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VAPOR INTRUSION WHITE PAPER

Steady-state considerations in vapor intrusion study design

Vapor intrusion (VI) is a potential exposure pathway at contaminated sites that involves the migration of volatile chemicals from soil or groundwater into overlying buildings. Guidance for VI investigations has been published in the U.S. by the United States Environmental Protection Agency (USEPA, 2015a; USEPA, 2015b) and by 42 States (Eklund, Beckley, and Rago, 2018). The guidance documents generally set forth procedures that have the goal of collecting data that are representative of average, long-term conditions or are biased high (i.e., biased toward worst case), with a strong preference for avoiding low bias. This is consistent with the USEPA's recent focus on indicators, tracers, and surrogates (ITS) for VI, which also has a preference for high bias. This is reasonable, given that VI investigations tend to involve relatively small data sets, and important risk management decisions regarding potential inhalation exposures may be based on only a few data points.

The evaluation of VI often involves determining concentrations of volatile organic compounds (VOCs) in shallow soil gas and/or indoor air. Sampling is generally expected to be performed under steady-state, representative conditions. In this context, steady-state means that the dependent variable is not changing with time or over time. In this paper, steady-state generally refers to vapor-phase concentrations remaining constant over a specified time frame of interest.

> **This white paper examines the basis for various approaches often followed in contemporary vapor intrusion guidance. Where possible, recommendations are made to improve the current standard practice.**

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At steady-state conditions, the system is stable. For example, VI is said to be at "steady-state" when the amount of mass entering the vapor phase in the soil due to volatilization is equal to the mass of VOCs migrating through the subsurface at any soil layer between the vapor source and the atmosphere. Steady-state conditions differ from chemical equilibrium in terms of thermodynamics; a system at steady-state may have energy inputs and be maintained at a higher Gibbs-free energy state than at equilibrium.

When a system at steady-state is perturbed, the system reacts and eventually reaches a new steady-state. While this adjustment is taking place, the system is said to be in a transient state. Testing under transient conditions typically should be avoided because the data collected may be neither representative nor reproducible. Therefore, VI guidance often includes explicit assumptions about how long it takes for steady-state conditions to be established after a system is perturbed (e.g., how long to wait to sample after installing a probe or removing an indoor air emission source). VI guidance also often includes implicit assumptions about chemical kinetics (which are assumed to be very slow) and phase partitioning (which is assumed to be essentially instantaneous). This translates to VI guidance that is prescriptive but based on flawed assumptions regarding what is required to avoid transient state, or alternatively – completely silent – in defining when sampling should be conducted to capture steady- state conditions. Either way, it is important to consider the rate of change when examining the time required for a new steady-state condition to be become established after a system is perturbed. This paper addresses a series of questions that concern timing of sampling to avoid transient conditions in VI assessments and provides recommendations for improved VI assessment practices that are based on sound science.

1) How long do you need to wait to collect an indoor air sample after removing a potential indoor air emission source?

2) How long should you wait to collect an indoor air sample after adjusting the heating, ventilation, and air conditioning (HVAC) system?

3) How long should you wait to sample after turning off the HVAC system?

4) Should the collection times for outdoor air samples be simultaneous with indoor air samples?

5) What collection times for soil vapor samples and indoor air samples are effectively concurrent?

6) What sampling duration should be employed for soil vapor samples? How long do you need to wait to sample after a new probe or well is installed?

7) How long should you wait after soil vapor extraction (SVE) system shutdown to ensure representative soil vapor data?

8) How long should you wait for biodegradation processes to be established?

DISCUSSION

Each of the questions listed above is discussed in turn below. In each case, recommended guidance is provided that is an improvement and a defensible alternative to existing published guidance.

Topic #1 – Removal or addition of potential indoor air emission sources

Indoor air concentrations may change if we add or subtract sources of VOCs. **If we remove potential indoor air emission sources, such as cans of paint or spray cans of degreaser, what time interval is necessary between the removal of the potential sources and the start of sampling?** Existing VI guidance that addresses this issue provides blanket, prescriptive waiting periods (see text box). However, the best answer is related to the building ventilation rate, which typically is expressed in air changes per hour (ACH). From this value, the flow rate of air moving through the space (e.g., cubic meters per hour [m^3/hr]) can be calculated if the volume of the space is known.

> Excerpt from existing VI guidance
>
> *USEPA: In residential settings, EPA generally recommends that potential indoor sources be removed from the structure and stored in a secure location at least 24 to 72 hours prior to the start of sampling, based on an approximate air exchange rate of 0.25 to 1.0 air changes per hour in residential settings.*

A building can be thought of as a continuously stirred tank reactor (CSTR). An example of a CSTR is a bathtub with water flowing through it but maintaining a constant water level, where the rate of water being added is equal to the rate of water being drained away. If we begin to add hot water to a draining bathtub full of cold water, it takes some time for the temperature of the water in the tub to equal the temperature of the water being added (assuming an adiabatic system). The same concept holds true if instead of changing temperature, we start adding salt water, thereby changing the concentration of anions and cations dissolved in the water in the tub. As shown in Figure 1, it takes about four change-outs of the volume of water in the tub (assuming a constant water level) for the concentration of anions and cations in the tub to be about the same as the concentrations in the salt water being added.

