

APPROACHES FOR VAPOR-FORMING CHEMICAL SOURCE DETERMINATION FACT SHEET



Introduction

Understanding the source of vapor-forming chemicals (VFCs) observed in environmental samples is a key component of site characterization and, as such, is critical to the site vapor intrusion (VI) conceptual site model. VFC source determination can be supported through the use of data interpretation, including the systematic and scientific evaluation of physical, chemical, and historical information for the purpose of source identification and attribution (after Morrison 2017). It is, in a way, another form of multiple lines of evidence like those discussed in the [Multiple Lines of Evidence Fact Sheet](#). A wide variety of techniques are available for the purpose of environmental data interpretation. These approaches attempt to determine the source of detected volatiles through a detailed study of the nature of contamination with a focus on lines of evidence to potential sources. Traditional environmental site assessments focus on the nature and extent of contamination as determined by common methodologies developed to provide data for regulatory purposes. Other environmental data interpretation approaches are more sophisticated techniques that can produce chemical “fingerprints” that are source specific.

Environmental data interpretation is a developing approach that may continue to develop as technologies change. This fact sheet introduces several of these approaches for VFC source identification. Additional methods are described in the scientific literature (e.g., USDOD 2019; Ma et al. 2020).

Example Source Determination Methods

Constituent Ratios

Evaluating the ratio between concentrations of different VFCs in groundwater, soil vapor, sub-slab, and/or indoor air may help to identify potential vapor intrusion contributions or to screen out background sources. For many VFCs, the background concentration ratios are distinct from groundwater-derived VFC ratios. This characteristic allows the volatile chemical ratios from other media to be used to eliminate indoor air constituents that may be due to background sources.

Concentration Ratios of Different Chemicals

Example: If the concentration of trichloroethylene or trichloroethene (TCE) is 10 times higher than that of tetrachloroethene (PCE; also called perchloroethene and tetrachloroethylene) in groundwater, deep soil gas, and/or sub-slab soil gas but PCE has a higher concentration than TCE in indoor air, it is reasonable to conclude there is an interior or background source of PCE (e.g., dry-cleaned clothes, carpet spot remover). Check with the regulatory agency when using constituent ratios.

It is possible that, even if the ratio analysis suggests that indoor or background sources are likely responsible for some of the measured indoor air concentrations, subsurface sources may still be contributing to indoor air concentrations. If the ratios of constituents in the indoor air sample are similar to the ratios observed in the sub-slab soil vapor sample, one may conclude that the two are linked and that there is a contribution from the subsurface sources, especially if subsurface concentrations are significantly higher than indoor air concentrations.

Comparison of chemical ratios in groundwater to ratios in indoor air may also be considered. These ratios should be adjusted for different relative volatilities of the VFC using their respective Henry’s Law constants and, if significant, different rates of retardation and/or biodegradation in the vadose zone. The

comparison of soil vapor ratios to Henry's Law-adjusted groundwater ratios may be another line of evidence for assessing background contributions or vadose zone sources. It should be recognized that background sources might result in ratios that fall within the range predicted for groundwater or measured in soil vapor data. Therefore, ratios can screen out obvious background sources but will not necessarily confirm VI or eliminate the potential for background contributions. Other lines of evidence will be needed to support these conclusions.

Marker Chemicals

The presence of marker chemicals (constituents that are associated with subsurface contamination but are not typical background air sources, such as 1,1-DCE or radon) in indoor air samples is a good indication that intrusion is occurring and that the observed constituents are derived from the subsurface. The converse assumption may also be true—the absence of a marker chemical (sometimes known as a “surrogate”) in indoor air samples is a good indicator that little to no contamination is coming from the subsurface, suggesting that air contaminants observed are from background sources. This second assumption will depend on the relative abundance, volatility, diffusivity, and reporting limit of the marker chemical compared to other VFCs.

It should be noted that the use of radon as a marker chemical to identify VI depends on site-specific conditions and geology. For example, radon makes a poor indicator at sites where naturally occurring concentrations are low or nondetect, which is highly dependent on the site's geology. For a site with this condition, no detections of radon do not translate to no VI concern. Conversely, some building materials (e.g., granite countertops) can release radon, which can create false positives, as one cannot distinguish between radon coming from the subsurface and from said material. When using radon as a surrogate to evaluate VI, it is good practice to conduct multiple sampling events that show the relationship between it and VFC concentrations in indoor air. This will ensure that radon is the appropriate marker chemical for the site in question. Additionally, practitioners should always check with the overseeing regulatory agency to make sure radon is an approved surrogate for their project.

In theory, if a marker chemical is found in the subsurface and indoor air, the indoor air concentrations of other chemicals can be estimated by multiplying the subsurface concentration ratio (nonmarker/marker) by the indoor air concentration of the marker chemical. If the measured indoor air concentrations of the second chemical are greater than that predicted by this method, the additional amounts found in indoor air may be due to background contributions. See the [Tracers for Determination of Attenuation Factors and Ventilation Rates Fact Sheet](#) for more ways to use marker chemicals.

Compound-Specific Isotope Analysis

Compound-specific isotope analysis (CSIA) can be used in VI investigations to help determine the source of VFCs in indoor air (VI versus indoor VFC background source). The CSIA procedure relies on differences in the isotope signature between the subsurface VFC source and potential indoor VFC sources. Degradation of VFCs in the subsurface commonly results in an isotope fractionation effect. The Interstate Technology and Regulatory Council's (ITRC's) Environmental Molecular Diagnostics Fact Sheet discusses CSIA in further detail (ITRC 2011). In contrast, isotope signatures from indoor VFC sources tend to fall within a narrow, and different, range. Sites with evidence of degradation are, therefore, likely to have subsurface sources with isotope signatures that are distinct from potential indoor sources. The sampling protocol for a CSIA evaluation involves sampling the subsurface source (for example, groundwater or soil vapor) and indoor air, comparing the sample results, and comparing the indoor air results to the known isotope signature from indoor VFC sources (McHugh et al. 2011; Beckley et al. 2016).

Building Pressure Control Testing

Building Pressure Control (BPC) testing is detailed in [Section 7.7.2 Differential Pressure Monitoring and Building Pressure Control](#) and in the [Pressure Monitoring and Building Pressure Control Fact Sheet](#). In the BPC method, the differential pressure between indoors and outdoors (or indoors and sub-slab) is manipulated to either “induce” VI (i.e., create a vacuum in the building compared to the sub-slab) or “suppress” VI (i.e., create a positive pressure in the building compared to the sub-slab). VFC measurements in indoor air during these different conditions can be used to determine whether VFCs in indoor air originated from subsurface or indoor (background) sources (McHugh et al. 2012). Building pressure is typically controlled using fans (e.g., blower doors) or the heating, ventilation, and air conditioning system. Indoor air measurements can be collected using Summa canisters or on-site field instruments, provided that data quality objectives can be met. The use of portable instruments (e.g., portable gas chromatograph / mass spectrometer (GC/MS), gas chromatograph / electron capture detector (GC/ECD), gas chromatograph / cavity ring-down spectrometer (GC/CRDS) has the advantage of allowing screening and identification of indoor (background) sources prior to BPC testing (Beckley et al. 2014).

Continuous Multivariate Monitoring

Continuous spatial/temporal monitoring of VFC concentrations along with differential pressure over a relatively short period (i.e., three or four days) may allow practitioners to obtain important lines of evidence, including the location/identification of background sources and the location of vapor entry pathways, or to distinguish between VI and potential background sources. For more information, refer to the [Real Time Monitoring Fact Sheet](#).

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