be benefits to developing passive sampling protocols using quantitative passive samplers that are sufficiently hydrophobic to be used above and below the water table as a groundwater monitoring option. The benefit of this would be comparability between media, if a certain type of passive sampler could be shown to provide representative concentration data below the water table (i.e., groundwater concentrations), above the water table (i.e., soil gas concentrations), and inside buildings (i.e., indoor air concentrations). The University of Waterloo and Geosyntec recently submitted a proposal to the Ontario Ministry of the Environment to evaluate PDMS membrane samplers for this purpose.

5.1.2 Intensive Field Data Collection at a Limited Number of Sites

Much can be learned from detailed field studies conducted to improve the understanding of processes and site conditions affecting VI. A detailed study at one site or building can pay significant dividends in incrementally lower costs, particularly for entities like the Navy, which have very large

numbers of buildings. A few such studies have been conducted (e.g., Hers, Atwater, Li, and Zapf-Gilje, 2000; Luo *et al*., 2006; McHugh, Nickles, and Brock, 2007; McAlary *et al*., 2007; Ririe, Sweeney, and Daugherty, 2002; Grosse, 2006; Lundegard, Johnson, and Dahlen, 2008), but the amount of information currently available is limited and not all results are easily transferred to VI assessment in general because each study was motivated by, and focused on, a site-specific issue. Several knowledge and data gaps can be filled by additional detailed field studies, including:

- Whether soil conditions (moisture, oxygen and vapor concentrations) affecting vapor migration under buildings are significantly different than those adjacent to the building or farther away, and if both respond to change (e.g., rainfall events) in the same way.
- The degree to which different subsurface materials (e.g., sand, silt, clay, and homogeneous or layered conditions) affect the inherent temporal and spatial variability of soil gas concentrations.
- Whether different soil gas sampling methods are more appropriate for different geologic settings (i.e., low-permeability soils, cobbles, fractured rock);
- Whether confidence in assessment conclusions can be improved by using long-term sampling for managing temporal variability.
- Whether confidence in assessment conclusions can be improved by using large-volume soil gas samples for managing spatial variability.

If planned strategically, this research can be conducted with relatively low incremental cost by leveraging on-going regulatory-driven VI assessment activities at Navy sites. Of particular interest are conditions representative of settings that are common for the Navy, for example:

- Large buildings with slab-on-grade construction and commercial/industrial use.
- Buildings with positive pressure by design and operation of ventilation systems.
- Volatile chemicals in groundwater under residential buildings.
- Shallow water table sites, such as the eastern US coastal plain.
- Undeveloped parcels of land.
- Sites with moderate- to low-level VOC contamination.
- Residential buildings with crawl spaces.

Considering the differences between these types of sites, it may be appropriate to develop a screening process that is specifically designed to address the processes or mechanisms affecting vapor fate and transport in each scenario. This is consistent with the approach of developing a classification of VI sites suggested by Johnson (2008), and is consistent with the approach of developing a robust conceptual site model and designing an investigation approach based on the CSM. Examples of potential approaches for assessing each of the site conditions listed above are discussed below, although these are intended as examples and would often be customized to some degree. For any of these site conditions, a short-duration field-testing program could be initially conducted to compare conventional sampling and analysis with additional or customized methods to assess the cost and effectiveness of various investigative approaches.

5.1.2.1 Large Buildings with Slab-on-Grade Construction and Commercial/Industrial Use

Large buildings used for commercial/industrial purposes often have floor slabs that are constructed to a higher standard than domestic residences, and therefore less likely to be extensively cracked. In

addition, concrete floors in commercial buildings are often coated with slip-resistant coatings, which also help to seal the floor. To the extent that the floor slabs are less permeable, these buildings are better candidates for high purge volume (HPV) sub-slab soil gas sampling because the HPV test design assumes that downward leakage of air across the floor slab is a relatively small or negligible contribution to the flow of gas extracted from the gravel layer beneath the floor. Furthermore, exterior sampling is likely to be inappropriate for large foundations because there may be an area of elevated soil gas concentrations far from the building perimeter to be adequately represented by exterior soil gas sampling. Other sub-slab sampling techniques such as quantitative passive sampling and composite sampling may also be valuable. A head-to-head test of innovative sub-slab sampling compared to conventional sub-slab monitoring would provide useful data for assessing the relative merits of each of these technologies.

5.1.2.2 Buildings with Positive Pressure by Design and Operation of Ventilation Systems

Large buildings are typically ventilated using air-handling units that blow air into the building. In warm humid climates (like the Gulf coast), buildings often have slight positive pressure by design to prevent influx of warm, moist air, which leads to condensation, and associated problems with rot and mold. A consistent positive pressure sufficient to avoid influx of outdoor air is also likely to significantly reduce or substantially prevent subsurface VI. This is based on theory and building codes, but research is needed to verify this with data. An example approach for rapid and cost-effective screening of buildings with suspected positive pressure includes review of HVAC operations (interview with mechanical engineers and review of Test and Balance reports) and pressure differential measurements (micromanometers and pressure transducers attached to probes installed through the floor slab). This approach was successfully used to screen out the potential for VI at the Young Rainey Star Center in Pinellas, Florida, a former DoD site that has been redeveloped for multi-purpose commercial use.

Currently, there have been very few buildings where a detailed review of the air-handling units design and operation, building pressures, influences of weather factors over time, and net effect on indoor air concentrations of subsurface vapors has been documented to the level required to demonstrate the extent to which mechanical engineering data regarding ventilation system operation and building pressure can be used in the prediction of indoor air concentrations. To demonstrate to what extent positively pressurized buildings have a significantly lower potential for VI, a series of well-documented assessments would be valuable. These assessments can be accomplished at Navy sites where VI assessments are already planned by adding sufficient additional data collection, ventilation system assessment, pressure differential monitoring, and data analysis to produce an assessment procedure that would be acceptable by regulatory agencies.

5.1.2.3 Volatile Chemicals in Groundwater under Residential Buildings

This scenario is the one that corresponds to the majority of the high-profile VI cases, and yet after a decade of investigation at several sites, there are still differences of opinion regarding the most reliable and cost-effective method of screening and assessment. There are at least two schools of thought:

- Adopt a blanket approach of offering indoor air sampling and/or pre-emptive mitigation to all occupied buildings within the known and suspected distribution of VOCs in soil gas and shallow groundwater.
- Collect data to assess the subsurface nature and extent of vapors and understand the processes and mechanisms controlling vapor fate and transport then proceed with interior sampling or pre-emptive mitigation only where warranted.

