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# **ARIZONA DEPARTMENT OF ENVIRONMENTAL QUALITY**

## **SOIL VAPOR SAMPLING GUIDANCE**

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# Soil Vapor Sampling Guidance

## **1. Scope and Application**

1.1 This guidance describes procedures for collection of active soil vapor samples and does not address procedures for collection of passive soil vapor samples.

1.2 This guidance details sampling procedures to ensure delivery of soil vapor samples to the laboratory that will yield reliable and consistent results that are representative of actual conditions.

1.3 This guidance provides a methodology to estimate the total contaminant concentration in soil using soil vapor samples.

## **2. Definitions**

2.1 Dead Volume – volume of the sampling probe and the connected sampling tubing and equipment. The boring volume is not included in the calculation of dead volume, because the probe tip sand-pack space is assumed to have been allowed to equilibrate with surrounding soil formation before soil vapor sampling occurs.

2.2 Internal Volume – dead volume plus probe tip sand-pack volume.

2.3 Probe Driving System – hydraulic or hammer system used for installation of soil vapor sampling probes.

2.4 Soil Vapor Monitoring Well – a well constructed specifically to sample soil vapor from the vadose zone.

2.5 Soil Vapor Sample – a sample of soil vapor representative of the vadose zone at the sampled location.

2.6 Soil Vapor Sampling Port – any mechanical device (usually a ball valve with a hose barb) that allows a representative soil vapor sample to be collected from a soil vapor monitoring well.

2.7 Soil Vapor Sampling Probe – any mechanical device that allows collection of a representative soil vapor sample from a specified sampling depth.

2.8 Vapor Equilibration – the condition where vapor concentration entering a sampling probe is 95% or greater of vapor concentration in surrounding soil.

## **3. Considerations when Planning for Soil Vapor Sampling**

The collection and analysis of soil vapor samples, along with any existing soil and groundwater data or any reasonably obtainable data (e.g., soil solids and groundwater data), is useful for the objectives of site characterization, determination of potential pathways of exposure for health risk, optimization of remedial or mitigation systems design, and confirmation of compliance with remedial goals.

### 3.1 Temporal Variations in Soil Vapor Concentrations

Variations in soil vapor concentrations due to temporal effects are principally due to temperature changes, precipitation, and activities within any overlying structure. Variations are greater for samples close to the surface and vary less with increasing depth. There are a number of available studies on the temporal variation in soil vapor concentrations and more are currently underway or planned in 2007 by the EPA and independent groups. The results of these studies have shown that short-term variations in soil vapor concentrations at depths four feet or deeper are less than a factor of two and seasonal variations in colder climates less than a factor of five.

Descriptions of expected variations in soil vapor concentrations due to temperature variation and periods of heavy precipitation follows:

3.1.1 Temperature: Effects on soil vapor concentrations due to actual changes in the vadose zone temperature will be minimal.

3.1.2 Precipitation: Infiltration from rainfall can potentially impact soil vapor concentrations by displacing the soil vapor, dissolving volatile organic compounds, and by creating a “cap” above the soil vapor. In most settings, infiltration from large storms only penetrates into the uppermost vadose zone. Soil vapor samples collected at depths greater than 3 to 5 feet below ground surface (bgs) under foundations or areas with surface cover are unlikely to be significantly affected. However, soil vapor samples collected closer to the surface (<3 feet) with no surface cover may be affected. It is preferred that sample collection not occur if any precipitation is falling or has fallen within 24 hours. Difficult collection of soil vapor samples is typical when the moisture has penetrated to the sampling zone. Consider measured values as minimum values when encountering high vacuum readings when collecting a sample or when drops of moisture are evident in the sampling system or sample. Measurement of percent moisture of the soil may also be useful if shallow sampling is performed during or shortly after significant rainfall (>1.0 inch).

3.1.3 Pressure: Barometric pressure variations are unlikely to have a significant effect on soil vapor concentrations at depths exceeding three to five feet bgs and only a minor effect (less than a factor of 2) at shallower depths unless a major storm front is passing through the area. A recent study in Wyoming (Luo et al., 2006) has shown little to no relationship between barometric pressure and soil vapor oxygen concentrations.

Human induced influences to pressure are likely to have a bigger effect upon soil vapor concentrations. For example, pressure changes resulting from the on-off

cycling of an overlying building's heating or HVAC system and the ventilation of the structure due to open doors and windows can greatly influence soil vapor concentrations at locations near the building. In colder climates, greater impacts are most likely in the winter season. Literature suggests that temporal variations in the radon concentrations are typically less than a factor of two and seasonal effects less than a factor of five. (Vapor Intrusion Pathway: A Practical Guideline, January 2007 Interstate Technology and Regulatory Council)

### 3.2 Conditions Unsuitable for Collection of Soil Vapor Samples

3.2.1 Collection of soil vapor samples is not desirable if:

- a. Groundwater is very close to the ground surface (i.e., < 3 feet);
- b. Chemical(s) of concern is/are not volatile; and
- c. Moisture or unknown material is in the sample stream or sample container. This is a field sampling quality concern, not a laboratory concern.

Please note that due to increased diffusivity, advective flow, and temperature fluctuations at near surface boundaries, the collection of a soil vapor sample in near surface soils is not useful for the purpose of calculating total soil solid VOC concentrations.

### 3.3 Tests to Determine if Soil Vapor Sampling is Practicable

Some soil types (i.e., clay or silty clays) may not be conducive for soil vapor collection. Tests to ascertain if soil vapor collection is possible from the soils are below.

3.3.1 Qualitative – connect a gas-tight syringe to the soil vapor sampling tubing to determine if a sample can be withdrawn. Please note that the soil vapor sampling tubing must have a volume of less than the gas-tight syringe for a meaningful result.

3.3.2 Qualitative – follow the instructions below:

- a. Install a T-connection at the end of the soil-vapor-sampling tubing;
- b. Connect a vacuum gauge to one branch of the T-connection;
- c. Connect a syringe fitting and a 60-mL or larger syringe to the remaining branch of the T-connector;
- d. With the syringe connected, pull the plunger back to the full-scale reading and hold in that position; and then

- e. Monitor the vacuum created at the full draw position and during relaxation

If the vacuum does not relax (i.e. less pressure over time) within a few minutes to an hour, it is unlikely that soil vapor sampling is practicable at that particular location and other locations in the subsurface with similar soil characteristics.

- A vacuum conversion table is provided in Attachment 1 for convenience.

### 3.4 Confirmation Sampling

Soil vapor samples used to verify completion of remedial actions must verify that residual contaminant concentrations are at or below the corrective action standard for each chemical of concern in the contaminated soil as determined under A.A.C. R18-7-201 *et seq* (please refer to Section 6). Collection of soil vapor samples must occur throughout all areas previously reporting soil solid concentrations for chemicals of concern above applicable corrective action standards.

Utilization of soil vapor data collected for the UST Program as part of assessing vapor intrusion issues for LUST case closure purposes occurs by demonstrating that soil contaminant concentrations above an applicable residential soil remediation level (rSRL), as determined by soil solids analysis, does not pose an unacceptable vapor intrusion risk.

