United States Environmental Protection Agency

EPA/600/R-14/277

Engineering Issue

Challenges in Bulk Soil Sampling and Analysis for Vapor Intrusion Screening of Soil

TABLE OF CONTENTS

1 INTRODUCTION AND PURPOSE

This Engineering Issue Paper (EIP) discusses the benefits and limitations of using bulk soil samples to assess vapor intrusion (VI) risks from soil containing volatile organic compounds (VOCs). Analyses of factors controlling the VOC concentration distribution in soil and the sensitivity of current laboratory methods are used to show that while bulk soil sampling and analysis may help delineate source areas and determine the gross mass of contamination present in a source area, they cannot adequately assess potential VI exposures for most VOCs in undisturbed soil or in soil remaining after excavation. To address this information gap, this EIP also describes alternatives for monitoring soil VOCs and for enhancing remedies at sites where soil excavation is being considered or used for VOC-contaminated soils.

The U.S. Environmental Protection Agency (EPA) EIPs are a series of technology transfer documents that summarize the latest available information on selected treatment and site remediation technologies and related issues. EIPs are designed to help remedial project managers, on-scene coordinators, contractors, and other site managers understand the types of data and site characteristics needed to evaluate a technology for potential applicability to their specific sites. Each EIP is developed in conjunction with a small group of EPA scientists and with outside consultants and relies on peer-reviewed literature, EPA reports, web sources, current ongoing research, and other pertinent information.

Information in this document is for technical support and does not represent EPA policy or guidance. The reader is expected to have a basic technical background on the VI exposure pathway and how to use groundwater and soil gas data in the context of a VI investigation. For more information on the VI pathway, please refer to the EPA VI webpage.[1]

---

[1] http://www.epa.gov/oswer/vaporintrusion/.

2 BACKGROUND

The 2002 draft EPA VI guidance and the 2015 EPA *Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway* recommend against using bulk soil VOC concentrations for screening the VI pathway or for deciding when no further action is needed at VI sites (U.S. EPA, 2002b; 2015). The reasons for this guidance include VOC losses during bulk soil sampling and analysis and uncertainties associated with soil partitioning calculations.[2] However, both documents note that bulk soil samples are useful for determining the chemical composition and general location of contamination in soil including whether nonaqueous phase liquid (NAPL) is present.

VOC losses during sampling and analysis may be minimized by submersing bulk soil samples in methanol (U.S. EPA, 1996a; 2002c), but methanol's presence in the sample leads to higher analytical detection and reporting limits (i.e., lower sensitivity). Heterogeneity in soil properties poses additional challenges for bulk soil sampling because of the difficulty obtaining representative samples given their size (usually about 50 grams) relative to the scale of contaminant concentration heterogeneities and the amount of soil mass to be evaluated (Interstate Technology & Regulatory Council [ITRC], 2012). Another difficulty is that VOC bulk soil concentrations corresponding to soil vapor concentrations protective of the VI pathway can be lower than typical bulk soil analytical method detection and reporting limits for several common VOCs, including trichloroethylene (TCE) and perchloroethylene (PCE).

To better understand the difficulties described above of bulk soil sampling, this document provides information on:

- how contaminants may be distributed among the solid, liquid, and gaseous phases in bulk soil;[3]
- how partitioning equations can be used to calculate bulk soil concentrations from soil vapor screening levels;
- typical laboratory method detection limits (MDLs) for bulk soil analysis; and

3 HOW HETEROGENEITY IN SOIL PROPERTIES AFFECTS CONTAMINANT DISTRIBUTION IN SOIL. RELATIONSHIPS AMONG VAPOR AND OTHER PHASES IN SOIL (PHASE PARTITIONING)

VOCs in vadose zone soils partition among the solid, aqueous, and gaseous (vapor) phases and may also be present as a fourth, separate NAPL (Feenstra et al., 1991; Feenstra, 2003; U.S. EPA, 2012a). Methods for calculating bulk soil concentrations that correspond to soil vapor concentrations for VI assessment can be developed by applying commonly accepted equilibrium partitioning relationships. Although equilibrium between phases may not exist in the field, for example, where biologically degradable compounds such as petroleum hydrocarbons (PHCs) are present or where processes induce relatively fast contaminant transport (e.g., a soil vapor extraction [SVE] system), equilibrium partitioning is a widely used simplification in subsurface investigations and modeling studies.