Proponents of the first approach argue that the spatial and temporal variability in soil gas and groundwater concentrations are large enough that any reasonable number of samples will have an unacceptable probability of a false-negative determination (failing to identify VI when it does indeed pose unacceptable risks); therefore, a protective position should be adopted for all properties overlying a plume of VOCs in groundwater. Proponents of the second approach argue that there can be processes that attenuate VOC transport in some areas that are not as effective in other areas. For example, in humid climates with ample rainfall, infiltrating rainwater tends to suppress the release of vapors from groundwater, and this effect become more pronounced with increasing distance from the source. Geologic barriers to vertical diffusion of vapors may be intermittent and not laterally extensive across the area of the plume. Research to compare and contrast the two approaches would be very beneficial, because sites of this class can result in multi-million dollar investigations, so the potential benefits of improved pathway screening are very large. Currently, there are very few sites with enough data collected to compare and contrast the two approaches. Valuable information could be gained by a modest investment of incremental data at a site where a detailed assessment has been conducted using one or the other approach.

5.1.2.4 Shallow Water Table Sites, such as the Eastern Coastal Plain

The Navy has a large number of sites with shallow water tables because Navy facilities are generally located close to major water bodies. Conventional soil gas sampling for VI assessment is challenging at shallow water table sites, particularly if the building foundation extends to a depth similar to or deeper than the water table. There may also be preferential pathways for vapor entry such as sumps, seeps, and underground utilities. The relative importance of the potential preferential pathways at these sites has not been studied in detail, and the relative contribution from the preferential pathways compared to pathways that are more typical has not been demonstrated. There have been reports of elevated VOC concentrations measured in water and headspace samples collected from sumps, although the relative contribution from the preferential pathways compared to more typical pathways has not been demonstrated. A detailed assessment of at least one representative building would be a good starting point to assess whether additional research in this area is potentially valuable.

5.1.2.5 Undeveloped Parcels of Land

Vacant land does not pose a current risk of VI, but may pose a risk in the future if a building is constructed. This scenario is especially important for sites included in the BRAC program. In some cases, the potential for VI into a building is difficult to assess simply because there is no building, but suggestions have been made to develop “surrogate” surfaces (i.e., a concrete parking area to act as a surrogate floor slab) or buildings (i.e., construct a small shed and monitor indoor air quality as a surrogate for a larger building). Mathematical modeling can also be used to predict indoor air quality. This modeling can assess different scenarios such as varying degrees of remediation before redevelopment, different styles of building construction and ventilation, etc. Assessing the predictive capability of the model by comparing its results with actual measured concentrations at well-characterized sites would be valuable. To provide the data required for research in this area, VI assessment data could be collected before and after constructing a building in an area with potential for VI, and the information gained could be compared to mathematical model predictions with minimal additional expense compared to the redevelopment activities.

For undeveloped land, it may be cost effective to adopt a presumptive remedy strategy and build new buildings with a vapor barrier. The costs of a vapor barrier typically are not prohibitive compared with the total cost of construction. Barriers alone may not reduce VI to the degree necessary, depending on the concentrations in the subsurface and the indoor air target concentrations.

It may be necessary to include vent-pipes to allow a point of exit for vapors, and may be necessary to facilitate the flow with fans or blowers to varying degrees. Where various presumptive measures have been used, it may be worthwhile to collect performance data to establish expected ranges of control efficiencies (percent reductions in concentrations achievable by various technologies) and develop a cost-benefit comparison to guide future remedy selection.

5.1.2.6 Sites with Natural Barriers to VI

Some site conditions (confined aquifers, fresh water lens, low-permeability highly saturated layers above the source, biodegradation zones, etc.) act as partial or substantial barriers to VI. It would be valuable to identify conditions under which any such barrier is sufficient to reduce VI to a level of no significant risk and to develop characterization strategies and tactics to demonstrate the influence of the natural barrier. Because regulatory agencies often require a significant effort to demonstrate that there is no unacceptable VI risk whenever concentrations exceed conservative screening levels, evaluation of the effects of natural barriers on VI would be particularly helpful for sites (or portions of sites) with moderate to low concentrations of volatile chemicals in the subsurface. As an example of this concept, some states use soil gas or groundwater screening levels for biodegradable compounds that have been adjusted by a factor of 10 to account for vadose zone biodegradation. There are currently no such allowances for sites with low-permeability layers above the source or other potential barriers.

5.1.2.7 Residential Buildings with Crawl Spaces

Base housing or adjacent off-property residential buildings may be pier-and-beam type construction with crawl spaces. This construction type is particularly common in humid climates like the Gulf States, because this design helps to prevent issues with dampness, mold, and rot. Passive or active ventilation of the crawl space may substantially or completely reduce VI; however, current VI guidance typically assumes that crawl spaces have no added ventilation beyond that of the overlying building. Evaluating this scenario through tracer tests capable of measuring exchange rates in the crawl space and overlying building and the rate of flow of crawlspace air into the building would be relatively simple. In addition, these experiments could be combined with tests of semi-passive (wind-driven or solar-powered fan) and active (powered fan) ventilation of the crawlspace where vapor concentrations are high enough to pose a potential risk.

5.2 FOCUS AREA 2: RESEARCH OPPORTUNITIES FOR PASSIVE SAMPLING METHODS

Today, passive diffusive samplers are not widely used as anything more than a screening tool in VI assessments. This is primarily because of a lack of familiarity of many regulators and practitioners with the options available and a lack of comprehensive demonstrations of the passive samplers. However, passive samplers may be used for several kinds of monitoring that may be useful on many if not most VI assessments if the data support their reliability and the research is published in reputable scientific publications. ESTCP has recently funded research to assess the relative performance of four quantitative passive samplers for indoor air, outdoor air, and soil gas monitoring (GeosyntecConsultants, Inc., 2008). The research will include controlled laboratory experiments and field-testing of a wide range of compounds of different physical and chemical properties to assess the capabilities and limitations of the samplers for different classes of compounds. Testing will include methods designed to minimize the starvation effect (described above) during soil gas sampling. One or more field sites are needed for this testing program. The potential cost savings with this research are very large, and there is ~$1M in funding in place that makes the leverage on this opportunity very large.