## 4. **Installation Methods**

This section provides useful construction information and details for installation methods.

### 4.1 Sample Through Rods (also known as temporary probes)

This method is advantageous if only one sampling round is required. Also, minimal disturbance of the in-situ vapor occurs due to less material placed in the ground, which decreases the need for collection of blanks.

Consider the following construction details for the collection of a sample through rods:

4.1.1 Seal probes at the surface with bentonite before sampling;

4.1.2 Utilize small diameter tubing (e.g. nylon - preferred tubing when conducting risk assessments - polyethylene, copper or stainless steel) which will not react, absorb or interact with site contaminants. It is suggested to use new tubing for new field events or demonstrate that the tubing you are using is contaminant free; and

4.1.3 When using direct-push borings for the installation of soil-vapor-sampling probes, avoid lateral movement of the probes once they are in the ground to prevent atmospheric air from entering the sampling system.

## 4.2 Permanent Probes

4.2.1 Consider the following construction details for the installation of permanent probes:

- a. Use short discreet sampling intervals (e.g., 6 to 12 inches);
- b. Color code or tag tubing of probes at the surface to be sure that the sampling depth is easily identifiable for future sampling events;
- c. Complete and seal permanent probes at the ground surface (e.g., road boxes, locked caps, vapor-tight valves).

## 4.3 Types of Drilling

When using auger, air rotary, air knife, or roto sonic drilling methods for the installation of soil-vapor sampling probes, consider the following:

4.3.1 Install sampling probes with sand-pack intervals of approximately 1 foot;

4.3.2 Seal each sampling interval with bentonite or grout above and below the sand pack in the annulus of the boring. Take care to ensure that the seal material does not intrude into the sand pack;

4.3.3 If the boring contains dry bentonite, take care to fully hydrate the bentonite. Placing the bentonite in small increments (e.g., < 6 inches) followed by water is helpful. Alternatively, the bentonite can be added using a combination of dry and hydrated bentonite, or in slurry form if the boring is of sufficient diameter; and

4.3.4 For deeper probes, down-hole support rods may be necessary during probe installation, especially for tubing sized greater than 1/8-inch outside diameter (OD).

## 4.4 Equilibration Time

During probe installation, subsurface conditions are disturbed. For probes installed with auger, air rotary, air knife, or roto sonic drilling methods, purge volume test, leak test and soil vapor sampling should not be conducted for at least 48 hours (depending on site lithologic conditions and stage of investigation) following probe installation. When utilizing sample through rods, the recommended equilibration time is 20 to 30 minutes.

# 5. Sampling and Analysis

## 5.1 Sampling Containers

The sample containers chosen for a specific site will depend on the sampling equipment and analytical requirements. Select the final storage container prior to the initial sampling.

- 5.1.1 Examples of different sample containers include:
  - a. Tedlar™ bags;
  - b. 1.0 Liter (L) stainless steel canisters (e.g., Summa™ canisters). The lab is responsible for certifying the cleanliness of the canister and evacuating the canister before leaving the lab. It is strongly suggested that the lab be responsible for providing a record of the canister vacuum/pressure before and after sampling; and
  - c. Gas-tight syringes

All of the above listed sample containers are relatively simple to fill. Tedlar™ bags have a 72 hour holding time. Stainless steel canisters have a 30 day holding time. On-site analysis by a mobile lab typically utilize syringes for which the holding time should be as short as possible (less than 5 minutes for plastic syringes and less than 15 minutes for glass syringes). ADEQ does not recommend extending holding times by transferring samples to different container types.

ADEQ's UST Program recommends Tedlar™ bags for their soil vapor extraction (SVE) system influent or effluent sampling. Summa™ canisters certified as clean are the preferred sample container for soil vapor data used in risk assessments.

## 5.2 Shallow Samples

Observe care when collecting shallow soil gas samples to minimize atmospheric influence from the surface. If possible, avoid extensive purging or use of large volume sample containers (e.g. 6.0 L Summa™ canisters) for collection of near-surface samples.

## 5.3 Storage and Shipping Considerations

- 5.3.1 Do not put sample on ice;
- 5.3.2 Do not store sample exposed to light (keep sample in dark place);
- 5.3.3 Keep sample at standard temperature and pressure as much as practicable;
- 5.3.4 Do not ship Tedlar™ samples by airplane.

## 5.4 Sample Collection

ADEQ recommends use of the ADEQ QA/QC checklist for Soil Vapor Sampling when sampling (see Attachment 2).

- 5.4.1 Purging

Utilize purging to obtain a sample that represents equilibrated vapor concentrations of soil surrounding the sampling probe. Conduct the initial purge testing in an area where positive detections are most likely to occur.

The purged volume selected should be consistent for all sample locations across the site. Please consider the following procedure with respect to purging:

a. Remove three to five internal volumes of a sample system. This should ensure that vapor concentration entering a sampling container is 95% or greater representation of vapor concentration in surrounding soil; or

b. If vapor equilibration has occurred, remove one to five dead volumes;

Base the number of dead volumes requiring removal on procedures such as:

c. Analyzing the purged vapor with a field vapor analyzer (photoionization detector (PID) or flame ionization detector (FID)) until the concentrations stabilize and assess consistency across sequential purged volume samples; or

d. Conducting a purged volume test to determine the number of dead volumes to remove that corresponds to the highest recovered vapor concentrations.

#### 5.4.2 Purging Equipment

a. A vacuum pump with a flow controller and flow meter can be used when sampling large (> than 200 milliliters (mL) probe volume) or middle size probe. Use another device (e.g. syringe) for small size probes (less than 3 mL probe volume).

b. To evaluate lithologic conditions adjacent to the soil gas probe (such as no flow conditions due to clayey lithology), a vacuum gauge or similar device should be used between the soil gas sample tubing and the soil gas extraction devices (e.g. vacuum pump).

The whole purging device should be used at the end of the sampling train (after the T-valve and canister) to avoid field cross contamination from the device.

#### 5.4.3 Purging flow rate

a. 200 mL/min is the recommended default rate, unless a non-permeable cover is present.



- b. Modify the purge rate based on conditions encountered in individual soil gas probes, such as:
- The probe vacuum reading > 5 inches Hg (full vacuum reading is 29.9 inch Hg)
  - Condensation is present in the sampling train, or
  - The internal volume of the sampling train is very large (i.e., the purging time would be over one hour at 200 mL/min flow rate). If the purge time is longer than 30 minutes, re-evaluate sampling conditions.
- c. Document any modified rates.

#### 5.4.4 Purging time

- a. Determine the dead volume - the internal volume of the probe plus the internal volume of the tubing used to connect the probe and the sampling train.
- b. The dead volume divided by 200 mL/min or the appropriate purging flow rate is the purging time.

Please take care to not collect a sample under non-equilibrium conditions generated by high purge rates. Overpurging is a common mistake of soil vapor sampling.

#### 5.5. Leak Testing

Consider conducting a leak test where leakage may be a concern (i.e. at fitting junctures and anywhere leakage may occur).

