

Determining the Influence of Background Sources on Indoor Air Concentrations in Vapor Intrusion Assessment

Purpose

This fact sheet was prepared by the Department of Defense (DoD) Tri-Services Environmental Risk Assessment Workgroup (TSERAWG) and relates to Sections 3.3.4 and 3.5-1 and Appendix G of the DoD Vapor Intrusion Handbook (TSERAWG, 2009). These sections discuss methods for determining the influence of background sources. This fact sheet also complements and augments:

- Naval Facilities Engineering Command's (NAVFAC's) Interim Final Guidance for Environmental Background Analysis Volume IV: Vapor Intrusion Pathway (NAVFAC, 2011)
- Department of the Navy (DON) Policy on the Use of Background Chemical Levels (DON, 2004).

Introduction

Vapor intrusion (VI) assessment involves determining the contribution of volatile organic compounds (VOCs) in subsurface contamination to indoor air concentrations via vapor migration into occupied buildings. Many of the VOCs of concern for the VI pathway also have outdoor (ambient air) or indoor sources that are unrelated to the subsurface contamination. Common ambient air sources include nearby emitters (e.g., dry cleaners, air-stripper stacks, and industrial emissions) and/or vehicle exhaust. Potential indoor sources within buildings or attached garages include household degreasers, cleaning products, furniture, building materials, paint, varnish, lacquer, paint thinner, plastics, petroleum fuels, additives, and lubricants. There are thousands of consumer products that contain VOCs.

Emissions from background sources can lead to indoor air concentrations that are biased high, which can confound the interpretation of risks and result in false-positive risk determinations for VI. In some cases (e.g., gun cleaners or spot cleaners), only small amounts emitted from cleaning products can lead to exceedances of risk-based targets. It is important to account for background sources of VOCs when assessing VI because cleanup efforts should address only those risks associated with chemical concentrations that are elevated as a result of a site-related release—not background chemicals (DON, 2004). However, if unacceptable risks are shown to be associated with emissions from background sources, applicable policies require restoration program personnel to convey information regarding all identified risks to stakeholders (i.e., DON, 2008).

Indoor concentrations arising from background sources can be quite variable depending on emissions from regular periodic activities (e.g., weekly, monthly, seasonal), irregular releases from intermittent maintenance activities, or interruptions in regular work activities due to weather conditions. Additionally, typical background levels in indoor air are near or above risk-based screening levels for many common compounds of concerns (COCs) at DoD's contaminated sites, including, for example, benzene, carbon tetrachloride, chloroform, 1,4-dichlorobenzene, 1,2-dichloroethane, ethylbenzene, and tetrachloroethene (PCE) (Dawson and McAlary, 2009). The potential presence of these compounds at

concentrations above risk-based target levels arising from sources unrelated to VI needs to be considered in VI assessments.

This fact sheet describes forensic strategies for evaluating background including both field methods during a VI investigation and desktop methods after a VI investigation has been conducted. Field methods discussed include: real-time VOC monitoring, building pressure cycling tests, and stable isotope sampling and analysis. Desktop methods include comparison of compound ratios, evaluation of building attenuation factors for multiple compounds, and comparison to literature values of background indoor air concentrations.

Background Investigation Strategies

Strategies for determining the influence of background sources on indoor air differ depending on whether a background investigation can be carried out prior to or concurrent with a VI investigation, or if background influences are being re-assessed after a VI investigation has been conducted and there is concern that previously unidentified background sources are present.

Consider the following when planning a background investigation prior to or concurrent with a VI investigation:

- Focus the VI assessment on VOCs associated with a site release that are present in groundwater or soil underneath/near the building and pose a VI concern.
- Consider that VOCs associated with a site release can also be used as tracers (e.g., cis-1,2dichloroethene and 1,1-dichloroethene are common degradation products of TCE, but not common in consumer products and are potentially valuable for establishing a building-specific attenuation factor).
- Identify potential outdoor sources of VOCs of VI concern by sampling ambient air adjacent to air intakes and upwind of the building.
- Identify potential indoor sources by inspecting the building to determine what indoor sources of the VOCs of VI concern may exist. A field portable chemical detector (e.g., gas chromatograph [GC] - mass spectrometers [MS] or - electron capture detectors [ECDs]) can facilitate identification of sources. Consider building history and known uses.
- If possible, remove indoor sources before sampling or otherwise account for them in VI exposure sampling and analysis plans. It is important to recognize that not all interior sources can be removed (e.g., impregnated concrete, new carpets, furniture or other textiles, painted surfaces), although if feasible, immobile sources may be temporarily sealed.