Passive samplers have other potential applications and additional research may be appropriate in these areas as well. Passive samplers can be used to monitor long-term time-average concentrations

in vent-pipes of sub-slab venting systems to assess performance over time and provide documentation for use when a petition for closure is ultimately prepared. Passive samplers may also be used in flux chambers of various designs, since they can provide a longer-term average measure of flux, which will minimize variability imposed by short-term temporal variability. Qualitative passive samplers can also be used to assess relative concentrations of target compounds in several media (soil gas, sub-slab, and indoor air samples), which might be possible to analyze using compound ratios to assess whether VI is occurring, even without rigorously quantified concentrations. Research in these additional applications should be considered after more research has been conducted to demonstrate the capabilities and limitations of passive sampling in conventional applications.

5.3 FOCUS AREA 3: ASSESSMENT OF INDOOR SOURCES OF TARGET COMPOUNDS

Interpretation of indoor air sample results is often difficult due to the presence of indoor sources of compounds of interest for the VI investigation and the fact that risk-based indoor air target concentrations for several common compounds are within the range of typical indoor air concentrations in residences that are not associated with contaminated land. This is further complicated by the high levels of temporal and spatial variability in concentrations that have been observed using current industry standard sampling and analysis techniques. Research opportunities for Focus Area 3 include improved sampling and analytical techniques to provide more representative long-term average concentration data (subsection 5.3.1). Experience has shown that there may be advantages to a few different forensic techniques of data collection and analysis to resolve relative contributions of vapors from indoor and subsurface sources, and research opportunities for these are presented in Subsection 5.3.2.

5.3.1 Indoor Air Samples – Integrated versus Instantaneous Measurements

Research is needed to establish indoor air sampling methods that most effectively characterize the low indoor air concentrations appropriate for risk assessment purposes. This may be accomplished by developing new sampling methods for collection of time-integrated samples. Three possibilities for long-duration VOC sampling to measure total indoor air concentrations are as follows:

1. Adjusting flow-controllers on canisters to extend the sampling duration, although there are practical limits to the capabilities of flow controllers that make sampling over a period of a week or more difficult with currently available apparatus.
2. Using electronic mass flow controllers and data loggers with canisters to extend the sampling duration. This might involve collecting periodic sample aliquots (e.g., 1 minute per hour) rather than continuous sampling.
3. Using quantitative passive diffusive samplers (of which there are several varieties as discussed in more detail in Section 3.2).

In addition to long-term indoor air sampling, research opportunities exist for real-time instantaneous monitoring to help resolve the contribution of VI versus building background contribution to total indoor concentrations. The DOD has a significant investment in the Inficon HAPSITE® Smart Chemical Identification System, which is a field portable GC/MS designed for on-scene detection, identification, and quantization of toxic industrial chemicals (TICs) and chemical warfare agents (CWAs) at parts per trillion levels during field operation. Another new technology that is being marketed for this purpose is the Tiger GC™ by Analytical Specialists, Inc. (www.microfastgc.com). The manufacturer claims that the product can quantify individual compound concentrations essentially continuously at the low ppbv level using a small (size of shoebox), portable, battery-operated GC. Field-testing of these real-time monitoring instruments is needed to demonstrate their capabilities and limitations in the context of VI investigations.

5.3.2 Sub-Slab Soil Gas Samples – Passive, HPV and Composite

Research is needed to assess whether sub-slab soil gas samples can be collected in a manner that (1) minimizes spatial and temporal variability, (2) minimizes the potential for collection of vapors from sources originating inside the building, and (3) correlates more strongly to indoor air concentrations attributable to true VI from subsurface sources. In cases where sub-slab sampling is required or considered necessary or appropriate, several alternative strategies for collecting sub-slab soil gas samples exist that should be researched:

5.3.2.1 Quantitative Passive-Diffusive Sampling

Measuring a time-integrated sub-slab concentration using quantitative passive adsorptive samplers may provide representative long-term average sub-slab vapor concentrations and minimize temporal variability in the data. To successfully apply passive samplers to sub-slab measurements, a method must be developed to eliminate or minimize negative bias caused by the starvation effect, which occurs when the sampler removes VOCs from its air space faster than they are replaced. If significant starvation occurs, the calculated concentration is therefore representative of the average over a time of diminishing concentrations imposed by the sampler itself and not natural conditions. It may be possible to minimize starvation by creating a sub-surface void space of a certain volume such that the sampler can uptake mass from within the void space to the extent needed to obtain a sample. In this scenario, either the void space would need to be allowed to equilibrate with the surrounding soil gas prior to sampler deployment, or the void space would need to be purged prior to sampling. The exact design is a matter to be resolved by the research. Even if a minor amount of starvation occurs, the samples would still provide a screening-level measure of concentrations. If the starvation effect cannot be eliminated, passive samplers (qualitative or quantitative) may be useful as a relative method for compound ratio analysis to assess contributions of sub-surface and indoor sources because the magnitude of the starvation effects will be similar for VOCs with similar properties. Passive sampling in most applications provides a localized measurement, so multiple samples may still be required to assess spatial variability. Quantitative passive diffusive sampling will be evaluated in the current ESTCP research program ER-0830, in which the Navy may participate by offering a field-testing site.

5.3.2.2 High Purge Volume (HPV) Samples

Extracting a large volume of gas from beneath a floor slab may provide representative average concentrations that minimize spatial variability in the data and can minimize the potential risk of missing an area of elevated concentrations when using multiple discrete sampling locations. The volume of gas in a 6-inch thick gravel layer beneath a typical residence is a few thousand liters (L). In this context, the volumes of sub-slab soil gas samples that are currently collected for VI assessments ($\leq$ 6 L) are very small, and larger samples may provide more spatially averaged concentrations. HPV sampling may also show less temporal variability because the temporal variability observed at a few field test sites has been localized and is not uniform beneath a foundation.

The gravel layer beneath most floor slabs is highly permeable, so it is relatively fast, simple, and inexpensive to extract a large volume of gas and from that collect a slipstream sample for laboratory analysis. The slip-stream sample can be collected by attaching a “T”-fitting to the extraction line and connecting a Summa canister with a flow controller that will fill the canister over the proposed duration of the test by collecting a small fraction of the total flow being extracted, although other options may also be available. This approach might prove to be more cost effective and faster than collecting a large number of discrete samples. It also may avoid the potential risk of a false-negative outcome attributable to inadvertently collecting samples between areas of elevated concentrations.