The following are examples of procedures for checking below ground sampling equipment for leaks:

5.5.1 Use oxygen as a qualitative test for a high-end indicator of short circuiting. Elevated oxygen measurements in soil vapor analytical results may indicate significant short-circuiting. This, though, may not be true for shallow depths or in areas where there is only halogenated VOC contamination); and

5.5.2 Use tracer compounds (e.g., difluoroethane) to conduct leak tests. For example, apply the tracer at the surface where air could enter the soil vapor probes. When using helium as a tracer gas, use a shroud to keep the tracer gas in contact with the probe during the testing. Please note that helium is a common carrier gas during sample analysis, so it is not recommended for use as a tracer compound. If using difluoroethane, use it sparingly on a rag and do not use a shroud. Alternatively, use a shut in test to test for system leaks.

**NOTE** – Contact the lab with any specific questions regarding any further information on tracer compound and techniques.

5.5.3 Gently apply the tracer compound at the surface where air could enter the soil vapor probes (i.e. at the top of the probe) and at all the connections of the sampling train when the sampling starts. Never over apply. Over application of the tracer compound may cause cross contamination and failure to obtain usable results.

The Detection Limit for leak check compounds should be 10 parts per billion by volume (ppbv) or less in an undiluted sample. Analyze the soil vapor sample for the tracer compound using a method that can detect it as a calibrated analyte or as a Tentatively Identified Compound (TIC).

Take care that the tracer compound of interest and other co-existing volatile compounds in the tracer media are not target compounds of interest in soil vapors investigated at the site. Appendix D (pages D-9 and 10) of the January 2007 ITRC *Vapor Intrusion Pathway: A Practical Guideline* contains a discussion of advantages and disadvantages regarding different tracers.

#### 5.6 Sample Collection Flow Rates

Maintain flow rates should not exceed approximately 200 mL/min and vacuums to below 10 inch Hg if practical. Also, consider the following:

5.6.1 Minimize the sample collection flow rate for near groundwater situations to prevent groundwater from entering the sample container;

5.6.2 Measure and record the vacuum for each sampling probe at sample collection;

5.6.3 Use a calibrated flow controller supplied by the lab to provide a consistent flow rate for each sample collected. Use one flow controller for each sample collected.

#### 5.7 Sample Collection Procedure

The following are examples of sample collection procedures utilizing different types of sample containers:

5.7.1 Collection using Tedlar™ bags:

- a. Use a “T-coupling” to place the Tedlar™ bag in the sampling system ahead of the purging equipment used to purge vapor from the system. Appropriate compatible connecting threads will be required in order to use the Tedlar™ bag;

- b. Attach sample tubing to a vacuum box and pump;
- c. Open the valve on a clean dry Tedlar™ bag and attach it to the inside of the vacuum box;
- d. Close the vacuum box, close stopcock (3-way valve) between vacuum box and pump, then turn the pump on;
- e. Allow Tedlar™ bag to fill to 50 – 70% of capacity (do not overfill), shut off the pump, close the toggle switch (to prevent loss of sample), open the stopcock, and remove Tedlar™ bag from the vacuum box; and
- f. Label the bag accordingly and keep it in a dark area with the temperature as near as possible to the soil temperature at the time sampled (to avoid condensation) until analysis occurs. Analyze the sample collected in a Tedlar™ bag as soon as possible after collection.

#### 5.7.2 Collection using stainless steel canisters (e.g., Summa™ canisters):

- a. The lab should provide a pre-cleaned, certified for cleanliness Flow Controller with every canister to control the sampling flow rate equivalent to 200 mL/min or appropriate rate.
- b. Use a “T-coupling” to place the stainless steel canister in the sampling system ahead of the purging equipment used to purge vapor from the system. Appropriate compatible connecting threads will be required in order to use the stainless steel canisters;
- c. If necessary, use a vacuum gauge to verify the pressure inside the stainless steel canister prior to sampling to ensure the canister has arrived from the laboratory with the proper vacuum. Please note, any kind of vacuum gauge may have potential field cross contamination risk if not used properly. ADEQ recommends to check the clean canister with vacuum gauge just prior to sampling in the field. Due to cross-contamination possibilities, do not use the same vacuum gauge while collecting samples at multiple locations.
- d. Empty stainless steel canisters may not be stored for more than 30 days prior to sample collection. Once filled, properly label and package the stainless steel canisters for transport to the off-site laboratory. (Note: Only stainless steel canisters can be shipped by air freight to an analytical laboratory for analysis and should be analyzed within 30 days after sample collection.);
- e. Connect all parts of the sampling train in the following order:
  - top of the probe
  - tubing

- “T-coupling”
- purging pump

Place the Flow controller on the site of “T-coupling”.

For permanently installed probes, check the tightness of the probe, the valve on the top of the probe, and the presence of glue applied at the probe junctures. Fix any problems if possible before purging, and record on the Soil Vapor QA/QC form which is included as an appendix.

5.7.3 Open all the valves; turn on the pump at the appropriate flow rate for the calculated purging time. During the purge, take action if any of the following conditions are noted:

- a. The probe vacuum is > 5 inches Hg, or
- b. Condensate is present in the sampling train

To address condition “a”, close the T-coupling valve, turn off the pump, and extend the sampling time (e.g. from 5 minutes to 10 or 15 minutes). To address condition “b”, raise the canister as high as possible until the water evacuates the line. Record all observations and actions.

If the probe vacuum is < 5 inches Hg, finish within the purging time, close the T-coupling valve, and turn off the pump.

Connect the canister to the Flow Controller, open the canister valve. If a canister with a bayonet style quick connector is used, simply push the canister fitting into the flow controller until it securely seats. Apply the leak test tracer compound (as described in 5.5) immediately after the canister is connected or opened.

Allow the canister to fill for the appropriate time.

5.7.4 Disconnect the canister from the sampling train, replace the canister valve cap and complete the sample label (Note: Label the tag attached to the canister), do not write on the outside of the stainless steel canister itself.

5.7.5 Use the **equipment blank** to monitor any cross contamination from the sampling train. Use the same setup as outlined above, using clean cylinder air or nitrogen (preferred) as source gas.

5.7.6 A **background blank** will monitor any cross contamination from the surrounding ambient air. To collect a background sample, place the canister upwind and as close as possible to the probe location.

5.7.7 A duplicate or split sample should be collected every 20 samples or field sampling event. Please note that it is very difficult to have reasonable precision for sample duplicates if a T-manifold splitter is not used, especially for medium or shallow depth probes.

## 5.8 Analysis

Analysis of vapor samples can occur in the field (mobile laboratory) or at a fixed laboratory setting. Use of a mobile laboratory for vapor analyses can be practical in terms of data collection when making field decisions, especially during the investigative process. The intention of analyses in the field is to ensure a good data set that provides results in real time that adequately represents conditions at the site. A good field data set should result in less time spent during the site investigation process.

The following analytical methods are acceptable for soil vapor analysis. Analytical methodology will depend on the project's objective(s), reporting limits needed, and sample container type:

For VOCs:

5.8.1 8260BAZ (Modified for Vapor)

5.8.2 8021B (Modified for Vapor)

5.8.3 TO-15 (Preferred method for risk assessments)

5.8.4 TO-14A

NOTE: Please contact the regulating program for the appropriate analytical method. All COCs may not be included in the method target compound list.