---

[2] Phase partitioning calculations are used to calculate groundwater vapor intrusion screening levels (VISLs); however, VOC losses during groundwater sampling are less likely than losses during bulk soil sampling and analysis (Maskarinec et al., 1989; U.S. EPA, 2002a).

[3] In this paper, bulk soil concentration refers to the total mass of a contaminant in a specific mass of dry soil, most often with units of mg/kg (parts per million or ppm) or µg/kg (parts per billion or ppb). Also known as whole or total soil concentration, a bulk soil concentration includes contaminants that are sorbed to or within the soil mass (solid phase), dissolved in soil moisture (aqueous phase), present as vapors in soil gas (vapor phase), and present as a pure liquid (nonaqueous phase).

The mass of a VOC associated with the soil solid phase is controlled by the amount of organic carbon in the soil to which VOCs adsorb,[4] and the VOC's affinity for soil organic carbon, which is typically expressed in terms of the VOC's organic carbon partition coefficient (K_{oc}). The mass of VOCs associated with the soil aqueous and vapor phases is determined by the soil moisture content, the air-filled soil porosity, and the VOC's equilibrium partitioning relationship between vapor and water, as expressed by its Henry's Law constant (HLC) (Thomas, 1990).

If NAPLs are not present and the VOC concentrations in the soil phases are at equilibrium, the bulk soil concentration (C_{bulk}) corresponding to a particular soil vapor phase concentration (C_{vapor}) of interest can be derived from the soil-water partition equations and default soil properties provided in EPA's *Soil Screening Guidance Technical Background Document* (U.S. EPA, 1996b) as follows:

$$C_{bulk} = \frac{C_{vapor}}{HLC\ \rho_b}(K_{oc}\ f_{oc}\ \rho_b + \theta_w + HLC\ \theta_a) \qquad \text{Eq. 1}$$

where

C_{bulk} = bulk soil concentration (mass/mass), site specific
C_{vapor} = soil vapor concentration (mass/volume), site specific
HLC = dimensionless Henry's Law constant, chemical specific
ρ_b = dry soil bulk density (mass/volume), default = 1,500 kg/m^3
K_{oc} = organic carbon partition coefficient (volume/mass), chemical specific
f_{oc} = fraction of organic carbon in soil (mass/mass), default = 0.006 (0.6%)
θ_w = water-filled soil porosity (volume/volume), default = 0.15
θ_a = air-filled soil porosity (volume/volume) = $n - \theta_w$
n = total porosity (volume/volume), default = 0.43

These equilibrium partitioning relationships are also used in calculating the EPA Regional Screening Levels (U.S. EPA, 2014a).

If a pure-phase NAPL is present in the soil and the soil is considered to be a closed system, the vapor phase concentration (C_{vapor}), which is typically expressed as the mass of VOC divided by the total volume of the vapor phase, can be related to the pure or NAPL phase vapor pressure (Pv) by rearranging the ideal gas law to the following:

$$C_{vapor,NAPL} = \frac{MW \cdot P_v}{R \cdot T} \qquad \text{Eq. 2}$$

where

MW = molecular weight (g/mol)
P_v = vapor pressure (mmHg)
R = universal gas constant (62.36367 x 10^{-3} m^3 · mm Hg · K^{-1} · mol^{-1})
T = temperature (298.15°K = 25°C)