> Removal of potential indoor air emission or suspected “background sources” will not result in zero or ND results for all VOCs in subsequent indoor air samples.

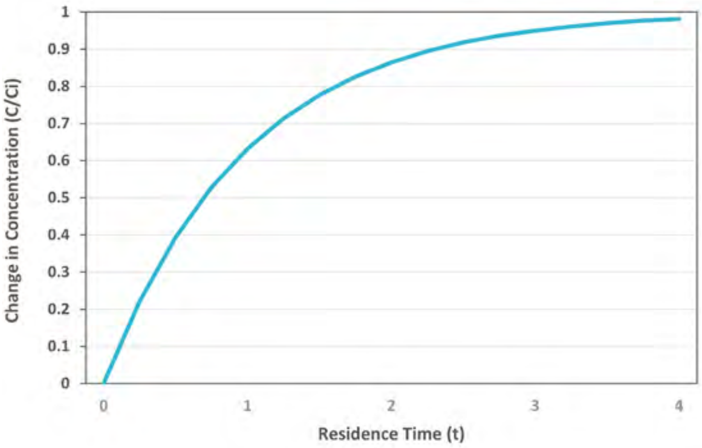

Figure 1. Increase in concentration as a function of time

The inverse happens when we remove an indoor air emission source from a building; it takes some time for the concentration in the indoor air to decay to the new steady-state concentration. The changes in concentration within a CSTR are well understood based on both theory and empirical data. The concentration changes exponentially as a function of time after the system is perturbed or changed:

Equation 1

$$C = \frac{1}{e^{t/x}}$$

where:
C = Concentration (parts per billion by volume [ppbv]);
t = time (hour [hr]); and
x = residence time for the system (hr).

In the equation below, the residence time for the system is designated by the Greek letter Tau (τ) and is dependent on the volume of the building and the rate of air flow entering the building:

Equation 2

$$\tau\ (\text{hr}) = \frac{Building\ Volume\ (m3)}{Building\ Ventilation\ Rate\ (m3/hr)}$$

The residence time is the reciprocal of the number of air changes per hour. For example, a typical single-family residential building with 0.5 ACH would have a residence time (t) of two hours, an office building with 1.0 ACH would have a residence time of one hour, and a warehouse with open bay doors with 1.5 ACH would have a residence time of 0.67 hours.

> Practitioners are cautioned that failure to remove potential indoor air emission or suspected "background sources" may result in data that are misleading, especially relative to potential indoor air impacts on sub-slab soil vapor.

As indicated by Equation 1, the relationship between concentration and time is exponential, not linear. The relationship is shown graphically in Figure 2. The y-axis is concentration at any time as a function of the starting concentration (C_i). It requires three or four residence times to approach the new steady-state value. The volume of the system is changed out three times to reach about 95 percent of the theoretical minimum concentration, and it takes four residence times to reach 98 percent.

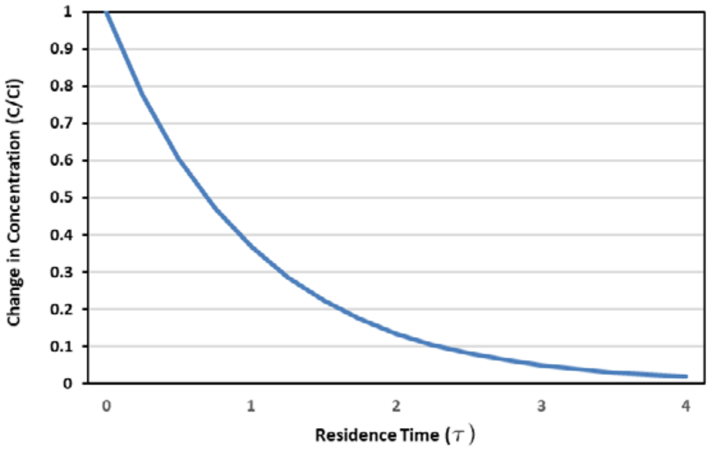

Figure 2. Decrease in concentration as a function of time

If potential indoor emission sources are removed from a building, the minimum interval before sampling should be at least 3 or 4τ to allow steady-state conditions to be achieved. Given the uncertainties involved, it is recommended to use 4τ as a minimum waiting time. As shown above, a single-family building with 0.5 ACH has a residence time of two hours, so 4τ = 8 hrs, and an office building with 1.0 ACH has a residence time of one hour, so 4τ = 4 hrs. This suggests that waiting overnight after sources are removed should be sufficient time and sampling can begin thereafter. If necessary, sources could be removed and sampling begin the same day, after waiting an appropriate interval. The USEPA recommendation for waiting periods of 24 to 72 hours prior to the start of sampling may be excessive.