## 5.9 Data Quality Objectives (DQOs)

Data quality objectives (DQOs) will vary with both the stage of investigation and the intended use of the data collected from soil vapor sampling. During screening or the initial stages of investigation, DQOs will be less stringent than those for confirmation of remediation or risk assessment for indoor air vapor intrusion. DQOs will determine the sampling method, the type of sample collected, the frequency of sample collection, sampling location, the number of samples to be collected, and the specific quality assurance (QA) and quality control (QC) necessary, both in the field as well as in the laboratory. Following DQOs will ensure that the data is useable for the intended purpose.

The most important QA/QC activities and parameters include:

5.9.1 Sampling method

5.9.2. Sampling equipment maintenance and calibration

5.9.3 Control samples, i.e., trip blanks, field blanks, method blanks

5.9.4 Standard Operation Procedures (SOPs)

- 5.9.5 Analyses method appropriate for target compounds
- 5.9.6 Sample holding times and transportation conditions
- 5.9.7 Analyses method with required practical quantitation level
- 5.9.8 Laboratory QC samples

## 5.10 Quality Assurance/Quality Control

### 5.10.1 Sampling QA/QC

Solid quality assurance and quality control procedures start with organized planning. A well thought out work plan will help to ensure collection of soil vapor samples in a manner resulting in data of known quality. Stated data objectives and quality control techniques are essential to the work plan. There are several quality control procedures to ensure collection of representative samples. Listed are some of those quality control procedures to consider:

- a. Purging (see Section 5.4.1)
- b. Leak Testing (see Section 5.5)

### 5.10.2 Analysis QA/QC

All soil vapor samples require analysis by an Arizona Department of Health Services (ADHS) certified laboratory and maintains a Quality Assurance Plan. Quality Control Procedures for analysis performed with soil vapor sampling should follow good laboratory practices and criteria within the specified methods and at a minimum include the following quality control criteria:

- a. Detection Limit Study
- b. Method Blank
- c. Calibration
- d. Calibration Verification
- e. Surrogates
- f. Duplicate (1 per 20 sample/field sampling event)
- g. Proficiency Test (PT) Samples

When QC criteria fall outside specified control limits, the analysis should be qualified using Arizona data qualifiers. The final report includes a case narrative for any event not describable by data qualifiers. Using the Arizona data qualifiers does not automatically qualify the data as acceptable to ADEQ. ADEQ expects that data reported utilizing these qualifiers, unless stated otherwise, is useable, scientifically valid and defensible.

### 5.10.3 Other Soil Vapor Analytes

Chemicals of interest for soil vapor sampling are specific for the type of contaminant release and breakdown products. They include both volatile organic and inorganic compounds, as well as some semi-volatile organic compounds. The method selected for laboratory analysis should be consistent with the stage of investigation and remediation, the volume of sample that is practical to collect, and the DQO's. Analysis of all samples collected to demonstrate compliance with regulatory requirements requires a laboratory licensed by the ADHS using an ADHS approved method.

The following table lists the types of compounds, methods, and ADHS approval status. Consult the laboratory for specific target list compounds, as well as detection limits. If using a particular laboratory analytical method not currently approved by ADHS for compliance samples, please contact ADEQ to begin an approval process through A.A.C. R9-14-610(C).

**Table 5.1 Analytical Methods**

<b>Compounds</b>	<b>Method</b>	<b>ADHS Certified</b>
Chlorinated VOCs and Petroleum VOCs BTEX/MTBE	TO-14A	Yes
Chlorinated VOCs and Petroleum VOCs	TO-15	Yes
VOCs	8260BAZ	Yes
VOCs	8021B	Yes

## 6. Relating Soil Vapor Concentration to Total Soil Concentration

Calculation of total soil concentrations using the method outlined below will vary depending on the input choice of chemical and physical values, such as soil adsorption coefficients ( $K_{oc}$ ) and soil organic carbon fractions ( $f_{oc}$ ). In this section, ADEQ provides a list of default values and methods to derive alternative values to be utilized in the three-phase partitioning equation outlined in Section 6.1. The listed default values are appropriate for use throughout much of Arizona and are conservative values so as to be protective of public health and the environment.

### 6.1 Three-phase Partitioning Equation

ADEQ accepts the following three-phase partitioning equation for the calculation of total soil concentrations which may occur in situ for a chemical. The basis of this equation is a

standard soil partitioning equilibrium model that assumes non-aqueous phase liquid (NAPL) is not present. Therefore, at soil concentrations exceeding the 3-phase saturation limit, measured soil vapor concentrations are inapplicable for calculating total soil concentrations using this equation. For a better understanding of when the 3-phase partitioning equation is not applicable, please see Section 6.5 of this document. The equations used that govern the equilibrium partitioning between phases are the linear sorption partitioning equation normalized with respect to organic carbon (Karichoff et al., 1979) and Henry's Law:

$$C_t = \frac{C_g [K_{oc} f_{oc} \rho_b / H_o + \theta_w / H_o + (\theta - \theta_w)]}{\rho_b}$$

where:

$C_t$  – Total concentration in soil (micrograms per kilogram ( $\mu\text{g}/\text{kg}$ ))

$C_g$  – Concentration in soil vapor (micrograms per liter ( $\mu\text{g}/\text{L}$ ))

$f_{oc}$  – Mass fraction of natural soil organic carbon content (grams (g)-organic carbon/g-soil)

$K_{oc}$  – Soil organic carbon-water partitioning coefficient (milliliters per gram ( $\text{ml}/\text{g}$ ))

$\rho_b$  – Dry Bulk Density (kilograms per liter ( $\text{kg}/\text{L}$ ))

$H_o$  – Henry's Law Constant (dimensionless)

$\theta$  – Total soil porosity (volume of voids/volume total)

$\theta_w$  – Volumetric Water Content (volume of water/volume of soil)

## 6.2 List of Default Values for the Soil Matrix

6.2.1. **Fraction of Organic Carbon in Soil ( $f_{oc}$ ).** 0.006 (0.6%) is the default value for fraction of organic carbon in soil for use in the equation.

6.2.2 **Soil Dry Bulk Density ( $\rho_b$ ).** -1.5  $\text{kg}/\text{L}$  is the default value for dry bulk soil density of 1.5  $\text{kg}/\text{L}$  for use in the equation. Dry bulk-densities for basin-fill deposits typically range from 1.3 to 1.8  $\text{kg}/\text{L}$ . The 1.5  $\text{kg}/\text{L}$  value is within this range.

6.2.3 **Total Soil Porosity ( $\theta$ ).** **0.43 (43%) is the default value for** total soil porosity selected for use in the equation. Its' basis is the default soil particle density ( $\rho_s$ ) of 2.65  $\text{kg}/\text{L}$  [ $\theta = 1 - \rho_b/\rho_s = 0.43$ ].



6.2.4 **Soil Volumetric Water Content ( $\theta_w$ )**. 15% (0.15) is the default value selected for use in the equation. Volumetric water content in basin-fill deposits typically range from 5 to 25 percent. The 15% value is within this range.