Where concentrations are high enough to be detected using portable instruments, monitoring the concentrations as a function of volume extracted can provide useful information (Creamer and McAlary, 2006). For example, if the concentrations increase with volume of gas purged, this indicates there are higher concentrations at a location some distance away from the point of extraction. If concentrations remain steady, this indicates that there is relatively little spatial variability in the sub-slab vapor concentrations, or the method is providing a blended concentration that is an average over the area evacuated (which may actually be more representative of what enters the building in the long term than any point-measurement). Recent experience in Florida using a comparable technique referred to as modified active soil gas sampling (MAGS), has demonstrated that this approach provides cost-effective useful information (Lewis, Folsom, and Moore, 2004, 2005). However, the MAGS approach has been limited mostly to dry-cleaner sites, with sandy soils and shallow water table conditions, so research is still needed to characterize the capabilities and limitations for a range of site conditions.

There is a significant research opportunity to apply this concept to sub-slab sampling or field screening in large commercial/industrial buildings where conventional sub-slab sampling data density would result in a prohibitively expensive program. The results could be compared with conventional sampling to see how the two data sets relate. This could be done at any such building where a conventional assessment was already planned with modest incremental cost and effort.

5.3.2.3 Composite Samples

Collecting aliquots from several locations and combining them into one sample for analysis may provide a more representative, spatially averaged concentration that will be less expensive and may be more representative of long-term average exposures than multiple discrete samples. This can be accomplished using Summa canisters and methods similar to those presented in current regulatory guidance documents. However, this approach for assessing average sub-slab concentrations may be subject to temporal variability from building pressure variability, and still requires drilling multiple holes through the building floor. Recognized cost savings would be limited to reduced analytical costs.

5.3.3 Pressure Cycling

The pressure cycling method requires manipulating the building pressure by adjusting the airflow into or out of the building and has been attempted with encouraging results (Berry-Spark, McAlary, Bice, and DeFlaun, 2004; McHugh, Nickles, and Brock, 2007). Research opportunities for pressure cycling include a series of tests to accomplish the following:

- Assess the practicability of pressure cycling for buildings of a variety of different sizes and construction types.
- Conduct comparative testing of sub-slab de-pressurization versus building pressurization to assess which approach is most cost-effective and provides the highest resolution.
- Develop a robust protocol that can be implemented consistently for different buildings by different practitioners.
- Research in this area could be combined with research into the building envelope mass balance strategies, described in the following sub-section.

5.3.4 Building Envelope Mass Balance Strategies

With a modest incremental effort beyond that required for pressure cycling tests, it is possible to collect sufficient data for independent verification of the relative contribution of background sources using mass balance calculations, which would constitute a second line of evidence, beyond the

indoor air concentration data. This may improve regulatory acceptance, since many regulatory guidance documents (USEPA, 2002; ITRC, 2007) recommend multiple lines of evidence be considered to reduce the uncertainty of the VI assessment. Buildings experiencing VI act essentially like a flux-chamber (upward flux of vapors is diluted within the building ventilation). Assessment is typically performed by measuring concentrations, but it may be possible to measure the mass flux of VOCs using the building itself as a flux-chamber.

A conceptual sketch of one potential implementation approach is shown in Figure 5-1. The image on the left shows the initial sampling of indoor air, providing time-weighted average concentrations of VOCs under normal conditions ($[VOCs]_1$). The second sampling event is shown on the right, where a pump is used to draw sub-slab soil gas to prevent soil gas entry into the building (10 L/min should be sufficient for most domestic residences according to Johnson [2005], although higher flow rates may be necessary), and concentrations are measured both in indoor air ($[VOCs]_2$) and extracted sub-slab soil gas ($[VOCs]_{ss}$).

The data can also be used to calculate the VOC concentrations attributable to VI ($[VOC]_{VI}$) from the mass flux (F), by dividing by the building ventilation rate ($Q_{building}$), which can often be estimated with reasonable accuracy, or can be measured using a tracer test:

$F = Q_{soil} \times [VOCs]_{ss}$

$[VOCs]_{VI} = F/Q_{building}$

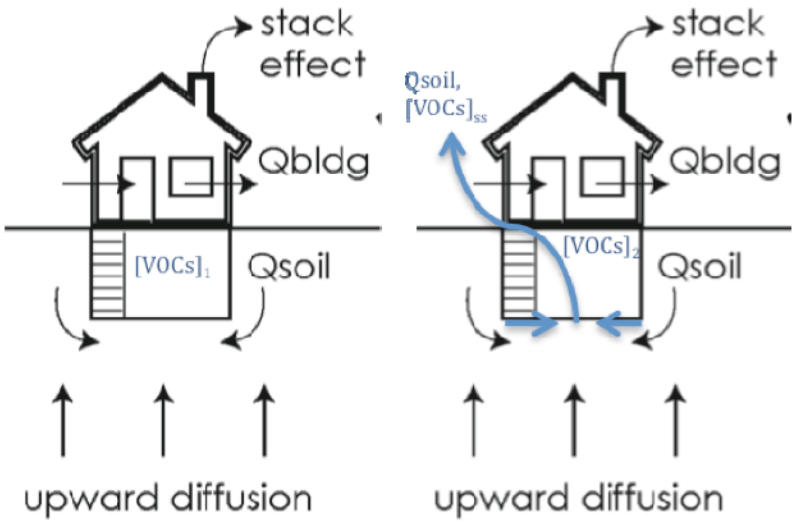

Figure 5-1. Conceptual sketch of one option for building mass balance assessment approach.

A second line of evidence for the indoor air concentrations attributable to VI is available from the same data set, based on a simple difference in the concentrations between the first and second indoor air sample:

$[VOCs]_{VI} = [VOCs]_1 - [VOCs]_2$.

If this method works as designed, it will accurately quantify the contribution of VI to indoor air with a single set of measurements, and a total cost that is similar or less than the costs of a single conventional monitoring event. As with any subsurface venting system, it will be necessary to determine the effectiveness of the control system across the entire slab footprint. It may be necessary to use multiple extraction points depending on the size of the slab, the number of slab elevations, the presence of any footing, or utilities beneath the slab, etc. Furthermore, the optimal duration of such a

test would need to be evaluated; shorter tests are less obtrusive to occupants, but the flux measurement would require some time for stabilization, and it may not be accurately measured if the test design is too aggressive.