The saturated bulk soil concentration ($C_{bulk,sat}$) above which NAPL is likely to be present in the soil is calculated by substituting $C_{vapor,NAPL}$ for C_{vapor} in Equation 1 (U.S. EPA, 2002c):

$$C_{bulk,sat} = \frac{C_{vapor,NAPL}}{HLC\ \rho_b}[(K_{oc}\ f_{oc}\ \rho_b) + \theta_w + (HLC\ \theta_a)] \qquad \text{Eq. 3}$$

where all other parameters are as defined above. In this case, the solid, liquid, and gas phases contain the maximum possible mass (at equilibrium) and are considered saturated. In other words, $C_{bulk,sat}$ is the bulk soil concentration that corresponds to the maximum (i.e., saturated) dissolved, sorbed, and vapor VOC concentrations in a soil. Any additional VOC mass would necessarily be present as a NAPL phase and will not result in higher vapor, dissolved, or sorbed concentrations. Note that at or below the saturated bulk soil concentration, most (>85%) of the

---

[4] Organic carbon is usually the dominant sorbent in a soil down to an organic carbon content of about 0.1% (Brusseau, 1994; Rorech, 2001). In very dry soils, VOCs can adsorb to mineral surfaces (Chiou and Shoup, 1985), but this is not usually a significant fraction of the total soil VOC mass because most natural soils are sufficiently moist.

VOC mass is present in aqueous and sorbed phases, whereas at concentrations above the saturated bulk soil concentrations, most of the VOC mass is present in the NAPL.

These relationships are used in Section 4 to calculate bulk soil concentrations corresponding to soil vapor concentrations of interest for VI assessments (i.e., soil vapor screening levels and soil vapor concentrations indicating NAPL is present), which will illustrate both the benefits and limitations of bulk soil sampling for the VI pathway.

4 CHALLENGES IN BULK SOIL SAMPLING AND ANALYSIS

4.1 Volatilization and Degradation Losses

There is a potential for significant losses of VOCs by volatilization, degradation, or a combination of the two when collecting bulk soil samples in the field, during storage prior to analysis, and during subsampling and sample preparation in the laboratory. Studies evaluating soil sampling and analysis protocols have shown that VOC concentrations can be biased low by a factor between 10 and 1,000 when methods to minimize VOC losses are not employed (e.g., U.S. EPA, 1993; 2002a).

Soil sampling using EPA's SW-846 Method 5035 specifies immediate immersion of the soil sample in methanol to minimize volatilization losses and degradation (U.S. EPA, 1996a), but a field technician needs to be vigilant and must work quickly (Indiana Department of Environmental Management, 2012). Additionally, the presence of methanol in the sample reduces analytical sensitivity and elevates MDLs[5] by one or two orders of magnitude. Methanol also is flammable and can be dangerous to transport.

Alternative Method 5035a provides for field sampling with certain sampling devices such as the EnCore and Associated Design & Manufacturing samplers[6,7] that allow analysis using purge-and-trap sample extraction techniques and do not involve methanol preservation (U.S. EPA, 2002a). These devices minimize VOC loss by confining the sample in a sealed zero headspace chamber, with storage for up to 48 hours before laboratory preservation and preparation for analysis. They function well for cohesive, uncemented soils but are not suitable for noncohesive or cemented soils that can cause headspace to develop within the device during or after sampling. The sensitivity of this method is greater than that of the methanol preservation approach, providing lower detection and reporting limits. However, the sample size is small for these devices,[8] so problems of representative sampling remain a limitation.

4.2 Sensitivity of Analytical Methods for Bulk Soil Samples

Bulk soil analytical methods have MDLs typically around 35 µg/kg or higher when methanol is used as a field preservative (e.g., EPA Method 5035; U.S. EPA, 1996a) and about one to two orders of magnitude lower when methanol is not used (e.g., EPA Method 5035a; U.S. EPA, 2002a). Table 1 compares typical MDLs for both analytical methods with bulk soil concentrations corresponding to target subslab soil gas concentrations (i.e., subslab vapor screening levels) from EPA's Vapor Intrusion Screening Level (VISL) Calculator[9] (U.S. EPA, 2014e; 2015). The bulk soil concentrations corresponding to

---

[5] The MDL statistically defines the minimum concentration of a substance that can be detected, with 99% confidence that the analyte concentration is greater than zero. The reporting limit is set by the analytical laboratory above the MDL to accommodate day-to-day variation in laboratory instrument sensitivity. In general, values between the MDL and the reporting limit represent true detections whose concentration cannot be reliably quantified.