### 6.3 Test Methods Required to Change Soil Matrix Default Values

This section specifies procedures and requirements to derive site-specific input parameters for use in the three-phase partitioning equation. Site-specific value substitutions for one or more of the following four input parameters are acceptable: soil dry bulk density, soil organic carbon content, total soil porosity, and soil volumetric water content.

6.3.1 **Deriving soil organic carbon fraction ( $f_{oc}$ )**. ASTM Method D2974 or other methods approved by ADEQ to derive site-specific soil organic carbon fraction values are acceptable. Using uncontaminated soil samples from lithologic zones that are representative of where the soil-vapor contamination is present is necessary to measure site-specific soil organic carbon content. Laboratory methods cannot include inorganic carbon in laboratory measurements.

6.3.2 **Deriving soil dry bulk density ( $\rho_b$ )**. ASTM Method D2049 or D2937 or other methods approved by ADEQ to derive site-specific soil bulk density values are acceptable.

6.3.3 **Deriving total soil porosity ( $\theta$ )**. ASTM Method D4404 or other methods approved by ADEQ to derive site-specific total soil porosity values are acceptable.

6.3.4 **Deriving soil volumetric water content ( $\theta_w$ )**. ASTM Method D2216 or other methods approved by ADEQ to derive soil volumetric water content values are acceptable.

### 6.4 List of Chemical Default Values ( $K_{oc}$ and $H_o$ ) for Selected VOCs

The VOCs listed in the following table provide soil organic carbon-water partitioning coefficients ( $K_{oc}$ ) and dimensionless Henry's Law constants ( $H_o$ ). ADEQ accepts these values, taken from *Soil Screening Guidance* (US EPA, 1996), for use in the three-phase partitioning equation. The chemicals shown are not a complete list of all potential VOCs encountered in contaminant releases, but represent those commonly encountered, those with greater potential to exist in the vapor phase, or those with greater toxicity relative to other VOCs.

Alternative  $K_{oc}$  and  $H_o$  values listed on the following table are substitutions for the values listed in the table on the next page when those alternative values more accurately represent conditions encountered at a site. Sources for these values may be obtained from the *Superfund Chemical Data Matrix* (US EPA, most current editions) and the EPA's

most recent version of Estimation Programs Interface Suite™ available at <http://www.epa.gov/opptintr/exposure/pubs/episuite.htm>.

Alternative  $K_{oc}$  and  $H_o$  values based on scientific literature are subject to ADEQ approval.

Table 6.1. List of Chemical Default Values for Selected VOCs

Compound	$K_{oc}$ (L/kg) <sup>1</sup>	$H_o$ (dimensionless) <sup>2</sup>
Benzene	5.89E+01	2.28E-01
Bromodichloromethane	5.50E+01	6.56E-02
Bromoform	8.71E+01	2.19E-02
Carbon disulfide	4.57E+01	1.24E+00
Carbon tetrachloride	1.74E+02	1.25E+00
Chlorobenzene	2.19E+02	1.52E-01
Chloroform	3.98E+01	1.50E-01
1,2-Dibromoethane (EDB)	2.81E+01	2.90E-02
1,1-Dichloroethane	3.16E+01	2.30E-01
1,2-Dichloroethane (DCA)	1.74E+01	4.01E-02
1,1-Dichloroethene	5.89E+01	1.07E+00
cis-1,2Dichloroethene	3.55E+01	1.67E-01
Trans-1,2-Dichloroethene	5.25E+01	3.85E-01
1,2-Dichloropropane	4.37E+01	1.15E-01
1,3-Dichloropropene	4.57E+01	7.26E-01
Ethyl benzene	3.63E+02	3.23E-01
Methyl bromide	1.05E+01	2.56E-01
Methylene chloride	1.17E+01	8.98E-02
Styrene	7.76E+02	1.13E-01
1,1,2,2-Tetrachloroethane	9.33E+01	1.41E-02
Tetrachloroethene (PCE)	1.55E+02	7.54E-01
Toluene	1.82E+02	2.72E-01
1,1,1-Trichloroethane	1.10E+02	7.05E-01
1,1,2-Trichloroethane	5.01E+01	3.74E-02
Trichloroethene (TCE)	1.66E+02	4.22E-01
1,2,4-Trimethylbenzene	3.72E+03	2.30E-01
1,3,5-Trimethylbenzene	8.19E+02	3.20E-01
Vinyl acetate	5.25E+00	2.10E-02
Vinyl chloride	1.86E+01	1.11E+00
Xylenes (total) <sup>3</sup>	3.86E+02	2.76E-01

Ref: U.S. EPA Soil Screening Guidance: User's Guide, 2<sup>nd</sup> Edition (July 1996)

<sup>1</sup> -  $K_{oc}$  = organic carbon partition coefficient

<sup>2</sup> -  $H_o$  = Dimensionless Henry's Law Constant ( $HLC[atm \cdot m] \cdot 41(25^\circ C)$ )

<sup>3</sup> -  $K_{oc}$  and  $F_{oc}$  values for total Xylenes represent average of values for *ortho*-, *meta*-, and *para*-Xylenes.

Supplied below are formula air unit conversions:

$$\text{ug/m}^3 = \text{ppbv} \times (\text{Molecular Weight}) / 24.45$$

$$\text{ppbv} = \text{ug/m}^3 \times 24.45 / (\text{Molecular Weight})$$

For example: 2.5 ppbv Benzene x 78.11 / 24.45 = 7.99 ug/m<sup>3</sup>

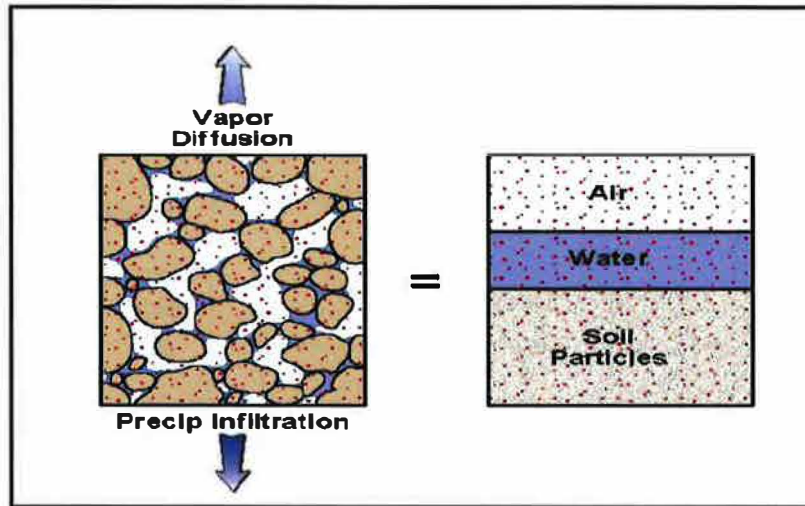
(Standard Condition: 1 atm, 25°C)

ppbv = parts per billion by volume  
 ppmv = parts per million by volume  
 1 ppmv = 1,000 ppbv  
 1 m<sup>3</sup> = 1,000 Liters  
 1 mg = 1,000 ug  
 1 mg/m<sup>3</sup> = 1,000 ug/m<sup>3</sup> = 1 ug/Liter