Several desktop methods can be used to help determine the influence of background sources on indoor air after VI data have been collected. These methods can be applied to historical data that may have been collected without the benefit of a site-specific background investigation. These methods may also prove useful when background impacts are suspected, but were not definitively identified in a background investigation. Consider the following desktop methods to evaluate background:

- Evaluate all chemicals associated with a site release, not just a single risk-driver, because the relative proportions of VOCs provide important information regarding potential sources.
- Compile available sources of local or regional measurements of ambient air concentrations for comparison to indoor air results (e.g., <u>https://www.arb.ca.gov/aaqm/aaqm.htm</u>).

- Focus the desktop evaluation on paired subsurface and indoor air samples collected relatively contemporaneously.
- Consider other lines of evidence (such as geologic features or building structure characteristics) that support or eliminate VI as a contributor to indoor air concentrations to help identify buildings with impacts from background sources.

Field Methods for Determining Background Contributions

Forensic field methods for determining background conditions can be conducted any time, but are most cost-effectively conducted during a VI investigation. Real-time VOC monitoring, building pressure cycling and stable isotope analysis can help identify background sources and, potentially, quantify the contribution of background sources to indoor air. Each of these approaches is described below.

Real-Time Monitoring of VOC Concentrations

Real-time VOC monitoring is useful for determining the presence of interior sources. A Fact Sheet on Real-Time Monitoring provides details on various tools for conducting real-time monitoring [link to <u>TSERAWG 2017</u>]. Instruments capable of detecting specific VOCs at concentrations as low as regulatory screening levels in indoor air include the HAPSITE^{*} GC/MS, field GC/ECD units, and the United States Environmental Protection Agency's (U.S. EPA's) Trace Atmospheric Gas Analyzer (TAGA) unit. Other instruments such as the Frog GC/photoionization detector (PID) can detect specific compounds at concentrations higher than the screening levels, so would need to be close to a background source (e.g., in a closet with cleaning products). Other photoionization detectors (PIDs) can detect total VOCs at concentrations down to about 0.1 parts per million vapor (ppmv) and can be used to identify areas for more detailed sampling and analysis. Small sources, such as aerosol cans that may be used in maintenance shops, can be placed in sealed vessels and the headspace gas can be sampled and analyzed for VOCs. This is especially useful as a screening tool where VOCs are suspected, but are not on material safety data sheets (MSDS). Emission rates can also be estimated from the measured concentration and the time period an item is in the vessel.

Building Pressure Cycling

Building pressure cycling (BPC) is a test method that can effectively distinguish between background and VI-related contributions to indoor air [link to TSERAWG 2017b]. BPC involves monitoring indoor air concentrations under both negative and positive building pressure conditions. VI through building foundation cracks, openings, and other preferential pathways is promoted during periods when the building is under-pressurized and inhibited during periods of over-pressurization. Sampling indoor air when the building is positively pressurized provides a building-specific measure of background concentrations without the influence of VI. The difference between the concentrations of VOCs in the indoor air samples collected during over- and under-pressurized conditions measures the contribution of vapors from the subsurface. This technique is particularly useful for distinguishing contributions to indoor air from VOC-impregnated building materials (e.g., due to spills from degreasing stations present in manufacturing and maintenance shops or impregnated organic materials like wooden beams). Real-time monitoring, as described above, can assist with identification of background sources or indicate when indoor air concentrations have stabilized following a change in building depressurization level.

Stable Isotope Analysis

Stable isotope analysis can assist in differentiating between VOCs emitted from manufactured products versus subsurface (aged) sources because biodegradation often changes the ratio of stable isotopes (microbes preferentially degrade lighter isotopes as shown in Figure 1). Carbon $({}^{12}C/{}^{13}C)$ isotope analysis is the most common stable isotope analysis used to differentiate sources, but chlorine (³⁵Cl/³⁷Cl) isotope analysis also has proven useful (Beckley et al., 2013). Analyses of hydrogen $({}^{1}H/{}^{2}H)$ and oxygen $({}^{16}O/{}^{18}O)$ isotope ratios also are possible, but not all compounds of interest contain oxygen and very high concentrations and/or sample volumes are required to obtain sufficient hydrogen for detection. A limitation of the methodology is that the instrument used for isotope analysis (GC isotope ratio mass spectrometer [IRMS] with combustion chamber positioned between the GC and IRMS) needs about 50 nanogram (ng) to detect the isotopes, which may require collection of very large sample volumes (hundreds of liters). Current best practice is to use sorbent tubes (such as used for TO-17 analyses) with a strong sorbent (such as Carboxen 1016) to concentrate isotopes from a large sample volume (for example, 1,000 L drawn at a rate of approximately 50 mL/min over approximately 2,000 minutes). The tube is then analyzed by thermal desorption and inductively coupled plasma mass spectrometry (ICP/MS). Retention and recovery studies, such as described in the Fact Sheet on Passive Sampling need to be conducted to obtain reliable results [link to TSERAWG 2017c].