[6] http://www.ennovativetech.com/non-methanol-sampling/en-core-sampler-information

[7] http://www.associateddesign.com/catalog.pdf

[8] For example, the EnCore device collects a single 5- or 25-g soil sample, and Associated Design and Manufacturing's device produces 5- and 10-g samples.

[9] EPA's VISL Calculator is available online at www.epa.gov/oswer/vaporintrusion/documents/VISL-Calculator.xlsm.

these subslab vapor screening levels were calculated using Equation 1, default values for soil properties from EPA's Supplemental Soil Screening Guidance (U.S. EPA, 2002c), and the chemical-specific Henry's Law constants (HLC) and soil/organic carbon partition coefficients (K_{oc}) taken from the VISL Calculator and shown in Table 1.

The calculated bulk soil concentrations corresponding to the subslab vapor screening levels are 30 to 80,000 times lower than the Method 5035 methanol MDLs for many VOCs, except for some VOCs that are not very toxic and have high screening levels. These bulk soil concentrations are also below the nonmethanol MDLs for constituents of most concern for VI, including TCE and PCE. Thus, for the VOCs that are typically of concern for the VI pathway, bulk soil samples analyzed using the currently available analytical methods cannot adequately assess VI risks.

Either the nonmethanol or methanol method is capable of evaluating the presence of NAPL sources in soil. Table 1 includes the saturated bulk soil concentrations (in column 6) calculated using Equations 2 and 3, above which NAPL would be expected to be present in the soil; in all cases, these concentrations are orders of magnitude higher than the MDLs. Soil with NAPL generally represents the bulk of the mass of VOCs in the vadose zone sources, so delineating and excavating the NAPL-containing soil represents the greatest opportunity for mass removal and is an appropriate application for bulk soil VOC analysis. The remaining VOCs in unexcavated soil can often be more cost-effectively remediated by polishing steps that may include natural attenuation, SVE, or bioventing; see Section 6 for additional information.

The calculated bulk soil concentrations listed in Table 1 were derived assuming equilibrium partitioning among phases, which is a widely used simplification when evaluating subsurface contaminant distribution, fate, and transport. Equilibrium partitioning is expected when concentrations are steady over time and sufficient time is available for equilibration among phases. In actuality, equilibrium conditions may not exist in the field because the kinetics of phase-transfer mechanisms may be slower than the rate of change in VOC concentrations in response to changes in atmospheric temperature and pressure, infiltration of rainwater, and water table fluctuations. Furthermore, phase partitioning may not be perfectly linear and reversible as the equations assume. For these reasons, the bulk soil concentrations corresponding to screening-level vapor concentrations presented in Table 1 are approximate and may be uncertain (i.e., generally lower than field measured values) by an order of magnitude or more (Carr et al., 2010).

4.3 Heterogeneity of Soil and Contaminant Distribution

Collecting bulk soil samples that represent the bulk VOC concentration in soil can be challenging because of heterogeneity in the soil properties (fraction of organic carbon, porosity, and moisture content) that control the mass of VOCs that can be held by a soil. The spatial scale of soil heterogeneities can vary from a few centimeters to a few meters depending on the origin and composition of the soil. Soil moisture can also vary temporally (Boulding and Barcelona, 1991; Payne et al., 2008). This heterogeneity poses a challenge for estimating average soil concentrations in unexcavated soil, given the typical size (40 g or less) and typical sampling density (often spaced meters apart) of bulk soil samples. VOC vapor concentrations in discrete soil samples may or may not be representative of larger-scale average VOC concentrations. Incremental sampling techniques such as those developed by Hewitt et al. (2008) can

Table 1. Calculated Example Bulk Soil Concentrations Corresponding to Generic Subslab Vapor Screening Levels, NAPL Saturation, and Detection Limits for Selected VOCs

