

Real-Time Monitoring for Vapor Intrusion Assessment

<u>Purpose</u>

This fact sheet prepared by the Department of Defense (DoD) Tri-Services Environmental Risk Assessment Workgroup (TSERAWG) relates to Sections 2, 3, and Appendix D of the DoD Vapor Intrusion Handbook, and reflects application of new technologies for vapor intrusion sampling.

Introduction

Real-time monitoring involves the collection of environmental data and reporting of sampling results in real time (i.e., within a very short timeframe on the order of seconds to minutes). Examples of vapor intrusion data that can be measured and reported in real time include: indoor air and soil vapor concentrations, building pressure differentials and ventilation rates, and tracer gas concentrations.

Potential Advantages

- Provides data that can be interpreted rapidly to accelerate and streamline the process of vapor intrusion assessment, which can save time and money and accelerate risk-reduction actions
- Provides quality assurance and quality control (QA/QC) data to verify and validate data integrity
- Provides data that can document cause-and-effect relationships to support the development of a conceptual site model (CSM) for vapor fate and transport

Potential Limitations

- Many instruments have either limited sensitivity, high cost, reliability issues or interferences
- Only provides data for a limited period, which may or may not represent longer-term conditions
- Mainly used to support other collection methods. Not usually reliable as a stand-alone method
- Limited spatial resolution. Real-time monitoring provides data specific to a finite space (i.e., a room, basement, office). The larger the area, the more uncertainty due to spatial variability

Keys to Data Quality

- Instrument calibration and maintenance
- Knowledge and avoidance of instrument bias and drift
- Operator awareness of expected readings and instrument behavior
- QA/QC protocols, such as inter-method duplicates, blanks, duplicates, inter-instrument checks, and periodic calibration verification

Rationale for Real-Time Monitoring

Vapor intrusion is a pathway of potential human exposure to volatile organic chemicals (VOCs) below buildings. The United States Environmental Protection Agency (U.S. EPA) issued guidance in June 2015 [link to OSWER 2015] for assessment of vapor intrusion at current or potential future occupied buildings

near volatile chemicals in the subsurface. Indoor air sampling and analysis by U.S. EPA Method TO-15 [link to EPA 1999] is currently recommended in most regulatory guidance documents and provides very reliable laboratory analytical data in most cases. However, there is a lag between sampling and interpretation of results that can be several days to several weeks. Real-time monitoring may not achieve the same level of precision, accuracy, sensitivity or temporal integration, but is often valuable as a component of a program of assessment with two or more supporting lines of evidence and can be used to:

- Provide critical information to support real-time decisions such as where and when to collect the samples for fixed laboratory analysis;
- Verify data quality (e.g., monitoring the efficacy of soil gas probe purging prior to sampling, providing leak checks, etc.); and
- Measure changes in VOC vapor concentrations in response to changes in building pressure, weather conditions or other factors affecting vapor fate and transport, which can support the CSM.

Recent advances in real-time monitoring since the publication of the DoD Vapor Intrusion Handbook [link to DoD 2009] are described in this fact sheet.

Vapor Intrusion Assessment Challenges Addressed with Real-Time Monitoring

Spatial and temporal variability are two common challenges with vapor intrusion assessment. Within a given building, the entry point(s) for vapors can be few or many, are generally irregularly spaced, and may be obscured from view by floor coverings, furniture or walls. Real-time monitoring provides a method to assess the spatial distribution of vapor concentrations, which may help to rapidly and efficiently identify the location of vapor entry points.

Indoor sources of volatile chemicals commonly confound the assessment of indoor air quality data, and real-time monitoring can potentially identify sources (consumer products such as aerosol cans, containers of solvents, glues, paints, lacquers, etc.), the compounds emitted from them and the magnitude of the concentrations, which can then be used to support forensic analysis of the relative contribution of vapors from the subsurface (if any).

Real-time monitoring can be used for QA/QC purposes, for example, monitoring soil vapor using a landfill gas meter for oxygen (O_2) , carbon dioxide (CO_2) and methane (CH_4) and a photoionization detector (PID) during purging to document steady readings before collecting samples for laboratory analysis. A helium shroud and portable helium meter can also be used to document the absence of leaks in the sample train.