Removal of indoor air emission sources also may have an effect on sub-slab concentrations because VOC transport can occur in both directions across a building slab. Indoor air concentrations will respond relatively quickly to source removal, but it may take several days to weeks for soil gas plumes created by indoor sources to dissipate (Johnson, et al., 2016). However, the VOCs detected in soil gas due to downward migration are generally not at concentrations that would be considered significant from a VI perspective given the much higher screening levels used for soil gas versus those used for indoor air. Therefore, waiting for soil gas concentrations to reach their new, lower steady-state concentrations after indoor source removal generally is not necessary.

Some state VI guidance suggests increasing building ventilation rates after removing potential indoor air emission sources (see text box). Note that changes in building ventilation also are considered to be perturbances to the existing steady-state conditions as discussed under Topic #2 below.

It should be recognized that removing indoor sources will not result in zero or non-detect (ND) results for all VOCs in subsequent indoor air samples. First, not all sources can be identified and/or removed. Second, outdoor air entering the building will contain VOCs. Third, in some cases, the building contents or construction materials may have adsorbed chemicals of interest and will continue to off-gas these chemicals for some time after sources such as paint cans have been removed. Building contents such as furniture cushions, carpet, and drapes may be low-level sources. These factors may confound VI investigations if substantial sources were present or if target VOCs of interest have especially low screening levels.

Excerpts from Existing VI Guidance

NJ: When background sources of indoor air contamination are identified and removed from a building, it would be prudent to ventilate the affected rooms in advance of the sampling event. Terminate this ventilation at least 24 hours before commencement of the IA sampling event to allow ventilation to return to normal operating conditions. As discussed in Chapter 4, these chemicals can be retained in materials found in the building (e.g., carpeting) and subsequently released over time.

NY: Once interfering conditions are corrected (if applicable), ventilation may be appropriate prior to sampling to minimize residual contamination in the indoor air. If ventilation is appropriate, it should be completed 24 hours or more prior to the scheduled sampling time.

Where applicable, ventilation can be accomplished by operating the building's HVAC system to maximize outside air intake. Opening windows and doors and operating exhaust fans may also help or may be appropriate if the building has no HVAC system.

Construction materials and building contents generally are not a significant issue for VOCs for existing construction; however, carpeting, fabrics, furniture, etc. may act as "sinks" that retain indoor air pollutants and subsequently release them over a prolonged period of time. This tends to be more significant for semi-volatile organic compounds (SVOCs), such as naphthalene, than for VOCs. For example, if a person formerly smoked in their house but then quit, the deposited and adsorbed SVOCs in the smoke may take weeks or months to off-gas and dissipate before new steady-state indoor air concentrations are established.

> We find that the recommendation of USEPA and many states for waiting periods of 24 to 72 hours prior to the start of sampling may be excessive.

Topic #2 – Changes in building ventilation

Indoor air concentrations are inversely correlated to the amount of building ventilation. If the building ventilation is changed, it will take some time for the indoor air concentration to adjust to a new steady-state value. **What time interval is necessary between a change in ventilation and the start of sampling?** If the HVAC settings are adjusted, or a door or window is opened or closed, the time for the system to reach a new steady-state condition depends on the new air exchange rate for the building. If the change increases the ventilation rate from 0.5 to 1.0 ACH, the average indoor air concentration will stabilize after 4τ, which in this case is four hours. Note that the time to reach steady-state conditions is independent of the starting rate. If the air exchange rate increases from 0.25 to 1.0 ACH, 4τ is still four hours.

It takes time for indoor air concentrations to stabilize after changes in building ventilation

> Practitioners are cautioned to that adequate time is needed for steady-state conditions to be reached after HVAC adjustments are made.

For commercial buildings where the HVAC system is shut down or operated at a reduced capacity overnight, getting representative data during the daytime may necessitate collecting samples during portions of the day when the indoor air concentrations may not be at steady-state.

The above examples assume a step-wise change in either source strength or ventilation rate. Different calculations are needed if the change is gradual rather than abrupt or if the value fluctuates, which is beyond the scope of this paper.

Topic #3 – Turning off building HVAC

An extreme example of a change in building ventilation is turning off the HVAC system and any exhaust or ventilation fans. **How long should you wait to sample after shutting off the building ventilation if characterization of indoor air under unventilated conditions is desired?** Obviously, it will take longer for the system to stabilize and reach a new steady state in this scenario than in the scenarios previously discussed, because as shown in Equation 2, Tau is inversely related to the rate of ventilation. A lower bound ventilation rate for an unventilated, closed space is thought to be about 0.05 ACH. That is the 5th percentile value for newer single-family houses (USEPA, 2018). If that value applies, there is about one air change per day, and a four-day waiting period is needed before steady-state conditions are achieved. Therefore, four days would be the optimal waiting time to sample an office building or other well-sealed building. A typical single-family house would likely have more ventilation due to leakage around doors and windows. Assuming 0.1 ACH, a 48-hour waiting period would be sufficient.