Chemical Name	Target Indoor Air Conc. @ TCR = 1E-06 or THQ = 1 (µg/m³)	Toxicity Basis C/NC	Target Subslab Soil Gas Conc. for AF = 0.03 @ TCR = 1E-06 or THQ = 1 (µg/m³)	Bulk Soil Conc. Corresponding to Target Subslab Soil Gas Conc. (Eq. 1) (µg/kg)	NAPL Phase Vapor Conc. @ 25°C (Eq. 2) (µg/m³)	Saturated (Eq. 3.3) Bulk Soil Conc. (Eq. 3) (µg/kg)	Typical Bulk Soil Method Detection Limit		Mol. Weight (g/mol)	Vapor Pressure (mm Hg)	K_{oc} (m³/kg)	HLC (-)
							Methanol (µg/kg)	Non-methanol (µg/kg)				
Benzene	3.6E-01	C	1.2E+01	5.4E-02	4.0E+08	1.8E+06	3.4E+01	3.7E-01	78	95	0.15	0.23
Carbon Tetrachloride	4.7E-01	C	1.6E+01	7.9E-03	9.5E+08	4.8E+05	3.4E+01	9.4E-01	154	115	0.044	1.1
Chloroform	1.2E-01	C	4.1E+00	8.7E-03	1.3E+09	2.7E+06	3.4E+01	1.1E+00	119	197	0.032	0.15
Dichlorobenzene, 1,2-	2.1E+02	NC	7.0E+03	2.1E+02	1.2E+07	3.6E+05	1.7E+01	5.4E-01	147	1.5	0.38	0.078
Dichlorobenzene, 1,4-	2.6E-01	C	8.5E+00	2.0E-01	1.4E+07	3.3E+05	4.7E+01	6.5E-01	147	1.7	0.38	0.10
Dichloroethane, 1,1-	1.8E+00	C	5.8E+01	8.5E-02	1.4E+09	2.1E+06	3.4E+01	7.2E-01	99	272	0.032	0.23
Dichloroethane, 1,2-	1.1E-01	C	3.6E+00	2.6E-02	4.2E+08	3.0E+06	3.4E+01	1.3E+00	99	79	0.040	0.048
Dichloroethylene, 1,1-	2.1E+02	NC	7.0E+03	3.2E+00	3.3E+09	1.5E+06	2.9E+01	9.2E-01	97	634	0.032	1.1
Ethylbenzene	1.1E+00	C	3.7E+01	3.3E-01	5.5E+07	4.8E+05	3.4E+01	4.0E-01	106	9.6	0.45	0.32
Tetrachloroethane, 1,1,2,2-	4.8E-02	C	1.6E+00	7.2E-02	1.2E+08	5.4E+06	5.0E+01	4.5E+00	168	13	0.095	0.015
Tetrachloroethylene	1.1E+01	C	3.6E+02	4.0E-01	1.7E+08	1.8E+05	3.4E+01	2.1E-01	166	19	0.095	0.72
Toluene	5.2E+03	NC	1.7E+05	1.0E+03	1.4E+08	8.1E+05	3.7E+01	3.4E-01	92	28	0.23	0.27
Trichloroethane, 1,1,1-	5.2E+03	NC	1.7E+05	1.2E+02	8.9E+08	6.3E+05	4.6E+01	1.3E+00	133	124	0.044	0.70
Trichloroethane, 1,1,2-	1.8E-01	C	5.8E+00	8.2E-02	1.7E+08	2.3E+06	7.0E+01	5.9E-01	133	23	0.061	0.034
Trichloroethylene	4.8E-01	C	1.6E+01	2.1E-02	4.9E+08	6.5E+05	5.0E+01	5.2E-01	131	69	0.061	0.40
Vinyl Chloride	1.7E-01	C	5.6E+00	2.2E-03	1.0E+10	3.9E+06	5.5E+01	9.4E-01	63	2980	0.022	1.1
Xylenes	1.0E+02	NC	3.5E+03	4.0E+01	4.8E+07	5.5E+05	3.4E+01	4.2E-01	106	8.4	0.38	0.21

TCR = target cancer risk; THQ = target hazard quotient; AF = subslab to indoor air attenuation factor; C = cancer; NC = noncancer; NAPL = nonaqueous phase liquid; K_{oc} = organic carbon/water partition coefficient; HLC = dimensionless Henry's Law constant.

