

Innovative Vapor Intrusion Site Characterization Methods

Introduction

Vapor intrusion (VI) is the migration of volatile chemicals from soil and/or groundwater into the indoor air of overlying buildings. Volatile organic compounds (VOCs) have been released into the subsurface from historic waste disposal practices at sources such as leaking underground storage tanks, dry cleaners, gasoline stations, or industrial processes. VOCs typically associated with VI are chlorinated solvents including carbon tetrachloride, tetrachloroethene (PCE), trichloroethene (TCE) and 1,1-dichloroethylene (1,1-DCE), and petroleum hydrocarbon compounds such as benzene and toluene. Inhalation exposure to such VOCs can cause adverse health effects if subsurface VOCs present in the subsurface migrate into indoor air at concentrations above acceptable risk levels.

This fact sheet was prepared for Remedial Project Managers (RPMs), practitioners (contractors), and other stakeholders to provide an overview of several emerging and innovative methods for the characterization of indoor air at potential VI sites. These methods include passive sampling, use of a portable gas chromatography/mass spectrometry (GC/MS) instrument, use of building pressure control techniques, hydrocarbon fingerprinting, compound specific isotope analysis (CSIA), and radon sampling. These innovative techniques allow for a better understanding of VI given the natural, inherent temporal variability of the phenomenon and can help to improve the understanding of potential background sources of VOCs. Two case studies where innovative VI site characterization techniques were applied at Navy sites are also discussed.

Conventional methods for identifying potential VI issues rely primarily upon the comparison of conservative VI risk-based screening criteria to groundwater data collected through conventional field sampling investigations. Typically, a preliminary conceptual site model is developed through the identification of potential vapor sources in soil/groundwater, preliminary exposure pathway(s), potential receptor(s), and building characteristics. Subsurface-to-indoor air attenuation factors or a VI model can be applied to VOC concentrations in groundwater to predict indoor air concentrations, which

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can be compared to generic risk-based screening values. Or, conversely, an acceptable groundwater concentration can be back-calculated from an acceptable indoor air concentration through application of attenuation factors or a VI model for comparison to site groundwater concentrations. If screening results suggest elevated levels, a site investigation will be warranted involving direct measurement of several environmental media which may include soil gas samples taken near the building, sub-slab soil gas samples (immediately beneath the building), indoor air samples, and/or outdoor air (sometimes referred to as “ambient air”) samples. However, conventional VI indoor air sampling approaches present a significant technical challenge in distinguishing between VI and potential background sources of VOCs in indoor air. This may confound the determination of whether or not VI is occurring in the building. More information on conventional VI sampling techniques can be found in the Department of Defense (DoD) [Vapor Intrusion Handbook \(2009\)](#).

Innovative Sampling Techniques for VI Site Characterization

Innovative sampling techniques for VI site characterization include passive sampling and the use of a portable GC/MS for real-time measurements. Passive sampling results can inform decision-making by obtaining longer-duration measurements that are less impacted by temporal variability. In addition, the use of real-time measurements of VOC concentrations with a portable GC/MS can help to cost-effectively optimize site characterization efforts, as well as help to identify background sources of VOCs.

Passive Sampling

Passive sampling allows the measurement of contaminant concentrations in sampling devices without active movement of air through the device. The device is capable of taking samples of gases or vapors from the atmosphere at a rate controlled by a physical process such as gaseous diffusion through a static air layer or a porous material and/or permeation through a membrane. Passive technologies rely on sampling devices being exposed to the target media at a discrete location during the sampler deployment period. When selecting a sampling technique (passive versus active), potential benefits must be carefully considered and weighed against potential limitations.

There are several advantages for the use of passive samplers for indoor air and soil gas monitoring as listed below:

- They are less expensive (from 30% to 50%).
- They can be successfully used with minimal training.
- Their deployment is less intrusive.
- Samples span longer periods of time providing long-term average concentrations (over 3 to 14 days compared to the 3- to 24-hour time span for a sampling canister).
- Allows for assessing risks over longer exposure periods, while helping to minimize the effect of temporal variability (McAlary, 2012).