> In our opinion, collecting indoor air data when the building HVAC is shut off as a routine element of a VI study may be misleading.

In some guidance documents (e.g., USEPA, 2015a), there may be recommendations to turn off any HVAC system and collect samples under supposed "worst-case conditions." In reality, there may be competing processes, and unventilated conditions may not be representative of worst-case conditions. It depends on whether operation of the HVAC system typically results in positive or negative pressure within the building relative to the subsurface. Whereas turning off the HVAC greatly reduces the building ventilation and decreases dilution of any vapors that enter the building, the lack of operating ventilation fans may change the pressure differential across the building slab. If the building is typically positively pressurized, turning off ventilation fans will increase the rate of VI and will tend to increase the indoor air concentrations, further reinforcing the trend due to lesser diluent air. If the building is typically negatively pressurized, turning off fans will decrease the rate of vapor intrusion and will tend to decrease the indoor air concentrations (e.g., a restaurant kitchen with exhaust hoods). When there is less dilution air but also lower rates of vapor infiltration, it is difficult to predict which process will predominate and whether indoor air concentrations will exhibit a net increase or a net decrease versus baseline conditions.

As noted above, the waiting times for steady-state conditions to be achieved may be up to four days for a well-sealed building (e.g., 0.05 ACH). Asking building occupants to do without ventilation for that period of time is not reasonable. One option that practitioners may consider is to not wait for steady-state conditions and instead collect indoor air samples after some fixed time period after the HVAC is shut off, while the system is in a transient state. As noted above, sampling during such transient conditions may yield ambiguous results.

Collecting indoor air samples long before the new steady state is achieved increases the likelihood that the change in indoor air concentration versus baseline concentration will fall within the measurement variability. Typical analytical methodology uncertainty is about ±30 percent for most target compound list VOCs based on laboratory control checks. Unless the HVAC-on and HVAC-off concentrations are substantially different from one another, the two results may fall within this range of uncertainty and complicate evaluation of the effects of HVAC operations on indoor air quality. The same may be said when both results approach the method reporting limit where precision and accuracy may suffer and analytical uncertainty is greater.

Lastly, it also should be recognized that the usual assumption that the indoors is a well-mixed space may not hold true with the shutdown of HVAC or other building ventilation. There likely will be greater stratification in air concentrations within the building, making it more difficult to assess whether the results that are obtained are representative of a larger area.

Although sampling in non-residential settings with the HVAC off is recommended in some guidance documents, in the opinion of the authors, collecting indoor air data when the building HVAC is shut off may be misleading. Multiple lines of evidence should be used in data reduction when employing this as a routine element of any VI study. If there is a need to augment data collected under potential worst-case conditions, an option would be for practitioners to manipulate the building pressure to directly determine the effect of that variable on measured indoor air concentrations.

Topic #4 – Timing of outdoor air samples

Given the air turnover rates in typical buildings, the indoor air is routinely replaced with outdoor air every hour or two. Therefore, whatever VOCs are present in outdoor air will tend to find their way into the indoor space. The indoor (I) and outdoor (O) values can be compared to evaluate what fraction of the indoor air concentration originates from outdoor sources versus VI or indoor emission sources. An I/O ratio of approximately one suggests that all of what is detected indoors is attributable to outdoor (ambient) air. This is commonly observed for compounds such as chloromethane, carbon tetrachloride, and various chlorofluorocarbons, which are commonly detected but are often found at the same concentration indoors as in outdoor air.

> In our opinion, it is recommended that the outdoor air sample be the first sample started during a sampling event.

To account for the contribution of outdoor air, it is common practice to collect an outdoor air sample in conjunction with any indoor air samples. The outdoor air sample can be collected at the air intakes of the building if those exist and are accessible. Alternatively, the outdoor air sample can be collected a short distance upwind of the building at a location that meets USEPA air monitor siting guidelines (e.g., a specified distance away from trees, walls, and other obstructions to free air flow) and minimizes the impacts from any localized air emission sources such as roadways.

When and for how long should outdoor air samples be collected? Indoor air samples are point-in-time determinations of air quality. Air concentrations inside residential buildings may exhibit some short-term temporal variability due to changes in the activities of occupants (e.g., cooking, sleeping) and changes in building operation (e.g., HVAC cycling on and off). These variations are assumed to average out over a 24-hour diurnal cycle, so the standard practice is to collect 24-hour time-integrated samples to address residential exposures.[1] For non-residential buildings, the standard practice is to collect 8-hour time-integrated samples (i.e., the length of a typical work shift). The sampling duration for outdoor air samples should match whatever sampling duration is used for the indoor air samples. In most cases, that means collection of 24-hour outdoor air samples for residential buildings and 8-hour outdoor air samples for non-residential buildings such as offices, factories, shops, stores, and schools.