Figure 1: Conceptual diagram of use of stable isotope analyses to distinguish between background and subsurface sources of VOCs (Modified from Beckley et al., 2013)

Desktop Methods for Determining Background Contributions

Forensic desktop methods for determining background contributions often use data from previous investigations that may not have included the field methods described above.

The influence of background sources on indoor air can be determined in clear-cut cases where, for example, the concentration of a chemical is elevated in indoor air, but is not present or is negligibly present in sub-slab vapor. In that case, the elevated concentration of this chemical in indoor air is more likely to have arisen from indoor sources than from VI. Similarly, where VOCs are detected in outdoor air and indoor air at similar concentrations, but are not present in sub-slab vapor or are present in the sub-slab vapor at a concentration similar to indoor air, the presence of the chemical in indoor air is more likely to be due to outdoor sources (i.e., ambient air) than from VI.

In many cases, however, the influence of background sources is not so transparent. Even when a background investigation was conducted prior to or concurrent with the VI investigation, additional evaluation methods are sometimes needed to determine their influence. Desktop methods presented in this fact sheet include comparison of compound ratios, evaluation of building attenuation factors for multiple compounds, and comparison to literature values of background indoor air concentrations as described below.

Compound Ratio Comparisons

Comparison of compound ratios in subsurface vapor and indoor air is useful for identifying which of several reported compounds may be influenced by background and to what extent. In theory, most recalcitrant VOCs, such as trichloroethene (TCE) and PCE, have similar mobility in the subsurface and are expected to enter an overlying building at similar rates. Therefore, the relative concentrations among these VOCs in subsurface and indoor air samples should be similar if subsurface VI is the dominant contribution of vapors to indoor air. This may not be true of petroleum hydrocarbons, which can biodegrade in the vadose zone where oxygen is present, but will apply when comparing sub-slab and indoor air data. Comparison of compound ratios is facilitated by using the dominant VOC (e.g., VOC with the generally highest concentration) as the denominator for calculating both soil gas and indoor air compound ratios. For groundwater sources, the groundwater concentrations are corrected to account for differences in volatility by using Henry's Law Constant before calculating the compound ratios. The most reliable compound ratios are obtained from paired data sets where both subsurface and indoor concentrations are above detection limits for the compounds being compared.

Compounds with indoor air concentration ratios greater than soil gas concentration ratios (e.g., PCE/TCE in indoor air versus PCE/TCE in sub-slab soil gas) are likely to indicate a contribution from a background source, especially where the difference between the two ratios is larger than can be reasonably explained with normal data variability (e.g., differ by more than a factor of 10). Figure 2 provides examples of options for illustrating compound ratios. In addition to the examples shown, a pie-chart of compound proportions also can be an effective method for evaluating the ratios of multiple VOCs.



Figure 2: Example illustration of compound ratios (Courtesy of Geosyntec)

Compounds that can aerobically degrade in the vadose zone (most petroleum hydrocarbons, vinyl chloride, methane, and others) may not be directly comparable to recalcitrant compounds for this analysis, depending on the separation between the soil gas sample(s) and the building, and the concentration of oxygen in the subsurface. This will not normally be an issue when comparing sub-slab samples to indoor air samples (as opposed to soil gas or groundwater samples to indoor air) because the opportunity for aerobic degradation across the slab is very limited. For deeper samples or samples outside the building footprint, aerobically degradable compounds should be excluded from the compound ratio analysis.