Research is needed to identify the most cost-effective way to conduct sampling with and without imposed pressure gradients that allow and prevent VI. It may be more efficient to manipulate building pressure or sub-slab vacuum, or both. It may not be necessary to install a full-scale sub-slab venting system to obtain data "before and after" cutting off the pathway. A temporary system may be sufficient because of the rate at which the indoor air is exchanged. In addition, since soil gas flow rates into buildings are typically low (<10 L/min), a temporary cut-off might be achieved with very modest equipment (a small pump attached to a sub-slab monitoring probe with a tube to an exhaust point outside the building). All of these aspects require testing to assess their importance and develop a cost-effective monitoring protocol, which could depend significantly on the building design, so field-testing in several building would likely be appropriate. This research could be conducted at any building where indoor air concentrations attributable to VI are higher than background levels. This has a high probability of providing good resolution of subsurface versus background sources. A test building with existing characterization data would be the ideal location to conduct applied research into the building flux and pressure differential measurement methods.

5.3.5 Compound-Specific Stable Isotope Analysis (CSSIA)

Some analytical techniques may be able to uniquely resolve the relative contribution of indoor and subsurface sources during VI investigations. Compound-Specific Stable Isotope Analysis (CSSIA) is used as a forensic tool in several environmental applications and has been demonstrated to provide a level of resolution that may not be available by other methods. The theory is relatively simple: stable isotopes of carbon and hydrogen occur in various VOCs at ratios that are diagnostic and can be measured very accurately. In the subsurface, many chemicals undergo transformations that affect the isotope ratios (e.g., biodegradation preferentially degrades molecules with the light isotopes of C and H, resulting in an enrichment of the remaining chemical mass in the heavier isotopes). The increase in proportion of heavier isotopes caused by biodegradation would not be seen in sources present inside the building. If samples can be collected for both indoor air and soil gas and analyzed by CSSIA methods, then it will be possible to assess whether the stable isotope ratios are similar for both samples. If different, it may be possible to use mass balance principles to calculate the relative contributions from both subsurface and interior sources to a particular indoor air sample.

The challenge with CSSIA is that a certain mass of the compound of interest must be supplied to the detector to avoid results below the limit of detection. Indoor air concentrations of interest for VI are typically very low, so the total mass within a 6-L Summa canister (common sampling vessel) is far too low for this method of analysis. Geosyntec has developed a sampling method to address this limitation with CSSIA, however, the method requires testing to demonstrate the performance. The incremental cost of the sampling activity is negligible, so this could easily be added to any investigative program. Laboratory method development is the more significant component of this research, and Geosyntec is currently developing a proposal in collaboration with a leading university in CSSIA research, so there may be an opportunity for leveraged funding in this area.

5.3.6 Using Naturally Occurring Radon as a Tracer

In buildings where the concentration of radon is elevated above background, it may be possible to use naturally occurring radon as a tracer to help resolve VI of VOCs from background sources.

This method would require the following actions:

- Measurement of both radon and VOC concentrations in samples of sub-slab soil gas and indoor air.
- Calculating the radon attenuation factor (indoor air radon concentration divided by the sub-slab radon concentration).
- Multiplying the radon attenuation factor by the sub-slab concentrations of VOCs as an estimate of the indoor air concentrations of those VOCs attributable to VI.

This approach depends on the similarity between radon and VOCs in their distribution in the sub-surface and transport across the slab to indoor air. Since radon and VOCs have different sources, their subsurface distributions may not be similar. Furthermore, all of the same issues of spatial and temporal variability in sub-slab and indoor air sample collection apply equally to the use of radon as a tracer. The options for alternative sub-slab sampling strategies described in Section 3.1.2 may also be applicable for radon assessment. In any event, research would be needed to demonstrate whether representative samples can be collected and to demonstrate the extent to which radon and VOC distributions are similar or different to make this method feasible. The necessary data collection could be added on to a VI investigation in any area where naturally occurring radon concentrations are elevated.

6. SUMMARY AND CONCLUSIONS

This report describes the current best practice, knowledge and data gaps, and research opportunities for the three Navy-identified VI focus areas. Section 3 provides a resource to Navy site managers to standardize current assessment approaches with respect to these areas, and should enable VI to be assessed as quickly as possible with methods that are reasonably familiar to regulatory agencies and accepted by the scientific community. Nevertheless, the challenges described in Section 4 will impose uncertainties that will continue to make the assessment of VI a complicated and expensive undertaking, particularly for responsible parties with large numbers of sites each with large numbers of buildings, such as the Navy.

Table 6-1 provides a summary of the study team recommendations for future VI research opportunities from Section 5 for the Navy to consider. The significance of each topic is ranked (high, medium or low), opportunities for synergy with existing research programs is indicated, costs are ranked (high, medium or low), and a general timeline for implementation for each research area is also provided. In conclusion, the recommended areas for research are as follows:

- Intensive field data collection at field sites with the following conditions:
    - Large (slab-on-grade) buildings – to assess the utility of high purge-volume (HPV) soil gas sampling to integrate soil vapor concentrations spatially, and potentially assess conditions between and beyond access points for probe installation, including assess conditions beneath a building by withdrawing gas from locations beside the building, and HPV sub-slab sampling.
    - Positively-pressurized buildings – to develop an assessment protocol and decision framework satisfactory for regulatory approval to demonstrate which buildings are protected against VI by their existing HVAC system design and operation.
    - Shallow Water Table sites – the Navy has many of this class because their sites are often at the coast, and a few well-documented studies would help to select the tools that are most suited to assessment in this scenario.
- Quantitative passive samplers:
    - ESTCP project ER-0830 will need field sites for the demonstration phase in mid-2009, and Navy sites could potentially benefit from collaboration. Testing is needed to demonstrate capabilities and limitations and head-to-head performance of multiple alternative designs to support regulatory acceptance.
- Pressure cycling and building mass balance strategies:
    - This strategy has been shown in a very limited number of cases to provide a very clear indication of VI and resolution of background contributions, but more work is required to develop a protocol accepted by regulatory agencies. ESTCP Project ER-0707 will characterize building foundation permeability through induced depressurization.