Outdoor air samples are generally collected concurrently with indoor air samples. In some jurisdictions, it has been suggested that outdoor air sampling should be started one hour prior to the start of indoor air sampling to account for the time lag for any changes in outdoor air concentrations to reach steady-state conditions within the building. While this is the technically correct approach, it is generally unnecessary in actual practice. For the vast majority of VOCs, the outdoor air concentrations are too low to be significant. For the few VOCs where outdoor air concentrations can be an issue, the outdoor air values reflect regional or area background levels, and the concentrations will be reasonably constant over the time frame of sampling.

If there is a localized outdoor source that has significant fluctuations in strength over very short time periods, a single outdoor sample will likely not be sufficient to characterize the outdoor air quality (whether it is started at the same time as the indoor air samples or started one hour prior to them). The changes in source strength combined with changes in meteorology will result in increased spatial variability compared with a constant-strength source.

In the field, it typically takes at least a few minutes to sequentially turn on each of the samplers due to the time for the sampling crew to move from one sampling location to another, record information, etc. It is recommended that the outdoor air sample be the first sample collected during a sampling event.

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[1] Changes in local meteorology such as wind direction, wind speed, atmospheric stability, solar radiation, and precipitation will not average out over periods of 24 hours or less; therefore, it is good practice to record readings for those variables during the sampling period and in the days immediately prior to the sampling period to aid in evaluating the sampling results.

Topic #5 – Timing of soil vapor samples

When should soil vapor[2] samples be collected? Existing guidance documents generally suggest that "concurrent" indoor air and soil vapor samples be collected; however, they do not explicitly define what is meant by the term. To reach a defensible answer, it is necessary to consider the sources of variability and how they may differ for different types of samples.

> There is no need for the sampling duration of soil vapor samples to exactly match the sampling duration of indoor and outdoor air samples. Indoor air samples and soil vapor samples collected within a few days of one another should be considered to be concurrent for VI decision-making purposes.

For indoor air, there may be short-term temporal variability in the concentrations being measured, so it is advisable to collect time-integrated indoor air samples to account for this variability. On the other hand, below the slab, the concentrations are typically very stable over time periods of days or weeks, and collection of time-integrated soil vapor samples to account for temporal variability is not necessary (Swanson, et al., 2010) (USEPA, 2012). However, there can be large amounts of spatial variability below the slab. To account for this variability, one can sample at more locations and/or bias the sampling locations toward known or suspected worst-case locations.

Consideration of variability

Aboveground, temporal variability is the main concern. Below the slab, spatial variability is the main concern.

Indoor air samples and soil vapor samples collected within a few days of one another should be considered to be concurrent for VI decision-making purposes. Furthermore, as discussed below, there is no need for the sampling duration of soil vapor samples to match the sampling duration of indoor and outdoor air samples.

Topic #6 – Partitioning in the subsurface

VOCs released into the subsurface will partition among various phases. This happens continually from the time of the original release. There is never just a single phase present in the subsurface, there is always partitioning. However, in some cases, it may not be readily apparent because VOC methods for soil and water samples are considerably less sensitive than VOC methods for gas phase samples. A given VOC may be detected only in soil vapor and be ND in soil and groundwater even though partitioning has obviously occurred.

When a given mass of VOCs is released into the environment, only a small fraction of the VOCs in the subsurface are present in the vapor phase. One rule-of-thumb is that the vapor phase typically represents about 1 percent of the total VOC mass with the vast majority of the mass present in the dissolved phase. Additional mass may be present bound to organic carbon in the soil, and at some sites, as free liquid. The dissolved phase includes VOCs dissolved in groundwater and VOCs dissolved in interstitial or pore water in the vadose zone.

> Collection of time-integrated soil vapor samples is unnecessary and grab sampling approaches should be acceptable and equivalent.

Perturbations to the system such as infiltrating rainwater will result in changes in the relative partitioning as the system moves toward a new steady-state distribution of the VOCs. Partitioning can be modeled using Henry's Law for dissolved phase VOCs, Raoult's Law for free liquid mixtures, and the organic carbon partition coefficient (K_{OC}) for sorption of VOCs onto soil organic matter. The rate at which partitioning occurs is not addressed in simple VI models, but it can be a significant factor. For example, the mass transfer from dissolved phase to gas phase for VOCs may take weeks to reach steady-state conditions in response to a system perturbance.

In aboveground sources such as lagoons, impoundments, and tanks, any VOC emissions are dependent on the amount of mixing that takes place due to wind and wave action, mechanical aeration, etc. The rate-limiting step is for VOCs

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[2] In typical use, soil vapor and soil gas are equivalent, interchangeable terms, though a distinction is sometimes made based on whether a given chemical may be either a gas or a liquid at room temperature (soil vapor) or is only a gas (soil gas).