6.5 Inappropriate Situations in which to apply the Three-Phase Partitioning Equation to calculate total contaminant concentrations in soil

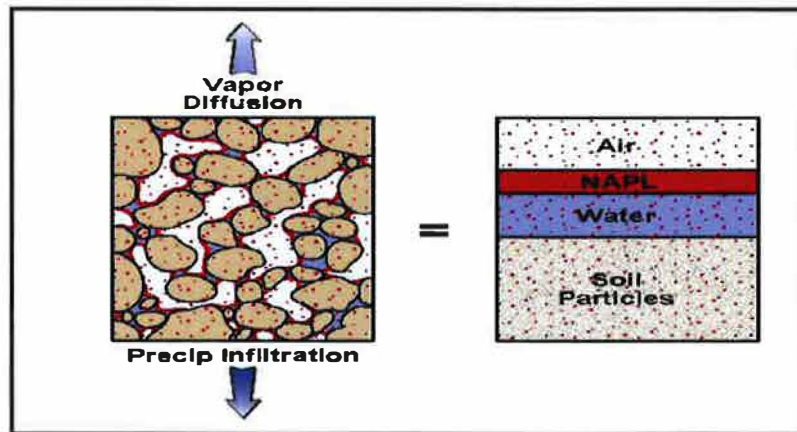
6.5.1 The Presence of NAPL

Section 6.1 indicates that the three-phase partitioning equation is not applicable when NAPL is present. The following diagrams illustrate this inapplicability:

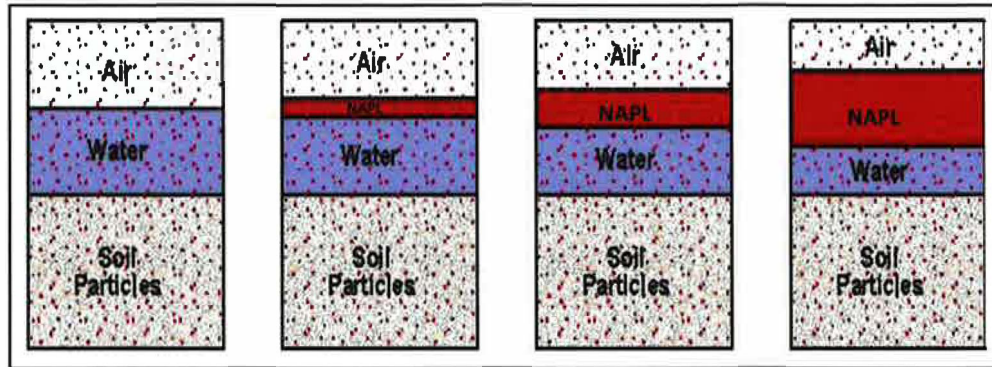


The red dots represent contamination. The red dots placed on the soil grains represent the sorbed phase contamination. The red dots placed on the soil moisture represent the dissolved phase contamination. The red dots placed in the open spaces represent the vapor phase contamination.

If a vapor sample was collected in this type of situation, where there are only 3 phases present, the 3-phase partitioning equation could be used to calculate a total contaminant concentration in the soil. The next diagram is the same as the previous with NAPL added.



The 3-phase partitioning equation is not applicable in this type of situation. This next diagram helps explain why this is so.



<b>Vapor Conc 1</b>	<b>=</b>	<b>Vapor Conc 2</b>	<b>=</b>	<b>Vapor Conc 3</b>	<b>=</b>	<b>Vapor Conc 4</b>
<b>Dissolved Conc 1</b>	<b>=</b>	<b>Dissolved Conc 2</b>	<b>=</b>	<b>Dissolved Conc 3</b>	<b>=</b>	<b>Dissolved Conc 4</b>
<b>Adsorbed Conc 1</b>	<b>=</b>	<b>Adsorbed Conc 2</b>	<b>=</b>	<b>Adsorbed Conc 3</b>	<b>=</b>	<b>Adsorbed Conc 4</b>
<b>Total Conc.1</b>	<b>&lt;</b>	<b>Total Conc 2</b>	<b>&lt;</b>	<b>Total Conc 3</b>	<b>&lt;</b>	<b>Total Conc 4</b>

The key to understanding the above diagram is first understanding the concept of saturation with respect to contamination in a given volume of soil. Saturation is a comparison between the degree to which something is dissolved, absorbed, or volatilized and the maximum dissolution, adsorption, or volatilization, respectively, possible.

When adding a contaminant to a given volume of soil, that contaminant, over time, will separate and equilibrate into the vapor, dissolved and sorbed phases. Each phase, though, can only accept so much contamination. Once these three phases accept the maximum possible amount of contamination, they will not accept additional contamination and is in a state of saturation. When adding a contaminant to a given volume of soil already saturated with that contaminant, the additional contaminant will remain as Non-aqueous phase liquid contamination.

Example:

Please consider the four situations depicted in the diagram above. The saturation value for PCE in a typical Arizona soil is about 61 mg/kg. A PCE vapor concentration from the 1<sup>st</sup> volume of soil plugged into the 3-phase partitioning equation would result in a total contaminant concentration of 61 mg/kg – which is a true value for that volume of soil.

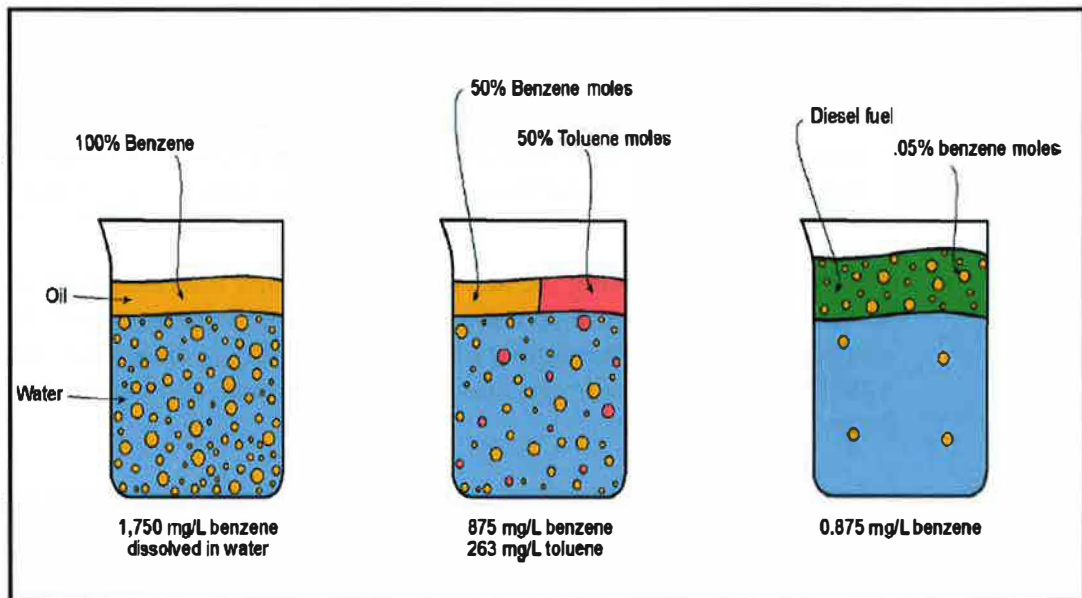
Now consider a vapor sample collected from soil volume #3. A PCE vapor concentration from the 3<sup>rd</sup> volume of soil plugged into the 3-phase partitioning equation would still result in a total contaminant concentration of 61 mg/kg - which is not a true value for that soil volume #3.