Some of the limitations for the use of passive samplers for indoor air and soil gas monitoring are listed below:

- Innovative technology that must be demonstrated and approved by project stakeholders to show equivalent results versus conventional sampling.
- Uptake rates, collection and desorption efficiencies vary both by compound class, by time, and also by deployment location of the passive samplers.

The use of passive samplers for air sampling in VI investigations is being investigated under the DoD Environmental Security Technology Certification Program (ESTCP); (McAlary, 2012). The research was designed to test the applicability of passive samplers for both indoor air and soil gas monitoring. A comparative study was performed to determine if passive

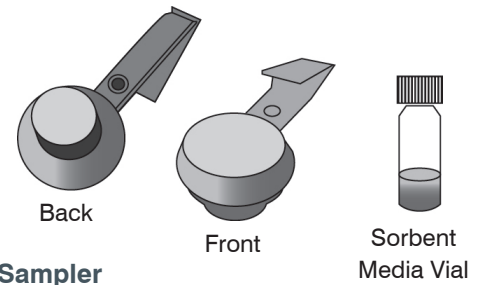


Figure 1. Passive Sampler

samplers would provide data of sufficient quality to be accepted by regulatory agencies in place of conventional sampling results. The project used four distinct types of passive diffusive samplers against two active gas sampling methods (e.g., TO-15 with sampling canisters [U.S. EPA, 1999a] and TO-17 with active sampling onto sorbent tubes [U.S. EPA, 1999b]). The four passive sampling devices tested include polydimethylsiloxane (PDMS) membrane samplers, automated thermal desorption (ATD) passive samplers, and two commercial samplers. An example schematic of a passive sampler is shown in Figure 1. The samplers were tested under both controlled laboratory conditions and field conditions at different VOC concentrations, temperatures, humidity, and sample durations. The data indicated strong positive correlation between passive sampler and conventional sampling canister results. Temporal variability for indoor air was also minimized when the sampling was integrated over time. The longer duration deployment meant that lower reporting limits could be achieved compared to those attainable using sampling canisters. The passive samplers could also be placed in locations that weren't accessible with conventional sampling such as mitigation system vent piping. More information on the final results of this project is pending publication on the ESTCP Web site (McAlary, 2012).

Portable GC/MS for Real-Time Sampling

Field portable GC/MS instruments are designed for on-site analysis of air and water samples (see Figure 2). The GC/MS unit is typically transported in a suitcase-sized shipping container and includes a user interface. It facilitates rapid on-site analysis of indoor, outdoor, or subslab air samples and can be used in a survey mode to help to distinguish between VI and

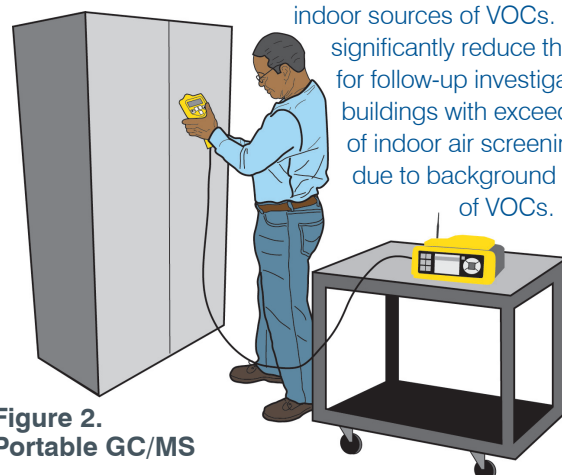


Figure 2. Portable GC/MS

indoor sources of VOCs. This can significantly reduce the need for follow-up investigations at buildings with exceedances of indoor air screening levels due to background sources of VOCs. It can be used to

select the location for sampling canisters or it has the potential to replace the traditional sampling canister collection and off-site TO-15 analysis, thereby reducing costs by 50% or more (McHugh, 2012a). These units can accurately measure VOCs present in air samples at concentrations as low as $1 \mu\text{g}/\text{m}^3$ when operated in the quantitative GC/MS mode (McHugh, 2012a).