> Although often repeated in guidance documents, the specification to purge and/or sample at rates of less than 200 mL/min is without technical basis and is not necessary.

to migrate from the bulk liquid to the boundary layer.[3] Once at the boundary layer, mass transfer to the gas phase occurs relatively rapidly. In the subsurface, on the other hand, there generally is no mixing, and VOC transport in water is dependent solely on diffusion (Fick's Law). The transport distances may be relatively short, but diffusion in water is very slow. Diffusion through air is considered to be a slow process, but for VOCs of interest for VI (e.g., trichloroethylene [TCE] and benzene), their diffusivity in water is about 8,000 times slower than their diffusivity in air. The result is that partitioning from liquid to vapor is not instantaneous, and in fact, can be quite slow.

The relatively slow partitioning to the gas phase discussed above has implications for soil vapor sampling. **What sampling conditions are appropriate for soil vapor samples?** Most VI guidance specifies an upper bound purging and/or sampling rate of 200 milliliters per minute (mL/min), but there is no technical basis for this value. Partitioning is very slow relative to the duration of sampling, so there should be no difference in concentration between time-integrated and grab samples for soil vapor. This has proved to be true in field tests where grab samples and time-integrated samples had about the same relative percent difference as duplicate time-integrated samples (Eklund, 2011). Another field study found that changes in sampling rate did not result in changes in photoionization detector (PID) readings or USEPA Method TO-3 results (McAlary and Creamer, 2006).

Some current guidance recognizes that time-integrated sampling is not necessary. The USEPA Office of Solid Waste and Emergency Response (OSWER) guidance (USEPA, 2015a) indicates that soil vapor samples are typically collected as grab samples. The current ASTM standard for soil vapor sampling (ASTM, 2018) also indicates that grab samples are an acceptable, equivalent sampling approach.

The same considerations discussed for soil vapor sampling also apply to purging of soil vapor probes prior to sampling. There is no technical basis for limiting purging to a rate of 200 mL/min. For example, a USEPA field study that collected samples over varying purge flow rates showed generally stable concentrations (USEPA, 2007). A separate field study showed the number of purge volumes did not have an effect on the measured concentrations after at least one purge volume was removed (USEPA, 2006).

Another question related to partitioning is: **How long to wait to sample after a new probe or well is installed?** In our view, waiting is irrelevant if sufficient purging has been performed and soil vapor readings have stabilized (or after purging a minimum of three void volumes). This purges out any soil vapor immediately around the probe or well that was affected by the installation process and replaces it with representative soil vapor from the surrounding area. The assumption is that the probe or well is representative of the area immediately around it (otherwise, what's the point of collecting data at that location?). So, there is no benefit in waiting some set number of hours or days after installation before purging and sampling.

> Extended pre-sampling waiting periods cited in guidance for soil vapor are not needed if sufficient purging has been conducted.

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[3] Mass transfer is often described using the two-film theory, where mass transfer from one phase to another involves transport from the bulk of one phase to the phase boundary or interface, then movement from the interface into the bulk of the 2nd phase.

Topic #7 – Rebound time

The slow rate of partitioning discussed above also has implications for operation of SVE systems. The fact that the mass of VOCs in the vapor phase is a small fraction of the total implies that the system must be operated for an extended period of time to be effective. Removing just one or two soil air-filled pore space volumes will not result in complete mass removal. The fact that phase partitioning is a relatively slow process implies that continuous operation will tend to remove mass from the pore spaces faster than it is replenished. This is evidenced by declining soil vapor concentrations over time and lower rates of mass removal. Therefore, pulsed SVE operation may be a more cost-effective option than continuous operation. After the SVE system is temporarily shut down, there can be an increase or "rebound" in soil vapor concentration back to near the original, starting concentration.

When SVE has reached the point of diminishing returns, the system may be shut down permanently. A typical requirement is to wait an appropriate amount of time, then test soil vapor to assess whether the soil vapor concentrations are at acceptable levels after any potential rebound has occurred. The question is: **How long do you need to wait after SVE system shutdown before testing for rebound in soil vapor concentrations?**

The following discussion assumes that rebound is dominated by diffusive transport. The time estimates will be conservative if advective or other transport mechanisms are the dominant mode of transport, such as might be the case at fractured bedrock sites or sites with other preferential pathways.

The key is understanding and defining the transport distance between the source of the vapors and the monitoring location and depth. For example, if there is a groundwater or soil source at 6 meters (m) and nested soil vapor probes at 1.5 and 3 m depths, the transport distance to the deeper probe is 3 m and the transport distance to the shallower probe is 4.5 m. So, we would expect to see new steady-state concentrations sooner at the deeper probe than at the shallower probe. But recognize that if the source of vapors is interstitial pore water, the transport distance may be relatively short and may be the same for both probes.

Two predictive tools for estimating rebound time for various distances are presented. The Jury method (Devitt, et al., 1987) is based on the diffusivity in air for a given compound and distance:

Equation 3

$$t = \frac{L^2}{Di}$$

where:
t = time (in seconds [sec]);
L = distance (in centimeters [cm]); and
Di = Diffusivity in air (square centimeters per second [cm^2/sec]).