Real-time monitoring can provide valuable information regarding the extent and rate of biodegradation of VOCs, particularly petroleum hydrocarbons. Landfill gas meter readings of O_2 , CO_2 and CH_4 are useful indicators of biodegradation, because O_2 is consumed and CO_2 is produced as hydrocarbons degrade aerobically and CH_4 is produced when hydrocarbons degrade anaerobically. Biodegradation is often the single most important process affecting the fate of petroleum hydrocarbons, and may be sufficient to reduce concentrations to levels that pose no significant risk, so understanding the O_2 and CO_2 distribution is very important.

Tracers such as sulfur hexafluoride (SF₆) and electronic pressure transducers with data loggers are commonly used to provide real-time monitoring of building ventilation systems, including the building

pressure and air exchange rate, both of which have an important influence on vapor intrusion. A separate fact sheet is available on the topic of tracer testing [link to TSERAWG 2017].

Description of Real-Time Tools

Indoor Air Quality Monitoring

Indoor air quality monitoring for vapor intrusion assessments requires instruments that are highly sensitive (able to detect very low concentrations) because many of the common chemicals of concern for vapor intrusion assessments have indoor air screening levels less than $1 \mu g/m^3$. Indoor air quality data are used to assess health risks to occupants, so it is important to avoid false-positive and false-negative results through the accuracy and precision of the indoor air sample analysis. Instruments that have been demonstrated to provide acceptable sensitivity, precision and accuracy include:

- Trace Atmospheric Gas Analysis (TAGA) Unit, owned and operated by the U.S. EPA and available only to federal agencies (including the DoD). The TAGA Unit has a dual quadrupole mass spectrometer, which is connected to a very long hose through which air is pumped. The instrument can quantify concentrations for more than one compound continuously in real time at <1 part per billion by volume (ppbv).
- 2) Portable gas chromatograph/mass spectrometer (GC/MS), which is battery powered and contained within a suitcase-sized enclosure. The GC separates compounds and the MS quantifies their mass. The sensitivity is enhanced if a pre-concentrator is used, which is a sorbent trap through which air is drawn for a period of time to trap a larger mass of the target compounds. Because of the time required to pre-concentrate with the trap and separate with the GC, the GC/MS usually requires 10 to 15 minutes per measurement to achieve reporting limits lower than indoor air screening levels (IASLs), but can be run continuously in a scan mode with higher reporting limits for reconnaissance or background source surveys.
- 3) Transportable GC with electron capture detector (ECD), which can be shipped from site to site, but remains in a fixed location when operating. The ECD is not compound-specific, so the GC is needed to separate compounds, which requires a runtime of about 10 minutes or more, depending on the compounds of interest. The ECD is very sensitive to chlorinated compounds, but generally not as useful for petroleum compounds. The ECD also responds to all compounds within a defined elution time, so false-positive results can occur if non-target compounds co-elute with target compounds.

GC/photoionization detector (PID) is less expensive than the other instruments listed here; however, the PID is less sensitive than the MS or ECD detectors, so the GC/PID is not sensitive enough to provide reporting limits lower than IASLs for all compounds of interest for vapor intrusion assessments. Nevertheless, the GC/PID could be used to test areas of potentially elevated vapor concentrations (floor drains, perimeter cracks, utility penetrations, etc.), instead of the general breathing zone.

Others: Proton Transfer Reaction Mass Spectrometer, Fourier Transform Mass Spectrometer and Cavity Ring-Down Mass Spectrometer all show promise, but have yet to be demonstrated and validated for vapor intrusion assessments. An example of the real-time continuous monitoring for trichloroethene (TCE) is shown in Figure 1. The letters across the top of the chart represent a series of locations identified as the operator traversed the interior of a business within one of the buildings. The quantitation limit (QL) was about 0.3 ppbv (~1.5 μ g/m³) and the average concentration in the office area was barely above the QL. The average concentration in the warehouse area was approximately 10X

higher, and there were notably higher concentrations emanating from some toolboxes. Real-time monitoring was able to pinpoint an interior source of TCE vapors that had been confounding the conventional Summa[®] canister samples for years.