A portable GC/MS can not only characterize the potential VI impacts on indoor air, it can also aid in the identification of background sources. A portable GC/MS was utilized at Hill Air Force Base (AFB) to identify and remove indoor sources of PCE that confounded the evaluation of VI. The indoor sources included a waste container and a floor drain. The concentration of PCE was lowered once these indoor sources were sealed (NAVFAC RITS, 2011). Further investigation of the use of a portable GC/MS for VI assessment is ongoing under DoD's ESTCP (McHugh, 2012a).

Background sources can include consumer products such as adhesives, degreasers, paints, and solvents. If such sources are identified, a chamber test may be performed to measure the emission rates of the VOCs from the products. VOC emission rates are subsequently scaled to account for the volume and air exchange rate of the indoor space in order to approximate if the product is the primary source of the VOC (or if other sources, such as VI, may also contribute to observed indoor VOC concentrations). More information on this technique can be found in McHugh et al. (2011b).

Emerging Techniques for Distinguishing Background VI Sources

Emerging techniques that involve distinguishing background VI sources include the use of building pressure control, hydrocarbon fingerprinting, CSIA, and radon sampling as discussed below.

Building Pressure Control

Temporal variability and varied indoor sources of VOCs can complicate the evaluation of VI. An investigation utilizing building pressure control can provide an improved understanding of the potential for VI to occur (see Figure 3). Building pressure control involves inducing a negative and then a positive pressure on a building. Induced negative building pressure enhances the potential impact of VI by ensuring that building pressure conditions favor the occurrence of VI. Similarly, induced positive building pressure prevents or minimizes the impact of VI by suppressing the transport of soil gas into the building. The pressure control method can also be used to identify buildings where foundation permeability does not support VI. Evaluation of the changes in mass discharges under induced positive and negative pressure may help to determine whether or not VI is the predominant source of VOCs to indoor air. It can also

help to evaluate if background sources (indoor or outdoor) are substantial contributors to the observed indoor concentrations (MacGregor et al., 2011; McHugh et al., 2012d).

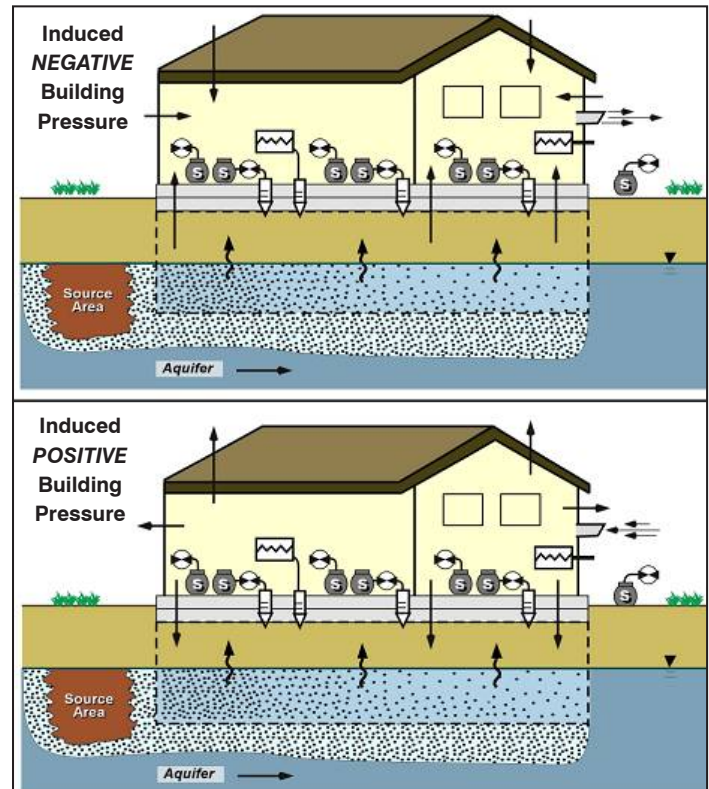


Figure 3. Building Pressure Control for VI Assessment
(Courtesy of DoD ESTCP)