Attenuation Factor Comparisons

Comparison of calculated compound attenuation factors offers an alternative approach to determining the influence of background sources. This method has the advantage that it can elucidate the influence of both ambient background and building-specific background conditions. Attenuation factors are calculated, by convention, as the ratio of the concentration of a given compound in indoor air to its concentrations in subsurface vapor. Where there are no background sources, empirically calculated attenuation factors provide a measure of the concentration dilution that occurs as soil vapor diffuses upward through soil to a building foundation and then mixes with the large volume of indoor air after it enters the building. For residential buildings (U.S. EPA, 2012), sub-slab to indoor air attenuation factors are typically in the range of 0.001 to 0.00001. Lower attenuation factors are likely for commercial/industrial buildings with heating, ventilation, and air conditioning (HVAC) units, or open bay doors that provide substantial ventilation, such as are common at DoD facilities.

An advantage of using attenuation factors to evaluate background sources is that the influence of lowlevel ambient air concentrations can be determined (and often is significant), especially where the source strength is low (as shown in Figure 3).



$$AF_{EMP} = AF_{VI} + \frac{C_{Ambient}}{C_{Subslab}}$$

Ambient Concentrations:

- PCE (0.3 μg/m³ dashed line)
- TCE (0.1 μ g/m³ dot-dashed line)
- 11DCE (<0.01 μg/m³- dotted line)

Note: AF_{EMP} is the empirically calculated attenuation factor. AF_{VI} is the "true" VI attenuation factor, $C_{ambient}$ is the ambient air concentration and $C_{sub-slab}$ is the sub-slab vapor concentration.

Figure 3: Sub-slab to indoor air attenuation factors as a function of source strength showing the influence of various levels of background concentrations on empirical attenuation factors (Courtesy of Geosyntec)

As with compound ratios, attenuation factors calculated from a single paired set of subsurface and indoor air samples should be similar (i.e., within the bounds of analytical variability, which for VOCs in air at low concentrations can be as much as a factor of two or three) for all non-degrading compounds (see Figure 4 (a)). Where background sources are present, however, empirical attenuation factors are biased high by the contribution of those sources to indoor air (see Figure 4 (b)). Inconsistent attenuation factors therefore suggest the presence of background sources and the greatest influence from background occurs for the compounds with the highest attenuation factor. There are few if any biases that would cause attenuation factors to be lower than the "true" value (i.e., the value represented by compounds not impacted by background sources), so the most reliable estimates of the VI attenuation factors are the lowest values.



Note: 11DCA = 1,1-dichloroethane; 11DCE = 1,1-dichloroethylene; 11DCE = 1,1-dichloroethylene; cis12DCE = cis-1,2-dichloroethylene; FREON = 1,1,2-trichloro-1,2,2-trifluoroethane; PCE = tetrachloroethylene; 111TCA = 1,1,1-trichloroethane; TCE = trichloroethylene

Note: (a) Attenuation factors are similar for all chemicals in Residence 002, indicating little or no background influence. (b) The attenuation factors for PCE and Freon are significantly higher than those for 111-TCA and TCE in Residence 005, suggesting there is background influence on PCE and Freon.

Figure 4: Empirical attenuation factors for individual chemicals in two buildings at the Endicott, NY Site (U.S. EPA, 2012)

Comparison to Literature Values

Indoor air sampling results can be compared to literature values to determine the likelihood of impacts from background sources. If measured indoor air concentrations fall within the historical range of background levels, such as for residences as reported in U.S. EPA's 2011 report on "Background Indoor Air Concentrations of Volatile Organic Compounds in North American Residences," there is a greater likelihood that the indoor air concentrations may be influenced by background levels, there is a greater likelihood that the indoor air concentrations exceed the historical range of background levels, there is a greater likelihood that a strong subsurface source exists and that indoor air concentrations are the result of VI. U.S. EPA tabulated background indoor air data for many VOCs in North American residences (U.S. EPA, 2011). In addition, typical background levels in indoor air are near or above risk-based screening levels for many COCs as shown in Figure 5 (Dawson and McAlary, 2009). Local/regional ambient air data sets are potentially pertinent for some compounds and are available in many urban areas.



Note: The risk-based concentrations shown are based on U.S. EPA Regional Screening Levels for Chemical Contaminants assuming a cancer risk range of 1E-06 (solid red circle) to 1E-04 or hazard quotient of 1 (horizontal bar).

Figure 5: Residential indoor air concentration statistics compared to risk-based concentrations (RBC) for selected VOCs (Modified from Dawson and McAlary, 2009; Based on May 2016 U.S. EPA Regional Screening Levels)

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