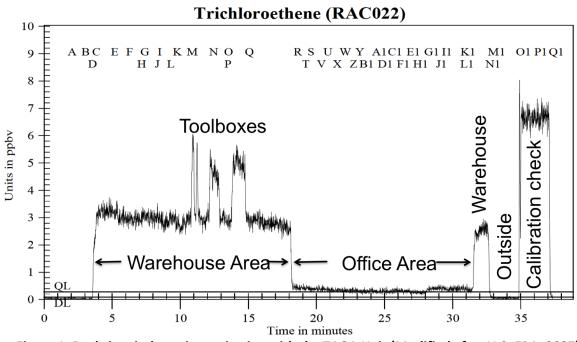


Figure 1: Real-time indoor air monitoring with the TAGA Unit (Modified after U.S. EPA, 2007)

Soil Vapor Monitoring

Soil vapor screening levels (SVSLs) for vapor intrusion are higher than IASLs because there is always a reduction in concentration between soil vapor and indoor air (usually a factor of 10 to 100,000). As a result, less sensitive instruments can be used for soil vapor monitoring, which also generally reduces the cost and complexity of the instrument and operation (e.g., the instruments listed above for indoor air monitoring can also be used for soil vapor monitoring, provided the concentrations are within the instrument range and can be assessed using a PID or FID). Monitoring of soil vapor includes the VOCs of concern, and can also include fixed gases and tracers. The most common instruments include:

- 1) Photoionization Detector (PID): ionizes all VOCs with ionization potentials lower than the power of the lamp, so the reading represents total VOCs. Each compound has a unique response factor, so calculations are needed to correlate PID readings to laboratory analyses (multiply the concentration measured in the laboratory by the response factor for each detected compound and sum the products to derive a value to be compared to the PID). Moisture can pose interference, particularly if the instrument is cold and condensation occurs on the lamp. Some PID manufacturers claim to be able to measure to ppbv levels, but accuracy and precision are less reliable below about 100 ppbv. Fortunately, this is sensitive enough to be very useful for soil vapor monitoring in vapor intrusion assessments.
- 2) Flame Ionization Detector (FID): preferred over a PID for petroleum hydrocarbons because some hydrocarbons are not ionized by a PID (notably methane). Readings made through a carbon filter can be used to discern the proportion of the total instrument response attributable to methane (methane is not adsorbed appreciably by activated carbon filters, whereas other petroleum hydrocarbons are). If the oxygen concentration is low (very

common when hydrocarbon concentrations are high), the FID flame may extinguish, and no reading can be recorded; however, this is seldom problematic because this condition almost always corresponds to VOC vapor concentrations far above screening levels.

- 3) Landfill Gas Meter: provides measurement of fixed gases O₂, CO₂ and CH₄, which can be used to verify stability after purging and before soil gas sample collection, and to assess the significance of aerobic and anaerobic degradation of hydrocarbons in the subsurface.
- Tracer gas meters (Helium, primarily): provides measurement of tracers for leak detection (e.g., helium shroud method), effective diffusion coefficient measurement (Johnson et al., 1998), aerobic degradation respirometry test, and sub-slab velocity and radius of influence for mitigation systems [ESTCP ER-201322].

For subsurface gas samples, the sample collection protocols must be designed and executed to provide representative, reliable and reproducible samples. Leak checks using a tracer gas are an example of how real-time instruments can verify sample integrity prior to sample analysis.

Building Pressure and Ventilation Monitoring

Building pressure can promote subsurface vapor entry (negative pressure) or suppress vapor entry (positive pressure). Measuring the differential pressure across the floor slab therefore provides very valuable information to understand whether a particular building is susceptible to vapor intrusion. It is also important to understand whether building pressure changes over time with daily, weekly or seasonal changes in operations of the building's heating, ventilating and air conditioning (HVAC) systems, and the influence of other factors such as wind load on the building and the "stack effect" (thermal convection). Some buildings are reasonably air tight and a small net influx or exhaust of air can create positive or negative pressure, whereas other buildings are very leaky and remain consistently neutral. Exhaust fans can create strong negative pressure inside the building, supply fans can create positive pressure, and the fans may operate on different schedules, so the building pressure may change systematically over time. Building pressure is especially important in assessing vapor intrusion in a workplace setting, where workers are present only during working hours and the HVAC system may operate in a diminished capacity when the building is vacant. Building pressure can be manipulated to induce or suppress vapor intrusion as an assessment technique, which is described further in a separate fact sheet on building pressure control [link to TSERAWG 2017].