This innovative VI site characterization method was tested under the U.S. Environmental Protection Agency (U.S. EPA) Environmental Technology Verification (ETV) Program as discussed in the case study below (MacGregor et al., 2011). This methodology was further refined under DoD ESTCP by validating site-specific screening criteria based on aquifer characteristics (e.g., confined versus unconfined), building characteristics, building foundation parameters, and other relevant site characteristics (McHugh et al., 2011a). Two methods validated were:

- A Tier 2 screening procedure from VOCs in groundwater at sites with fine-grained soils at the top of the water table; and
- A Tier 3 investigation program using building pressure control for application at sites requiring building-specific investigations.

The Tier 2 screening procedure was demonstrated at seven sites and the Tier 3 investigation procedures were demonstrated at six sites (McHugh et al., 2011a). Tier 3 involved the collection of indoor air samples under controlled negative and positive pressure building conditions.

The results from Tier 2 demonstrated higher attenuation of VOCs from groundwater to deep soil gas at sites with fine-grained soil at the water table. Based on the results from the demonstrations, the groundwater screening concentrations at fine grained soil (soil permeability of less than 1×10^{-9} cm²) sites was recommended to be increased by 100 times over the default Tier 1 screening values.

The results from the Tier 3 procedures demonstrated that a building-specific investigation program utilizing controlled building pressure conditions provides an understanding of VI processes in the building. The results confirmed that the indoor air concentration of VOCs originating from aboveground sources did not show much difference between the negative and positive pressure conditions (McHugh et al., 2011a). Visit the ESTCP Web site for more information on the final results of this project (McHugh, 2012b; McHugh et al., 2012d).

Hydrocarbon Fingerprinting and Forensic Analysis

Forensic analysis can be applied to better understand soil gas chemistry and VI for petroleum compounds. Advanced forensic analysis can also be used for estimating vapor phase chemical composition from the volatilization of subsurface non-aqueous phase liquid (NAPL) contamination.

The conventional whole-air sample analysis TO-15 has a relatively limited suite of petroleum-derived hydrocarbons and gasoline-additive analytes. It does not allow for the differentiation of petroleum residues from background sources. A forensic air analysis method called "Forensic TO-15" was developed to better characterize the nature and type of hydrocarbon sources in soil gas, indoor, and ambient air. One of the primary differences between conventional TO-15 and forensic TO-15 is that the latter has a greatly expanded target analyte list including paraffin, isoparaffin, aromatic, naphthalene, and olefin (PIANO) compounds. Analysis by forensic TO-15 provides a more distinct hydrocarbon fingerprint that facilitates source identification by matching the observed patterns of VOCs in the subsurface (potentially impacted by biodegradation) to the patterns observed in indoor air. An example is shown in Figure 4 of Forensic TO-15 histograms for indoor air versus soil gas (Plantz et al., 2012). The histogram illustrates that the soil gas signature has a unique pattern from the indoor air signature, thus confirming that soil gas is not the predominant source of the hydrocarbon VOCs observed in indoor air. Conventional TO-15 analysis can be used as a preliminary screening tool and the data can be used to determine the need for detailed hydrocarbon fingerprinting. Typically, the forensic analysis can be conducted from the same canister as conventional TO-15.

Predicted equilibrium chemical fingerprints can also be compared to soil gas and indoor air VOC chemical profiles to determine if subsurface NAPL is a source of indoor air contamination (Uhler et al., 2010).