Vapor samples collected from each of the volumes of soil depicted here have the same concentrations because the volumes of soil are at or over their saturation

limit of 61 mg/kg PCE. The sorbed, dissolved and vapor phases in all of the volumes of soil cannot accept any more contamination. Calculating a total contaminant concentration for soil volumes 2, 3 and 4 using only vapor data will not yield an accurate result.

### 6.5.2 Single vs Multiple Chemical Contaminant Mix

The presence of NAPL is not the only factor to be aware of when using soil vapor data to calculate total contaminant values. Multiple chemical mixes are also a consideration. Saturation values for chemicals change when a contaminant mix has additional chemicals added.



**Adding additional chemicals to the contaminant mix changes individual chemical saturation values.**

To illustrate how saturation values change when multiple chemicals are in the contaminant mix, consider these three beakers with different combinations of chemicals in them.

The first beaker contains only one chemical in the contaminant mix - benzene. The water can only dissolve so much contamination before a state of saturation occurs. Since this beaker contains benzene as the sole contaminant, 1,750 mg/L of benzene dissolves into the water – this represents the benzene saturation value when no other chemical is present in the contaminant mix.

The second beaker contains two chemicals in the contaminant mix – benzene and toluene in equal molar amounts. No matter how many chemicals are in the contaminant mix, the water can still only dissolve the same amount of contamination as the first beaker before a state of saturation occurs. Since there are equal molar amounts of benzene and toluene in the contaminant mix, an equal amount of benzene and toluene moles dissolve in the water. This effectively cuts

the amount of dissolved benzene in half compared to the first beaker. The saturation value for benzene has changed compared to the first beaker.

The third beaker contains diesel fuel for the contaminant mix. Diesel fuel is composed of several dozen chemicals. In this example, the diesel fuel contains .05% benzene moles. This means that the water in this beaker will only contain a dissolved benzene concentration of 0.875 mg/L ( $1,750 \text{ mg/L} \times .05\% = 0.875 \text{ mg/L}$ ). 0.875 mg/L represents its saturation value for this contaminant mix.

Although this illustration focuses on the dissolved phase, the same concept holds true for the vapor phase. This is an important concept with respect to using the 3-phase partitioning equation. One needs to know the contaminant mix concentration in order to derive saturation values for individual chemicals. If only vapor sample collection occurs in places of saturation value exceedances, calculated total contaminant concentrations will be inaccurate.

## 7. Procedure References

7.1 Karichoff, S.W., D.S. Brown, and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. *Water Resources Research* 13, no. 3: 241–248.

7.2 Luo, H., P. Dahlen, P. Johnson, T. Creamer, T. Peargin, P. Lundegard, B. Hartman, L. Abreau, and T. McAlary. 2006. “Spatial and Temporal Variability in Hydrocarbon and Oxygen Concentrations Beneath a Building Above a Shallow NAPL Source.” Presented at Remediation of Chlorinated and Recalcitrant Compounds, Monterey, Calif.

7.3 U.S. EPA Soil Screening Guidance: User’s Guide, 2<sup>nd</sup> Edition (July 1996)

7.4 Vapor Intrusion Pathway: A Practical Guideline, January 2007, Interstate Technology and Regulatory Council.

### Other useful references

Atlantic RBCA Version 2.0 for Petroleum Impacted Sites in Atlantic Canada, User Guidance, Appendix 9 – Guidance for Soil Vapor and Indoor Air Monitoring Assessments

California Regional Water Quality Control Board, California Department of Toxic Substances Control. Advisory – Active Soil Gas Investigations January 28, 2003. Hartman, Blayne (2006). Part 4 – “How to Collect Reliable Soil-Gas Data for Risk-Based Applications, Specifically Vapor Intrusion: Updates on Soil-Gas Collection and Analytical Procedures.” LUSTLine Bulletin 53 September 2006

Wilson, L. H., P. C. Johnson, and J.R. Rocco (2005). Collecting and Interpreting Soil Gas Samples from the Vadose Zone: A Practical Strategy for Assessing the Subsurface-

Vapor-to-Indoor-Air Migration Pathway at Petroleum Hydrocarbon Sites. API Soil Gas Sampling May 2005 Pre-Publication Version.



## Attachment 1

### *Vacuum Conversion Table*

Vacuum	In Hg (rel)	ft H <sub>2</sub> O (rel)	Torr (abs) mm Hg (abs)	mbar (abs)	psia (abs)
0%	0.00	0.00	760.0	1013.3	14.70
10%	2.99	3.39	684.0	911.7	13.23
20%	5.98	6.78	608.0	810.4	11.76
30%	8.98	10.17	532.0	709.1	10.29
40%	11.97	13.56	456.0	607.8	8.82
50%	14.96	16.95	380.0	506.5	7.35
60%	17.95	20.34	304.0	405.2	5.88
70%	20.94	23.73	228.0	303.9	4.41
80%	23.94	27.12	152.0	202.6	2.94
90%	26.93	30.51	76.0	101.3	1.47
91%	27.23	30.85	68.4	91.2	1.32
92%	27.53	31.19	60.8	81.0	1.18
93%	27.83	31.53	53.2	70.9	1.03
94%	28.13	31.87	45.6	60.8	0.88
95%	28.42	32.21	38.0	50.6	0.73
96%	28.72	32.54	30.4	40.5	0.59
97%	29.02	32.88	22.8	30.4	0.44
98%	29.32	33.22	15.2	20.3	0.29
99%	29.62	33.56	7.6	10.1	0.15
99.10%	29.65	33.59	6.8	9.1	0.13
99.20%	29.68	33.63	6.1	8.1	0.12
99.30%	29.71	33.66	5.3	7.1	0.10
99.40%	29.74	33.70	4.6	6.1	0.09
99.50%	29.77	33.73	3.8	5.1	0.07
99.60%	29.80	33.76	3.0	4.1	0.06
99.70%	29.83	33.80	2.3	3.0	0.04
99.80%	29.86	33.83	1.5	2.0	0.03
99.90%	29.89	33.87	0.8	1.0	0.01
<100%	29.92	33.90	0.0	0.0	0.00

Pressure measurement units:

In Hg - inches of mercury

ft H<sub>2</sub>O – feet of water

mm Hg – millimeters of mercury

mbar – millibars

psia – pounds per square inch absolute

Attachment 2

## Arizona Department of Environmental Quality QA/QC checklist for Soil Vapor Sampling

### Sampling Company

- 1 Date: \_\_\_\_\_ Start time: \_\_\_\_\_
- 2 Company Name: \_\_\_\_\_ Sampler's Name: \_\_\_\_\_
- Consulting Firm:**
- 3 Company Name: \_\_\_\_\_ Project Name: \_\_\_\_\_
- 4 Project Manager: \_\_\_\_\_ Project Number: \_\_\_\_\_

### Well's Information

- 5 Location: \_\_\_\_\_ Client ID: \_\_\_\_\_ Permanent  Temporary
- 6 Address: \_\_\_\_\_
- 7 ADEQ File Identification #(s) \_\_\_\_\_
- 8 Describe the probe location: \_\_\_\_\_
- 9 Probe Depth: \_\_\_\_\_ inch Probe ID: \_\_\_\_\_ inch **Probe volume: 0 inch<sup>3</sup> ( 0 ) mls**
- 10 Probe type: Tygon  Teflon  Vinyl  PVC  Metal  Other: \_\_\_\_\_
- 11 Is probe tested in the lab before installed? Y  N  NA  Don't know
- 12 Comments: \_\_\_\_\_

### Weather Conditions

- 13 Temperature: \_\_\_\_\_ C°  F°
- 14 Has there been significant rain or snow recent to the sampling event? Y  N
- 15 If Yes to Question 14 Date \_\_\_\_\_ Amount of Precipitate \_\_\_\_\_ inches

### Soil Conditions Information

- 16 Was a soil sample collected and analyzed for volumetric moisture content? Y  N  attach results if yes  
If yes, attach results  
If no, is the apparent moisture content dry  moist  saturated
- 17 What is soil type encountered at sample location? \_\_\_\_\_
- 18 Was sample collected beneath a surface cover (e.g. parking lot, sidewalk, road, building, other)? Y  N
- 19 Describe the surface cover, if any \_\_\_\_\_
- 20 Was the sample collected near a subsurface conduit? Y  N

Describe subsurface conduit, if any \_\_\_\_\_

### Sampling Train

- 21 Sample container: Canister : 1.0 L  6.0 L  Silanized: Y  N   
Other: \_\_\_\_\_  
Tedlar bag: Y  N  Gas tight syringe Y  N
- 22 Flow restrictor: On: 1000 mL/min  500 mL/min  200 mL/min  Other: \_\_\_\_\_  
One min = Taking one minute to fill one liter canister.
- 23 Tubing type: Tygon  Teflon  Vinyl  PVC  Other: \_\_\_\_\_
- 24 Tubing used from probe top to canister: Length: \_\_\_\_\_ inch ID \_\_\_\_\_ inch
- 25 **Tubing volume: 0 inch<sup>3</sup> ( 0 ) mls**
- 26 Are all parts of Sampling Train tested in the lab before sampling? Y  N

**Probe Purging Before Sampling**

- 27 Total volume: probe(v) + tubing(v) = Probe volume 0 + Tubing volume 0 = 0 ml
- 28 Total volume to be purged (ml): 1x 0  1.5x 0  2x 0  3x 0
- 29 Purging pump #: \_\_\_\_\_ Purging flow rate: \_\_\_\_\_ ml/min Purging time: \_\_\_\_\_ mins \_\_\_\_\_ seconds
- 30 Gauge reading: < 5 inHg  Other: \_\_\_\_\_ Comments: \_\_\_\_\_
- 31 Syringe Purging: NA  Dedicated Syringe  Re-used Surlinge  Volume \_\_\_\_\_
- 32 Is there condensation evident in the sampling train? Y  N
- 33 Post sample collection - Is there condensation evident in the sampling container? Y  N
- 34 **Leak Test** Y  N  If Yes, fill in the blanks blow: \_\_\_\_\_
- 35 Tracer compound: \_\_\_\_\_ Trade name: \_\_\_\_\_ Tested before use: Y  N
- 36 Locations applied: Probe top  Sampling train:  Other: \_\_\_\_\_
- 37 **Field Duplicate** Y  N  If Yes, fill in the blanks blow: \_\_\_\_\_
- 38 Used the Duplicate Splitter? Y  N  If no, describe the procedure: \_\_\_\_\_

**Other Information**

- 39 Identify the equipment and method used to install probe and collect sample \_\_\_\_\_
- 40 What was the equilibration time between probe installation and withdrawal of any soil vapor? \_\_\_\_\_
- 41 Sample storage /shipping temperature \_\_\_\_\_
- 42 Sample storage /shipping container \_\_\_\_\_
- 43 Sample transportation mode(s) \_\_\_\_\_
- 44 Was an equipment blank taken? Y  N  Was Tank air or Nitrogen used? \_\_\_\_\_  
**Note: Ambient air should not be used**
- 45 Was a field blank taken? Y  N
- 46 Was a background (upwind ambient) sar Y  N
- 47 Are there any potential VOC sources other than the identified release nearby?  
Groundwater/active fueling station/ dry cleaners/ dry wells/ other - please describe \_\_\_\_\_

**48 Well (Probe) Inspection Note:**

\_\_\_\_\_

\_\_\_\_\_

## Attachment 3

### 1.0 Directive Owner (Person Responsible for Implementing & Maintaining the Directive – Title/Unit/Section/Division)

WPD Environmental Associate Hydrogeologist

### 2.0 Audience

Stakeholders conducting Hazardous Waste, WQARF, UST and other remediation or corrective action

### 3.0 Communication & Training

The Waste Programs Division Environmental Associate Hydrogeologist will conduct a class within 45 days of the policy effective date and annually thereafter insure that employees that deal with soil vapor issues are familiar with the policy's content, including any procedures for internal compliance, audit and review. Concurrent with the 2<sup>nd</sup> class and annually thereafter, the Environmental Associate Hydrogeologist will review the policy for any needed changes or updates.

### 4.0 Compliance & Audit Plan

Prior to each annual review, the Environmental Associate Hydrogeologist will arrange for a records review or similar inquiry to estimate the number of corrective actions that have involved issues with soil vapor contained in the current policy. Each annual review shall evaluate whether applicable WPD personnel and external stakeholders are aware of the policy and explore methods to increase awareness if needed.


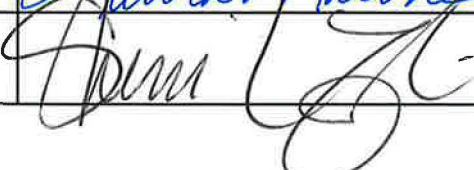
### 5.0 Review & Revision

This directive will be reviewed after the first year on an annual basis.

### 6.0 Additional Documentation

This policy complements the Site Investigation Guidance Manual.

### 7.0 Approved by:

Title	Name	Signature	Date
WPD Division Director	Laura Malone		3/31/17
Administrative Counsel (as to form)	Sherri Zendri		4/21/17

**11.0 Historical Note**

*[Describes the changes or updates to a directive, which serves as a reference for the reader to understand any past changes.]*

Date	Change	Ref. Section
July 10, 2008	Issued	
May 19, 2011	Revised	Grammatical changes and procedure clarifications
April 21, 2017	Revised	Grammatical changes and added Section 6.5