Table 6-1. Summary of recommendations to Navy for research and development on vapor intrusion.[1]

Research Area		Recommended Research Activities	Significance	Priority	Cost	Potential Collaboration	Estimated Time
Focus Area 1: Alternative subsurface sampling methods to reduce spatial and temporal variability							
Soil Gas	Sampling Protocols	Comparison of methods for high quality data for a wide range of site conditions	High	Medium	$$		4-12 Months
Groundwater	Passive Sampling – Above and below water table	Assess hydrophobic passive samplers in wells	Medium	Medium	$		Weeks to months
Focus Area 1: Intensive field data collection ant a limited number of sites to identify const-effective screening strategies for site –specific conditions							
Large Slab-on-Grade Buildings	HPV Screening	Collect a slip-stream of sub-slab soil gas, monitor discharge with portable meters	High	High	$$		Weeks
Pressurized Buildings	Pressure Differential Measurements	Assess HVAC design and operation vs. pressure	High	High	$	ESTCP ER-0707	Weeks to months
VOCs in Groundwater Beneath Buildings	Identify susceptible homes. Assess modeling vs. indoor air passive sampling	Testing of method similar to radon monitoring, using passive samplers for low-cost screening	Medium	Medium	$$	ESTCP ER-0830	Weeks to months
Shallow Water Table	Shallow groundwater, HPV sub-slab and pressure cycling sampling	Follow several lines of evidence and compare results to identify the best approach	High	High	$$		4-12 Months
Undeveloped Land	Model indoor air, develop surrogate surfaces, assess control efficiency	Identify best method for predicting whether VI will pose a risk in future buildings	Medium	Medium	$	BRAC	4-12 Months
Natural VI Barriers	Evaluation of attenuation factors	Evaluate attenuation by low-permeability layers, high-moisture content layers, or biodegradation	High	Medium	$$		4-12 Months
Buildings with Crawl Spaces	Passive vs. active ventilation mitigation	For consideration if assessment include large numbers of buildings with crawl spaces	Dependent on number of sites		$		4-12 Months
Focus Area 2: Passive diffusive sampling and analysis to obtain long-term average concentrations with simpler protocols and lower analytical cost							
Quantitative Passive Samplers	Demonstration of quantitative passive samplers	Identify building(s) with demonstrated VI and with existing data for field phase testing	High	High	$	ESTCP ER-0830	12-24 Months
Focus Area 3: Techniques to resolve relative contribution of indoor vapor sources							
Indoor Air Monitoring	Passive Samplers	Demonstration and validation in field testing	High	High	$	ESTCP-0830	12-24 Months
	Canisters – Extended Flow Control	Testing of two options to extend sampling	Medium	Low	$		Weeks to months
	Real-Time Portable GC Instruments	Monitoring comparison to conventional methods	High		$	ESTCP ER-0702	>1 year.
Sub-Slab Monitoring	HPV Sampling	Compare to conventional and composite samples	High	Medium	$$		Weeks
	Passive Samplers	Demonstration and validation in field testing	Medium	Medium	$	ESTCP ER-0830	12-24 Months
	Composite Summa Can Samples	Compare to conventional and passive samplers.	Medium	Medium	$		Weeks
Pressure Cycling and Mass Balance	Sampling under building-to-sub slab pressure differential,	Identify building with VI condition that can be resolved against background	High	High	$$	ESTCP ER-0707	Weeks to months
Stable Isotopic Ratios	C and H stable isotopes ratios in subsurface and indoor VOCs	Develop method for collecting sufficient mass from low concentration indoor air samples	Medium	Medium	$	Canadian Research Funding	4-12 Months
Radon as a Tracer	Comparison between subsurface distribution of VOCs and radon	Limited in application to areas where radon is naturally-occurring at levels above background	Medium	Medium	$		Weeks to months

[1] Cost: $ = <$50,000, $$ = $50,000 to $150,000

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APPENDIX A

SUGGESTED QUALITY CONTROL PROCEDURES FOR SOIL GAS SAMPLING

Soil gas sampling for VI assessment is more challenging than other soil gas sampling uses because the target concentrations are lower. To avoid some of the common contributions to data bias and variability, several quality control procedures should be considered:

1. Equipment blank sample: assemble a soil gas probe, and collect a sample through it before installing it in the ground. Repeat for representative number, depending on amount of probe construction material used.
2. Coring: collect soil core for visual inspection of texture and moisture at a minimum, also consider laboratory index tests for bulk density, grain density (collectively used to determine porosity), moisture content, and grain size distribution in select samples to provide information to support conceptual and mathematical models of the transport pathway.
3. Probe installation: probes can be temporary driven probes if the geology is well known and highly permeable. If the geology is unknown, it is usually better to core the soil, and install a probe in the corehole with a sand pack and annular seal. The preferred seal is a slurry of bentonite and water; however, alternating lifts of granular bentonite and water may be effective. Installing a probe with a good annular seal is minimal additional effort compared to a temporary driven probe, but provides a much higher protection against leaks, and will provide more representative samples, regardless of the gas permeability of the soil. Probes should be handled with clean hands, and since this is often challenging to maintain during drilling and related field work, it is often easier to put on a new pair of nitrile gloves before constructing and installing a probe. Adding some dry granular bentonite above sand pack helps prevent slurry from invading sand-pack, then either slurry seal or alternating lifts of dry granular bentonite and water.
4. If multi-level probes are installed in a single borehole, exert a vacuum on each probe in turn, and monitor vacuum in adjacent probes to assess integrity of seals (leaks are usually obvious).
5. Probe “Development”: purge air entrained during installation as soon as practicable after seals have been placed. If flow is sufficient to achieve this with modest vacuum, sampling can proceed thereafter. Otherwise, it may be good to leave overnight to re-equilibrate. If flow is too low to remove at least one pore volume of the sand-pack and tubing, allow several days or more for equilibration before sampling.
6. Measure flow and vacuum during purging to assess permeability and verify whether special procedures may be required for low-flow probes.
7. Purging: purge standing volume in the probe and sand-pack prior to sample collection, monitor Total VOCs with a photoionization detector (PID) or flame ionization detector (FID), as well as O_2, CO_2, and CH_4 with a landfill gas meter, and review the field screening data before collecting a sample for laboratory analysis. Parameters should be relatively stable and not trending up or down or erratic.
8. Sample collection: conduct vacuum leak check prior to sample collection, adjust fittings as necessary. Assemble all sampling fittings, then apply pressure or vacuum to the lines. Close valves at each end and monitor the pressure or vacuum over time for at least a minute. If the

applied pressure or vacuum does not hold, there is a leak and it should be fixed and re-tested before proceeding with sampling.

9. In low-permeability soils, sub-slab samples, or very shallow soil gas samples (<5 ft deep), the potential for leaks is higher, so a tracer is also a good idea. Place a shroud over the Summa can, flow controller and top of probe, add ≥ 10% He, purge through T-fitting to Tedlar bag in lung box to record field parameters plus He, and if He is <10% of the concentration in the shroud, the sample may be used for laboratory analysis.