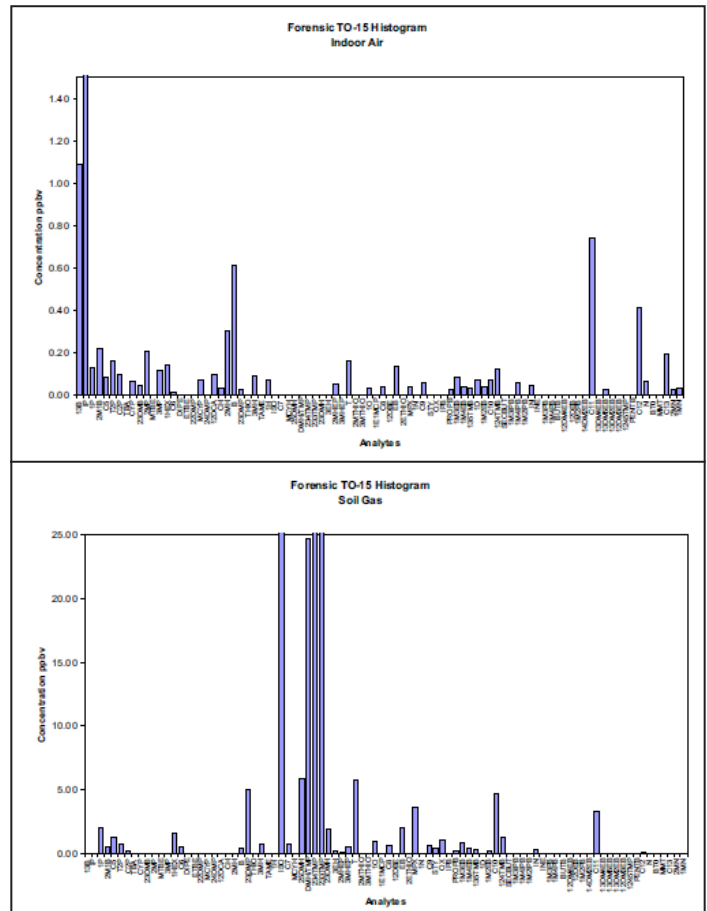


Figure 4. Example Histograms from Forensic TO-15 Analysis of Indoor Air vs. Soil Gas

(From Plantz et al., 2012; Reprinted with permission of the National Ground Water Association. Copyright 2007.)

Compound Specific Isotope Analysis (CSIA)

CSIA is a laboratory analytical method to measure the ratio of stable isotopes (e.g., ¹³C/¹²C; ³⁷Cl/³⁵Cl; D/H) in individual chemicals present in environmental samples. Table 1 provides the abundance of common isotopes in the environment. The differences in isotopic ratios between environmental samples are used to distinguish between different sources of environmental contaminants. In addition, CSIA may aid in the understanding of biodegradation and other transformation processes occurring in the environment. This method has already been used as an effective tool for distinguishing between different sources of VOCs in groundwater and has been adapted for VOCs in air.

Under DoD's ESTCP, research was conducted to evaluate and validate the use of CSIA to distinguish between VI and indoor sources of VOCs. The project validated the use of active sorbent samplers for the collection of vapor phase samples for CSIA

Table 1. Stable Isotope Abundance in the Environment

Element	Stable Isotopes	Abundance
Hydrogen	¹ H	99.985%
	² H	0.014%
Oxygen	¹⁶ O	99.750%
	¹⁷ O	0.037%
	¹⁸ O	0.204%
Carbon	¹² C	98.9%
	¹³ C	1.1%
Chlorine	³⁵ Cl	76.0%
	³⁷ Cl	24.0%
Sulfur	³² S	95.0%
	³³ S	0.8%
	³⁴ S	4.2%
	³⁶ S	0.01%
Nitrogen	¹⁴ N	99.6%
	¹⁵ N	0.4%

of VOCs containing carbon, chlorine, and hydrogen (e.g., for source attribution of PCE, TCE, and benzene).

The results from the validation study of active sorbent samplers indicated that accurate measurement of carbon, chlorine, and hydrogen isotope ratios could be performed by collection of the target VOCs onto adsorbent tubes packed with Carboxen 1016.

Carbon, chlorine, and hydrogen isotope ratios were measured in PCE, TCE or benzene found at low concentrations in indoor air and higher concentrations in soil gas samples. The study successfully developed an optimized two-dimensional GC method that provides reliable separation of the target analytes from non-target VOCs. Visit the ESTCP Web site for more information on the final results of this laboratory project (McHugh et al., 2012c).