If indoor air samples are collected under natural pressure gradients, it is valuable to collect building pressure data to help interpret the indoor air sample results. For example, if the building pressure was negative throughout the sample collection period, the indoor air concentrations may represent a reasonable maximum exposure (RME), as preferred for risk assessment (U.S. EPA, 2004), but if the pressure was positive for most of the sample period, the concentrations may not adequately represent the risks attributable to vapor intrusion. **Micromanometers with pressure transducers and data loggers** can be attached directly to a sub-slab probe to record the cross-slab pressure differential over time. Some pressure transducers allow integrated average readings over a period of time (e.g., 10 seconds) to minimize noise attributable to very short-term effects like wind gusts. Instruments with a sensitivity of 1 pascal or less are preferred and auto-zeroing is important to avoid instrument drift. Micromanometers are temperature sensitive, so the instruments should be allowed to equilibrate with room temperature before use. Figure 2 shows data from one building that generally operated under a negative pressure of at least 2 and up to 6 pascals because of exhaust fans, however when the external doors were opened, the magnitude of the vacuum rapidly decreased and returned again to the average level soon after the door was closed.

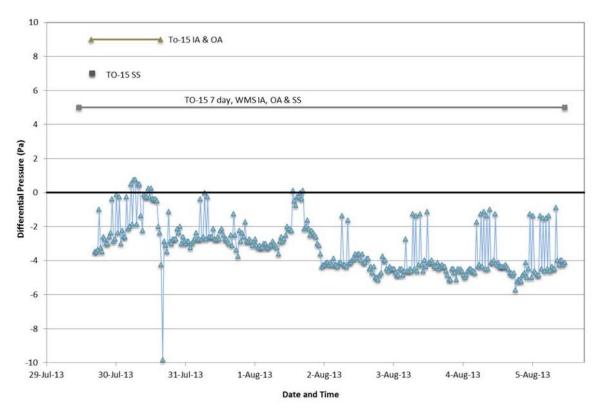


Figure 2: Cross-slab differential pressure (Courtesy of U.S. Air Force) (negative values indicated building pressure is lower than soil gas pressure)

HVAC system performance in large buildings is usually monitored using **electromagnetic flowmeters and thermal anemometers** and documented in a "Test and Balance Report", which is often available for review and provides data on the design specifications and operating performance for the building (NEBB, 2015).

Air flow between zones in a building or across the floor can also be measured using smoke pens, soap bubbles, and bubble flowmeters, all of which are specifically suited to visual observation of air flow where the flow rate or pressure gradient is very small. Smoke pens burn at a very low temperature to minimize thermal convection and the smoke flows in the direction of flow, which is usually assessed at the gaps in doors separating distinct air zones of a building, but can also be used to assess upward or downward flow through a sub-slab probe, floor joint, utility penetration, etc. Soap bubbles are used for detecting small leaks in pressurized containers or lines (tires, gas lines, etc.), and can also be used over a loose cap on a sub-slab probe. A bubble flowmeter is a glass tube through which air flows and the flow rate is calculated from the time for a soap bubble to travel between graduations on the tube. Understanding the rate and direction of gas flow between rooms or across the floor is an important component of the CSM and can provide valuable data to document the effectiveness of sub-slab venting systems. For example, if there is permeable gravel below a floor slab (a requirement in most building codes), there can be appreciable flow with minimal vacuum, so if the subfloor vacuum is too low to measure, the performance of a mitigation system could still be verified with a smoke pen. Locations for testing vapor entry to a building can be identified by depressurizing the building (adjust HVAC to achieve a negative pressure or use a door fan to exhaust air from the building) and using a thermal imaging camera to look for temperature anomalies across the floor and any below-grade walls.