APPENDIX B
TOOLBOX SUMMARY TABLES FROM ITRC GUIDANCE

Table title numbers in this appendix reflect the original numbers used in the ITRC Guidance document.

Table D-4. Matrix of various quantitative options to evaluate vapor intrusion

Measurement approach	Source at depth (> 5 feet) directly under building				Shallow source (<5 feet) under building				Source in vadose zone adjacent to building				Special conditions			
	Undeveloped site	Residential with basement or slab-on-grade floor	Residential with dirt floor or crawl space	Commercial/ industrial	Undeveloped site	Residential with basement or slab-on-grade floor	Residential with crawl space or dirt floor	Commercial/ industrial	Undeveloped site	Residential with basement or slab-on-grade floor	Residential with crawl space or dirt floor	Commercial/ industrial	Petroleum hydrocarbons	Vapor migration routes	Wet basement	Very-low-permeability soils
Shallow groundwater (near water table)	P	P	P	P	P	O	O	O	O	O	O	O	S	O	P	O
Deep (> 5 feet) soil gas	P	P	P	P	N	N	N	N	P	P	P	P	P	O	N	N
Shallow (5 feet) soil gas	P	P	P	P	P	P	P	P	P	P	P	P	P	P	N	N
Subslab soil gas	N	P	N	P	N	P	N	P	N	S	N	S	P	O	N	P
Vertical profile of soil gas	O	O	O	O	N	N	N	N	O	O	O	O	P	O	N	N
Indoor air	N	S	S	S	N	S	S	S	N	S	S	S	S	P	S	S
Ambient (outdoor) air	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Passive soil gas sampling	S	S	S	S	S	S	S	S	S	S	S	S	S	S	N	S
Emission flux chambers	O	N	S	O	O	N	S	O	O	N	S	O	O	N	N	O
Tracer testing for alpha factor	N	O	O	O	N	O	O	O	N	N	N	S	O	O	N	O
Tracer testing for ventilation rate	N	O	O	S	N	O	O	S	N	O	O	O	O	O	O	O
Pressure differential monitoring	N	O	O	O	N	O	O	O	N	O	O	O	O	O	N	O
Real-time analyzers	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O
Meteorological data	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O	O

This rating indicates that each tool can be used for the category lower in the hierarchy.

P = primary investigative tool, can potentially be used as a principal tool for assessing VI.

S = secondary investigative tool, can be used to develop CSM and/or as a line of evidence in support of another line of evidence.

O = Optional investigative tool, may be useful to further define VI pathway or as means to focus primary investigative tools.

N = not usually appropriate as an investigative tool for vapor intrusion assessment.

Table D-5. Pros and cons of various investigative strategies

Measurement	Relative Advantages	Relative Disadvantages	Comments
Deep soil gas (>5 feet below slab)	• Existing data may already be available for some sites • Less chance of short-circuiting by atmospheric air • Temporal variations in concentration minimal	• Data may not be representative of soil gas concentrations at shallower depths due to intervening soil layers • Does not account for aerobic biodegradation in shallower soil layers	When combined with other data, deep soil gas data can provide evidence of attenuation as a function of vertical transport distance. However, deep soil gas sampling is conservative for screening purposes.
Shallow soil gas (<5 feet below slab or basement floor)	• Standard equipment and approaches have been developed • Media most likely to intrude into receptors • Data can be collected outside the building	• Rate of vapor transport to the building must be estimated • May not reflect subslab concentrations • Greater temporal variability than deeper soil gas data	Building zone of influence must be taken into consideration in sampling design. Shallow soil gas sampling may not be conservative for screening purposes.
Subslab soil gas	• Provides more representative subsurface data for sites with surface releases (e.g., spills and leaks) • Gives concentrations immediately below building and receptors	• May contain contaminants from interior sources • Highly intrusive; requires building access and drilling through slab/floor • Rate of vapor transport into the building must be estimated • Conservative screening levels	Preferred approach of many regulatory agencies. Concurrent determination of slab-specific attenuation factor may be useful to interpret data.
Emission flux	• Measure actual contaminant emissions from subsurface • Takes into account all subsurface processes such as biodegradation, advection, sorption • Eliminates interpretation using attenuation factor or model	• Equipment and experienced staff may be difficult to find • Selection of representative sampling locations may be difficult • Biased low results if emission "hot spots" are not sampled • Not considered by most regulatory agencies	This approach is best suited for evaluating future-use scenarios on undeveloped land, houses with dirt floor basements or crawl spaces, and to confirm bioattenuation in shallow vadose zone (<3 feet bgs).
Soil gas attenuation (α) factors	• Quick and very easy	• Attenuation factors used for this purpose tend to be very conservative (e.g., <50^{th} percentile) • Empirical attenuation factors may be biased high due to sources other than vapor intrusion • No agreed-upon attenuation factors for many regulatory jurisdictions	Attenuation factors may be based on empirical measurements of concentration ratios at other sites or on assumed Q_{soil} and building ventilation flow rates.

Measurement	Relative Advantages	Relative Disadvantages	Comments
Slab-specific attenuation factor determination (from subsurface tracer)	• Naturally occurring compounds (e.g., Rn-222) can be used in some cases • Provides a direct measure of attenuation across a slab • Typical values often >10 times lower than default values	• Usually requires separate analytical method than that used for target compounds • If radon is used, investigator may find indoor concentrations exceeding health-risk levels • Radon not present everywhere at levels distinguishable from background	Method assumes that the tracer and subsurface contaminants move into the building at the same rate.
Indoor air	• Relatively simple to collect samples • Direct measurement of contaminant concentrations in buildings • May be more convincing to occupants	• Background sources complicate data interpretation • Requires access to indoor space • For residential sites, a building survey prior to sampling is often necessary • Very low reporting limits may be required for some compounds (e.g., TCE) • One-time sampling results may not be representative of long-term average concentrations • Poor sample control	Time-integrated samples are typically collected (e.g., 24-hour samples for residential sites and 8-hour samples for industrial sites).
Crawl-space air	• Simple to measure	• Background sources from overlying structure may complicate data interpretation	Most guidance uses an attenuation factor of 1.0 between crawl space and indoor air.
Pressure differential	• Relatively simple to measure • Can provide evidence of direction of vapor transport (in or out)	• Requires subslab port or other subsurface sampling point • Temporal variations complicate interpretation and often requires multiple sampling events	Detection levels down to 1 pascal can be obtained using inexpensive 0–0.25 inch H_2O magnahelic gauge.
Building ventilation rate	• Very simple to measure (standard ASTM method exists) • For many commercial buildings, rate is already known from design specifications • Value can be >10 times default parameters allowed in models	• For residences, seasonal variations may be large	Fewer sampling locations are needed if additional mixing of air within building is provided. Most commonly used for commercial receptors.