CSIA was implemented at five residences near Hill AFB, UT to investigate VI sources for TCE and PCE. Carbon and chlorine isotope ratios for TCE and PCE in indoor air samples were measured. These values were compared to the range of isotope ratios observed in the unaltered commercial products and the ratios measured in subsurface samples to identify the source of VOCs (see Figure 5). Isotope ratios of VOCs in the subsurface often show enrichment of heavy isotope species

(in comparison to isotope ratios in unaltered product) due to biological degradation in the saturated or vadose zone. The results indicated that the subsurface and indoor sources of TCE and PCE exhibited distinct carbon and chlorine isotope ratios. CSIA results provided a definitive identification of the VOC source in two of the five residences (VI in residence No. 1 and indoor source at residence No. 3). At residences No. 2 (indoor source) and No. 4 (sewer source), results indicated a likely source. The results for residence No. 5 were inconclusive as the chlorine isotope ratios showed no clear pattern (McHugh et al., 2011c).

The utility of CSIA at a site can be evaluated by measuring the isotope ratios for target VOCs in a small number of groundwater or soil gas samples in close proximity to the building of concern. If the results from the isotope ratio evaluation fall outside of the typical range for consumer products, then a larger scale investigation can be implemented to provide another line of evidence with respect to the impact of VI at the site.

Radon Sampling

Radon is a naturally-occurring compound in soil gas. Uranium is present in all soils and the decay of uranium-238 results in the emission of intermediate Radon-222 into the soil pore space. Typical radon concentrations in soil gas range from 240 to 2,400 pCi/L. Because of the subsurface source, this concentration range is much higher than typical atmospheric radon concentrations that range from 0.2 to 0.7 pCi/L. Radon serves as a naturally-occurring tracer for evaluating VI impacts since indoor sources have little contribution to the indoor radon concentrations. It is assumed that sources of VOCs and radon are similarly located and distributed beneath the building. Indoor to sub-slab attenuation factors for radon are calculated by measuring radon concentrations in soil gas below, inside, and outside of the building. The attenuation factors represent the ratio of the indoor air concentration within a building to the vapor phase concentration in the subsurface. These factors are then used to calculate the concentration of VOCs in indoor air attributable to VI. In addition, the vertical radon concentration profile adjacent to a building can be used to identify the sample depth at which VOC concentrations are most representative below the building. This can support the collection of soil gas samples for VOC analysis adjacent to rather than below a building. There are several methods to measure indoor radon concentrations including charcoal canisters, electret ion chambers, and alpha track detectors. These methods require long-term (48 hour to 3 months) exposure durations. However, none of these methods are suitable for VI investigations because they are relatively large and cannot be placed below a building foundation and are also adversely impacted by moisture conditions below ground. Therefore, grab soil gas samples are the best method to collect samples for measuring radon concentrations in soil gas (McHugh et al., 2008).

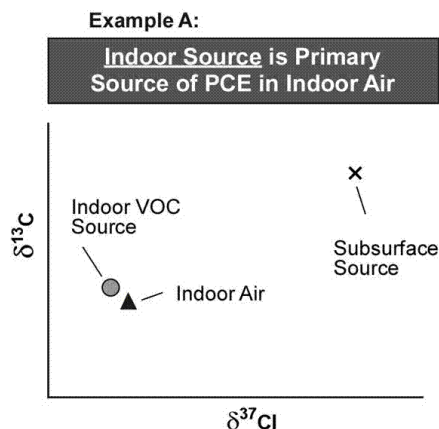


Figure 5. Use of CSIA for VI Assessment (McHugh et al., 2012c; Courtesy of DoD ESTCP)

Summary

The evaluation of VI can be complicated by various indoor sources, spatial, and temporal variability. If determined to be suitable for a given site, the innovative and emerging methods discussed here may be a cost-effective alternative for minimizing the ambiguity caused by indoor sources of VOCs, developing site-specific attenuation factors, and addressing temporal changes for a more realistic exposure scenario. Table 2 summarizes the status and use of each of these innovative technologies.