Tracer Test Monitoring

Portable instruments for real-time monitoring of tracer tests include **helium meters**, SF₆ meters, CO₂ **meters**, and **GC/MS** for detection of perfluorocarbon (PFC) tracers. Tracer tests include leak checks to verify sample integrity, building ventilation tests, and performance monitoring of sub-slab venting systems. A separate fact sheet provides details on tracer testing [link to TSERAWG 2017].

Guide to Selection and Use

Selection and use of real-time monitors should consider the capabilities and limitations of each line of evidence. For example, passivated canisters and TO-15 analysis may provide highly reliable indoor air concentrations, but cross-slab differential pressure monitoring helps verify whether the building pressure during the sample interval was conducive to vapor intrusion and real-time indoor air sampling and analysis could help identify potential background sources of vapors. Combining lines of evidence helps to overcome the limitations of one with the strengths of another.

Real-time monitors are often subjected to changes in temperature, moisture, or other factors that could cause interference or drift compared to fixed laboratory analytical instruments. Therefore, it is advantageous to include some inter-method duplicate samples as a QA/QC step. For example, if a portable GC/MS or transportable GC/ECD is used for indoor air quality monitoring, a percentage of samples should be collected as duplicates for analysis by a different method (e.g., collocated and synchronous samples for analysis by U.S. EPA Methods TO-15 or TO-17) to document the accuracy of the portable/transportable instrument. The results of the inter-method comparison will not be available for real-time decisions, but will support the decisions after the fact.

Selection and use of real-time monitors also depends on the sequence of events during an investigation. There are several strategies to choose from, and the optimal strategy depends on site-specific conditions and factors. For example:

- Some assessments proceed using a "bottom-up" approach, where the first stage is a mapping of the subsurface VOC vapor distribution (via soil vapor survey, for example), then indoor air samples are collected starting above the highest subsurface concentrations and moving outward. In this case, a landfill gas meter, PID or FID and a mobile GC/MS or ECD with one in 10 samples collected via passivated canisters for TO-15 analysis may be an appropriate selection for the first stage of soil vapor mapping.
- Some assessments proceed using a "top-down" approach, where the first stage is a mapping of the indoor air VOC vapor distribution using a TAGA Unit or mobile GC/MS or ECD. In this case, verification samples by passivated canister and TO-15 analysis may be appropriate in locations where the real-time readings are within a reasonable margin of error of the screening levels or above.
- Another strategy is to impose a negative pressure on a particular building as an initial
 assessment. If the indoor air concentrations pose an unacceptable risk, it may be sensible to
 proceed to mitigation system design. If the real-time monitoring under negative pressure
 indicates no unacceptable risk, the program may proceed to a periodic verification stage (e.g.,
 seasonal assessment), which may be best accomplished with less expensive methods (such as
 long-term passive sampling [see Tri-Service passive sampling fact sheet on passive sampling]).

For all real-time instruments, calibration and maintenance are important and periodic calibration tests are highly recommended. For example, if a helium tracer test is being performed at a large building and

two or more helium meters are in use, it is valuable to screen a select number of samples using all of the instruments to document whatever differences in their readings may exist. PIDs have lamps that periodically need cleaning, so the readings may drift over time, especially in heavy use, so periodic verification of the calibration (re-reading the span gas concentration and verifying outdoor air provides a zero reading) is valuable. For instruments that have a calibration procedure, it is best to calibrate the instrument on site at the beginning of the day of use, rather than relying on a calibration performed before the instrument was rented or the night before in a different location. Always allow instruments to acclimate to ambient temperature before calibration (for example, don't take an instrument from the trunk of a hot or cold car and calibrate without allowing it to cool or warm to room temperature). When using instruments outdoors, the calibration should be verified and adjusted if needed periodically as the temperature increases and decreases through the work day.