The transport distance is typically assumed to be several times the straight-line distance due to the tortuosity of the soil (i.e., the path that a VOC molecule takes through the interconnected air-filled pore spaces is two to three times longer than the straight-line distance).

An alternative approach is that of Johnson, et al. (1999). This method calculates the time required to achieve steady-state soil vapor concentrations for a specific constituent and takes into account soil type.

Equation 4

$$t = \Theta_a R_v L^2 / D_{eff}$$

where:
θ_a = air-filled porosity (unitless);
R_v = vapor-phase retardation factor; and
D_{eff} = effective diffusivity (cm^2/sec).

The air-filled porosity will vary with soil type as will the effective diffusivity, which is calculated based on the Millington-Quirk relationship. The retardation factor will be 1 for alkanes but may be between 10 and 100 for monoaromatic hydrocarbons because of their potential for aerobic biodegradation. Most chlorinated VOCs also should have a retardation factor of 1.

Results are plotted in Figure 3 for the two estimation approaches for TCE in a clay soil. The transport distance was assumed to be two times the straight-line distance for the Jury method calculations. The vapor-phase retardation factor was assumed to be 1 for the Johnson, et al. method calculations. The two methods show reasonable agreement for this soil type.

The required wait times for rebound to occur are less than one week for 1 m distances (6.7 days for Jury method and 3.8 days for the Johnson, et al. method) and less than one month for 2 m distances (27 days for Jury method and 15.3 days for the Johnson, et al. method). The wait for rebound to occur exceeds three months by either method for distances of 5 m, and the wait times exceed one year by either method for distances of 10 m. There are significant advantages in time to reach a decision if the monitoring locations are located close to the source of vapors.

Jourabchi and Lin (2021) recently refined the Johnson, et al. approach and demonstrated that the time to reach steady-state conditions is dependent on the distance of the entire pathway, not just the distance between the vapor source and the monitoring location. This difference is relatively insignificant when the distance between the vapor source and the monitoring location is only 1 or 2 m.

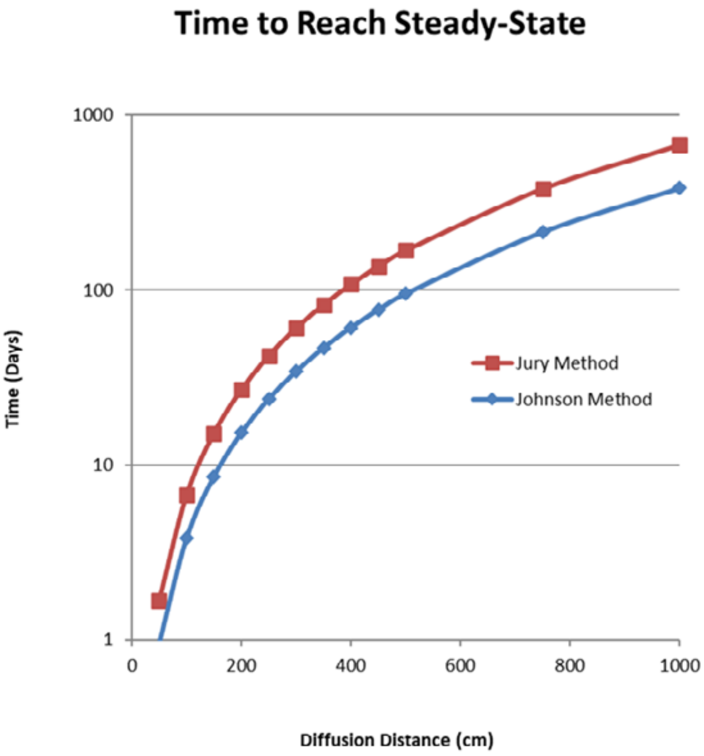


Figure 3. Time for SVE rebound to occur for TCE in a clay soil

The relatively long wait times associated with longer distances shown in the above Figure also have implications for how long it takes for sites with new releases to reach steady-state conditions. That is a complicated topic and outside the scope of this paper, but it should be recognized that sites may be under transient conditions for some number of months after a release occurs.

Also outside the scope of this paper is what time, if any, is needed to account for changes in environmental variables such as barometric pressure changes, temperature, rain events, etc. There, the key issues are the magnitude of the effect and how far it extends down into the soil column. For more information, see Eklund (2016).

Topic #8 – Chemical Kinetics

Chemical kinetics addresses the rate of chemical reactions. In VI studies, most VOCs are assumed to be inert and to persist unchanged in the subsurface over the time frames of interest. However, biodegradation and chemical reactivity are common exceptions that practitioners should keep in mind. These are discussed below.