Table 2. Summary of Innovative Vapor Intrusion Site Characterization Techniques

Technology	Status	Description	When to Use
Passive Samplers	Innovative; samplers and analysis are commercially available; collection of samples and interpretation of results requires specialized expertise.	Relies on the sampling device being exposed to indoor air at a discrete location and achieving equilibrium.	To obtain a sample integrated over time to manage temporal variability.
Portable GC/MS	Innovative; instruments are commercially available; their operation and interpretation of results requires specialized expertise.	Uses gas chromatography (GC) to separate volatile constituents for subsequent analysis and identification by mass spectrometry (MS).	Most reliable method to identify indoor sources of VOCs and obtain real-time results. Can be used to select locations for sampling canisters.
Building Pressure Control	Emerging; execution is complicated; data interpretation is highly specialized.	Uses changes in mass discharges under induced positive and negative pressure to determine whether VI or background sources are present.	Useful for evaluating diffuse indoor sources (e.g., carpet). Alters building conditions to promote VI (if present) so it can be measured during sampling event.
Hydrocarbon Fingerprinting and Forensic Analysis	Emerging; sampling media and analysis commercially available; sample collection is not complicated (sampling canisters); interpretation of results requires specialized expertise.	Facilitates source identification by comparing the observed patterns of VOCs in the subsurface to the patterns observed in indoor air.	Useful to identify source(s) of petroleum hydrocarbons detected in indoor air.
CSIA	Emerging; sampling media and analysis are commercially available; collection of samples and interpretation of results requires specialized expertise.	Relies upon the differences in isotopic ratios between environmental samples to distinguish between different sources of environmental contaminants.	Applicable to sites where an isotope shift may have occurred due to VOC biodegradation in groundwater.
Radon Sampling	Emerging; sampling media and analysis are commercially available; collection of samples and interpretation of results requires specialized expertise.	Radon serves as a naturally-occurring tracer for evaluating VI impacts since indoor sources have little contribution to the indoor radon concentrations.	Useful at sites with only one or two primary chemicals of concern for VI. Ratio analysis can be used as a line of evidence for VI potential.

Case Studies

Building Pressure Control at Hill AFB, Utah and Moffett Field, California

These case studies describe the use of the building pressure control technique at two buildings for the assessment of VI. The goal of the study was to obtain a better understanding of the VI process in buildings. The project was performed jointly under the DoD ESTCP and the U.S. EPA ETV Program; the results are available in two separate peer-reviewed publications (McHugh et al., 2012b; MacGregor et al., 2011).

The VI investigation was performed at Building 107 at NAS Moffett Field near Palo Alto, CA and the ASU house near Hill AFB in Layton, UT (see Figure 6), which were both impacted by subsurface sources of chlorinated solvents. The buildings were maintained for 24 hours at each of the three pressure conditions (e.g., baseline, negative pressure, and positive pressure). A tracer gas (SF₆) was released at each building over the entire duration of the testing to measure building ventilation rates. Each building atmosphere was allowed to come to equilibrium during the first 12 hours at each pressure condition. The next 8 to 12 hours was used to collect ambient air, indoor air, and sub-slab gas samples to characterize VOCs, SF₆, and radon in the building.



Figure 6. NAS Moffett Field and ASU Buildings for Pressure Control Testing
(From MacGregor et al., 2011;
Courtesy of US Navy and US Air Force)

Building pressure control was achieved under both negative and positive pressure conditions at each of the buildings. Outcomes of the study also included the qualitative demonstration that radon VI was enhanced under induced negative pressure and reduced under induced positive pressure. Other important qualitative observations included the following: compounds with expected subsurface sources (i.e., radon, TCE, 1,1-DCE, and PCE) had indoor air concentrations greater than ambient air in both of the buildings under induced negative pressure. Under induced positive pressure, indoor air concentrations in both buildings were similar to ambient air concentrations for the compounds with expected subsurface sources. Furthermore, these compounds with expected subsurface sources had patterns in their indoor air concentrations and mass discharges similar to radon, indicating that these VOCs are likely present in indoor air due to VI. Compounds with expected ambient sources (i.e., benzene and toluene) had similar indoor air concentrations to ambient air for all pressure conditions and had different concentration and mass discharge patterns compared to radon, suggesting that VI is likely not a concern for these compounds.