The more sophisticated instruments require more sophisticated calibration and QA/QC procedures. Depending on the site-specific compounds of interest, the calibration may require multiple chemicals, in which case, it may be valuable to purchase a prepared calibration gas mixture of known concentrations from which serial dilutions can be performed to generate a calibration curve. Periodic instrument blanks should be run to demonstrate that there is no carryover from one analysis to the next. If sampling equipment (such as syringes) is cleaned and re-used, then equipment blank samples should be run to document the efficacy of cleaning. Internal standards are sometimes added to assess instrument drift, otherwise continuing calibration verification (periodically running a sample of the calibration gas or an appropriate dilution) is valuable.

Disclaimer

This publication is intended to be informational and does not indicate endorsement of a particular product(s) or technology by the DoD, nor should the contents be construed as reflecting the official policy or position of any of those Agencies. Mention of specific product names, vendors or source of information, trademarks, or manufacturers is for informational purposes only and does not constitute or imply an endorsement, recommendation, or favoring by the DoD.

References

- Environmental Security Technology Certification Program (ESTCP). 2013. ER-201322 Demonstration/Validation of More Cost-Effective Methods for Mitigating Radon and VOC Subsurface Vapor Intrusion to Indoor Air. <u>https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Groundwater/Emerging-Issues/ER-201322/ER-201322</u>.
- Guo, Y., C. Holton, H. Luo, P. Dahlen, K. Gorder, E. Dettenmaier, and P.C. Johnson. 2015. Identification of Alternative Vapor Intrusion Pathways Using Controlled Pressure Testing, Soil Gas Monitoring, and Screening Model Calculations, Environ. Sci. Technol. 2015, 49 (22), 13472-13482.
- Holton, C. 2015. Evaluation of Vapor Intrusion Pathway Assessment through Long-Term Monitoring Studies, Arizona State University.
- Holton, C., Y. Guo, H. Luo, P. Dahlen, K. Gorder, E. Dettenmaier, and P.C. Johnson. 2015. Long-Term Evaluation of the Controlled Pressure Method for Assessment of the Vapor Intrusion Pathway, Environ. Sci. Technol. 2015, 49, 2091–2098.

- Johnson, P.C., C.L. Bruce, R.L. Johnson, and M.W. Kemblowski. 1998. In situ measurement of effective vapor-phase porous medium diffusion coefficients. Environ. Sci. Technol., 32 (21), 3405–3409.
- National Environmental Balancing Bureau (NEBB). 2015. Procedural Standard for Testing, Adjusting and Balancing of Environmental Systems. Eighth Edition. April.
- Tri-Services Environmental Risk Assessment Workgroup. 2009. DoD Vapor Intrusion Handbook. Available at: <u>http://www.denix.osd.mil/irp/vaporintrusion/unassigned/dod-vapor-intrusion-handbook/</u>.
- Tri-Services Environmental Risk Assessment Workgroup. 2017. Fact Sheet on Passive Sampling. Available at http://www.denix.osd.mil/irp/vaporintrusion/.
- Tri-Services Environmental Risk Assessment Workgroup. 2017. Fact Sheet on Tracer Testing. Available at http://www.denix.osd.mil/irp/vaporintrusion/.
- United States Environmental Protection Agency (U.S. EPA). 1999. Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-Prepared Canisters and Analyzed By Gas Chromatography/Mass Spectrometry (GC/MS), EPA/625/R-96/010b, January.
- United States Environmental Protection Agency (U.S. EPA). 2004. Risk Assessment Guidance for Superfund Volume I: Human Health Evaluation Manual (Part E, Supplemental Guidance for Dermal Risk Assessment) EPA/540/R/99/005, July 2004.
- United States Environmental Protection Agency (U.S. EPA), 2007. Final Analytical TAGA Report, ACOE Raritan Center, Edison New Jersey, August 2007. EPA Work Assignment No. 0-269, Work Order EAC00269, Document No. 269-DFA-081307.
- United States Environmental Protection Agency (U.S. EPA). 2012. Fluctuations of Indoor Radon and VOC Concentrations Due to Seasonal Variations, EPA/600/R-12/673, September.
- United States Environmental Protection Agency (U.S. EPA). 2015. Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air, OSWER Publication 9200.2-154, June.