Measurement	Relative Advantages	Relative Disadvantages	Comments
Forensics	• Can differentiate sources of contaminants	• Typically requires a significant amount of data • Methods still being developed • Background sources can complicate interpretation	Forensic approaches are not likely to be used until later rounds of an investigation.
Continuous analyzers	• Provide large amounts of data • Can help sort out temporal variations and background scatter	• Limited use	Larger data sets allow correlation to other variables such as pressure differentials, wind speed, and HVAC systems.
Soil physical properties	• Easy to measure • Enable site-specific values to be used in predictive models • Values can be >10 times default parameters in models	• Data collected near a building may not be representative of zone beneath building • Difficult to get rig near most residential buildings (e.g., lawns, landscaping, trees)	Most sensitive soil physical properties to measure are percentage of water content and permeability.
Groundwater data	• Monitoring wells already exist for many sites (previous data) • Acceptable to most agencies • Familiar media to most investigators • Temporal effects minimal	• Look-up values, attenuation factors, or models tend to be extremely conservative, so VI risk is often overestimated • Existing data may be from a well that is not optimally screened for upper water table	This approach often used as an initial screen.
J&E model with groundwater or soil gas data	• Quick and easy • Model can account for various site-specific factors • Potential future scenarios can be evaluated	• Default input values to model tend to be very conservative • Pressure differential always assumed to be present (i.e., Q_{soil} assumed to be positive value) • Model does not account for biodegradation of BTEX or other compounds • Model is designed to evaluate residential scenarios and has some added limitations if used for other scenarios • Regulators may not accept results if depth to groundwater is <5 feet	The accuracy of the model output is best if the pollutant transport distance is at a minimum (i.e., shallow soil gas is better than deep soil gas) and no partitioning calculations are needed (soil gas data are better than groundwater data).

APPENDIX C
LABORATORY BEST PRACTICES

Prior to collection of any samples, it is important to establish communications with the analytical laboratory and human health risk assessor, if necessary, to ensure that proper sampling and analytical methods are selected to meet the data quality objectives of the project. The compounds of concern and the required analytical sensitivity (i.e., target concentrations or screening levels) should be determined, and these choices largely drive the selection of sample collection media and methodology.

A detailed overview of sampling and analytical methods can be found in the ITRC VI Guidance Appendix D (2007). In general, compounds with vapor pressures greater than 0.1 Torr[3] at 25 °C are amenable to whole air sampling and analysis methods such as USEPA Compendium TO-15. Gas-tight syringes, Tedlar bags, and passivated canisters are commonly used to collect soil gas samples. The best approach for a given site often will depend on whether on-site data are being generated for screening purposes or off-site analytical data are being generated for input to a human health risk assessment. While convenient and inexpensive, disposable syringes are not inert and losses of VOCs have been observed for sample storage times of less than 5 minutes (Hayes, 2008). Tedlar bags are best used for applications in which parts per million by volume (ppmv) levels are expected and when short storage times of less than 72 hours are implemented. Summa polished canisters or other specially prepared canisters provide both low VOC background levels and acceptable inertness for a wide range of VOCs over storage times of 30 days. When collecting indoor and outdoor air requiring sub-ppbv target screening levels, canisters are the most appropriate container for whole air sample collection. Certifying each sampling train as clean below the analytical reporting limit prior to sample collection minimizes the presence of artifacts, which could lead to erroneous assessment of the health risk and vapor intrusion pathway.

USEPA Method TO-15 is the industry standard for indoor and outdoor air samples collected in canisters; however, several modified SW-846 methods are also options for soil gas analysis. SW-846 Method 8260 and Method 8021 were originally written for soil and water matrices and have since been modified by some laboratories to address soil vapor. Typically, calibration is performed using liquid-phase standards in the same manner as water and soil analysis. Vapor introduction systems and performance requirements are not described in the SW-846 methodology, so analyzing a National Institute of Standards and Technology (NIST)-traceable vapor phase standard is highly recommended to validate laboratory procedures for soil gas. The SW-846 methods may not meet the required soil gas screening levels due to their higher reporting limits relative to TO-15. Additionally, Method 8021 relies on less selective detectors than the mass spectrometer detector used for methods 8260 and TO-15. As a result, potential misidentification of compounds and/or quantification errors can occur when using 8021, especially when analyzing a complex sample matrix.

Compounds with vapor pressures lower than 0.1 Torr are generally referred to as semi-volatile organic compounds (SVOCs). If these analytes are compounds of concern, sorbent-based methods such as USEPA Compendium TO-13A and TO-17 may be required to provide acceptable compound

[3] 1 Torr = 1 mm Hg = 133 Pa

recovery. Method TO-13A uses XAD resin to capture compounds heavier than naphthalene. TO-17 uses a wide variety of carbon- or polymer-based adsorbents and can collect compounds from C_3 up to

C_{30} depending on the sorbent material. Both TO-13A and TO-17 are active sampling methods requiring a sample pump to pull a known volume through the sorbent, and the reporting limit is calculated by dividing the analytical reporting limit (micrograms) by the volume collected (cubic meters). The sampling flow rate, duration, and expected sample matrix should be discussed with the laboratory to ensure screening levels are met and a valid sample is collected. The TO-17 method utilizes thermal desorption to release the adsorbed compounds and TO-13A relies on chemical extraction. Because the analytical sensitivity of the TO-17 thermal desorption technique is several orders of magnitude higher than TO-13A, TO-17 is often preferable when sample volume is limited.

In addition to the selection of collection media and analytical method, the selection of the leak check compound can affect data quality. Some commonly used leak check compounds, such as isopropyl alcohol, are target TO-15 compounds and can interfere with the analysis. When applying essentially pure product on sampling equipment, even an inconsequential leak in the sampling train can introduce ppmv levels that may necessitate an analytical dilution. This dilution can elevate reporting limits such that screening levels are not met. Leak compounds such as helium present no analytical interference for any of the VOC or SVOC methods.

Reference for Appendix C

H. C. Hayes. 2008. “Evaluation of Disposable Syringes for the Collection of Soil Gas, Air Toxics.” White Paper, January.

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