While the qualitative study outcomes demonstrated the utility of the pressure control technique for overcoming issues with temporal variability and background sources on assessing VI impact, the quantitative study outcomes were less definitive, due in part to small sample sizes and the natural variability inherent in environmental sampling of VOCs at trace concentrations. More information on the study results can be found in MacGregor et al. (2011) and McHugh et al. (2012).

Radon Tracer Testing at Dry Cleaner Site

An innovative tracer technique was conducted as part of a VI assessment for a chlorinated solvent plume at a former dry cleaner site at Marine Corps Recruit Depot (MCRD) Parris Island, SC (see Figure 7). Radon was used as a natural tracer to determine whether or not subsurface contamination was causing indoor air impacts above levels of regulatory concern. The tracer study results were instrumental in developing a building-specific attenuation factor and demonstrating that the likely source of PCE in indoor air was tied to ongoing use of the building as a storage and transfer station for dry cleaned clothes.

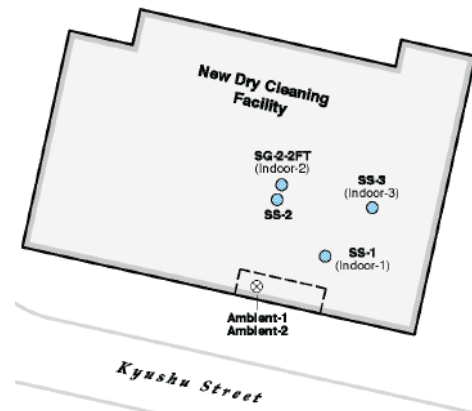


Figure 7. Dry Cleaner Site MCRD Parris Island, South Carolina
(Courtesy of US Navy)

Radon was used to compare attenuation and transfer of other volatile chemicals across building slabs. Additional data collected included sub-slab, indoor air, and ambient air samples. Radon concentrations ranged from 0.21 to 0.49 picocuries per liter (pCi/L) in indoor air. In comparison, radon concentrations below the foundation ranged from 2,073 to 2,752 pCi/L. For radon, the attenuation factors for the building ranged from 0.00011 to 0.00008. PCE concentrations in indoor air ranged from 11 to 54 $\mu\text{g}/\text{m}^3$. PCE concentrations below the foundation ranged from 74 to 240 $\mu\text{g}/\text{m}^3$. Attenuation factors based on PCE concentration data ranged from 0.06 to 0.6. This was three orders of magnitude less than the attenuation factor based on the radon data. Applying the average building-specific attenuation factor of 0.0001 based on radon data to the maximum PCE sub-slab concentration (240 $\mu\text{g}/\text{m}^3$) yielded an indoor concentration of 0.024 $\mu\text{g}/\text{m}^3$. This is below the U.S. EPA screening level for PCE in residential air of 9.4 $\mu\text{g}/\text{m}^3$, suggesting that the high indoor concentrations of PCE are not a result of VI. It is likely from indoor sources such as dry cleaned clothes, which continued to be brought into the facility as a dry cleaning transfer station.

The MCRD Team was able to work together to develop the multiple lines-of-evidence approach for the VI assessment. The team estimated building-specific attenuation factors and considered other building factors (such as the storage of treated garments in the facility and the air exchange rate in the building). The building-specific attenuation factor was instrumental in demonstrating that subsurface contamination was not impacting the indoor air quality at the dry cleaner facility. This innovative approach allowed the Navy and U.S. EPA to move forward to remedy selection without further VI evaluation required during the remedial investigation phase.

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