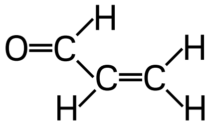
It has long been recognized that petroleum hydrocarbons are amenable to aerobic biodegradation and therefore exhibit different behavior in the subsurface than most other VOCs. Compounds such as benzene and ethylbenzene will readily undergo aerobic biodegradation if sufficient oxygen is available. For these compounds, the vadose zone essentially acts as a giant biofilter. At steady-state conditions, the removal is essentially instantaneous and complete. Certain other VOCs, such as vinyl chloride, exhibit similar behavior and also are aerobically degraded under these conditions. For these VOCs, groundwater or deeper soil gas may exceed screening levels, but shallower soil gas and indoor air are unlikely to be impacted.

For chemicals that undergo aerobic biodegradation, the key is collecting samples at the proper depth. At some depth in the soil column, there will be a zone of active biodegradation. Above this zone, the soil vapor will be depleted of aromatic petroleum hydrocarbons (and vinyl chloride) and have "excess" available oxygen. Below this zone, the soil vapor will be relatively high in aromatic petroleum hydrocarbons and depleted of oxygen. Collection of field parameters such as oxygen, carbon dioxide, and methane concentrations is recommended to support multiple lines of evidence evaluations.

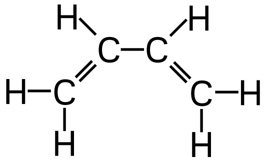
How long do you need to wait for biodegradation processes to reach steady-state conditions? For biofilters, a three- to six-week conditioning period is needed to allow the microorganisms to adapt to the gas-phase compounds being treated (Janni, et al., 2011). A similar time frame is assumed to apply to natural aerobic processes in the subsurface.

Some chlorinated VOCs such as tetrachloroethylene (PCE) and TCE will undergo anaerobic biodegradation in oxygen-limited environments. That process tends to be relatively slow, and soil gas concentrations generally are expected to be stable over time frames of months.

Highly reactive chemicals tend to have relatively low screening levels if they can react with lung or other bodily tissue and result in potential adverse health effects. However, this same reactivity leads these chemicals to have relatively short half-lives, which limits their transport in the subsurface. Two examples of reactive chemicals that sometimes are an issue in VI studies are acrolein and 1,3-butadiene. These chemicals are produced during combustion processes and both are unsaturated (i.e., have carbon-carbon double bonds). The double bonds contribute to their reactivity.



Acrolein



1,3-butadiene

For example, 1,3-butadiene sometimes is detected in soil vapor samples initially collected after probe installation through tight soil formations using direct-push approaches. It is believed that heating due to friction during the probe installation process produces the 1,3-butadiene. Subsequent sampling invariably shows that the 1,3-butadiene does not persist. In this scenario, 1,3-butadiene is formed as a result of the sampling process and is therefore a sampling artifact; its steady-state concentration in soil vapor is essentially zero.

Acrolein is sometimes detected in soil vapor samples, and it too can be a sampling artifact. Acrolein concentrations may increase over time in TO-15 canisters that contain relatively high concentrations of polar compounds (e.g., alcohols, ketones). Low humidity in the samples and heating of the canisters during the cleaning process are contributing factors to rates of acrolein formation (Shelow, et al., 2009) (Swift, et al., 2006) (Whitaker, et al., 2015). If acrolein is detected in soil vapor, it may be formed endogenously in the canisters and can therefore be a sampling artifact; its steady-state concentration in soil vapor is essentially zero.

Summary

A conceptual site model (CSM) summarizes key information about a site so that stakeholders have a common understanding of what is known about the VI pathway for a given site. A robust CSM is especially needed in VI studies to guide the design of any testing to be performed. As new information becomes available, it is compared with the CSM and the CSM is adjusted as appropriate. When developing a CSM for vapor intrusion, the importance of steady-state conditions is often overlooked. The consideration of steady-state conditions and incorporation of this information into the CSM is important for designing defensible, efficient VI studies. The key points addressed in this paper are summarized in Table 1.

Table 1. Summary of recommendations to address the need for steady-state conditions

Topic	Recommendation	Comment
Removal of a VOC source from inside a building	Wait a minimum of 4 residence times to sample	Indoor surfaces may continue to emit SVOCs for several days or weeks
Changes in building ventilation	Wait a minimum of 4 residence times to sample	
Turning off building HVAC	Wait up to 4 days to sample an office building; wait up to 2 days to sample other building types	This type of testing is not practical or easily implemented and other options should be considered
Timing of outdoor air samples	Collect concurrently with indoor air samples	
Timing of soil vapor samples	Indoor air and soil vapor samples collected within a few days of one another should be considered concurrent	It also is not necessary that indoor air and sub-slab soil samples have the same sampling duration
Partitioning in the subsurface	Soil vapor can be collected as a grab sample No minimum wait times are needed after probe or well installation if adequate purging is performed	
Rebound time	Use Jury and/or Johnson, et al. method to estimate	Collect soil vapor as close to the source of vapors as is feasible
Chemical kinetics	Assume 3 to 6 weeks for microbes supporting aerobic biodegradation to become established Do not include acrolein or 1,3-butadiene in VI evaluations	

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