NOTE: The target indoor air subslab soil gas concentrations were calculated using EPA's Vapor Intrusion Screening Level Calculator, which is available at www.epa.gov/oswer/vaporintrusion/documents/VISL-Calculator.xlsm. The bulk soil concentrations corresponding to the target subslab soil gas concentrations were calculated using Equation 1. The NAPL phase vapor concentrations were calculated using Equation 2. The saturated bulk soil concentrations were calculated using Equation 3. All bulk soil concentrations in Table 1 were calculated as example values only for the purposes of this document. They were calculated using default values from U.S. EPA (1996b; 2002c) for the variables listed in Equations 1 through 3, which may vary from actual site-specific conditions. The resulting values should not be applied to specific sites without a thorough review of the assumptions and defaults on which they are based.

minimize the influence of heterogeneity (ITRC, 2012) but are subject to the same challenges as other soil samples preserved in methanol, including detection limits that are not low enough to fully assess VI risk.

In summary, representative average bulk soil concentrations can be difficult to achieve for a given volume of soil because of the spatial heterogeneity of VOC concentrations in the soil, the volume of typical soil samples relative to the soil volume that needs to be characterized, and issues with VOC losses during sampling and analysis.

5 ALTERNATIVE OPTIONS FOR MONITORING VOCS IN BULK SOIL

Despite its limitations, bulk soil sampling can help delineate heavily contaminated (e.g., source) areas and confirm that high-VOC soil has been removed prior to other management options such as polishing remediation techniques or redevelopment with appropriate building mitigation systems. Other methods to define soil source area or excavation limits include visual inspection, field headspace screening, and soil gas monitoring.

5.1 Visual Inspection for Black Stains (PHCs) or Sudan IV Dye Testing (PHCs and Chlorinated Solvents)

PHCs associated with crude oil can readily be identified by a characteristic black staining of soil. The presence of chlorinated solvents and free-phase fuel products that do not exhibit black staining can be detected by testing with Sudan IV dye. Soil is placed in a clear glass jar with water, and Sudan IV dye is added to color the hydrocarbons red, which allows them to be distinguished from water (U.S. EPA, 2004).

5.2 Field Headspace Screening of Soil Samples

Field headspace screening can be conducted by placing 0.5 kg to 2 kg of excavated soil (or soil from sidewalls or floors of excavated area) to about half fill a sealed container and measure the VOCs in the headspace over time (Fitzgerald, 1993; U.S. EPA, 1997; South Dakota Department of Environment and Natural Resources, 2003). If pure-phase hydrocarbons are present and the VOC concentration in the headspace drops well below the NAPL vapor concentration shown in Table 1, one can check for rebound by closing the container, waiting a few hours or agitating it for a few minutes, and retesting. If after a few hours the VOC concentrations are back up above the NAPL vapor concentration, the soil likely has NAPL source material, and excavation of such material will significantly reduce the overall VOC mass in the soil. Temperature, soil and container volume, equilibration time, and inertness of the container material all need to be specified and kept as consistent as possible during field headspace screening to minimize error and obtain consistent and comparable results (Fitzgerald, 1993; U.S. EPA, 1997; South Dakota Department of Environment and Natural Resources, 2003).

Field screening of headspace and soil gas probe samples for total hydrocarbons can be conducted using a photoionization detector (PID) for chlorinated VOCs or a flame ionization detector (FID) for PHCs. A field gas chromatograph can be used to measure individual VOCs. In the vicinity of a NAPL, PID or FID readings will likely go off-scale (e.g., > 10,000 ppmv on a PID), or the FID may flame out because there is not enough oxygen. The range of these portable instruments is several orders of magnitude, so they are easily sensitive enough for source delineation. For example, the ITRC guidance on petroleum VI recommends a value of 500 ppmv as a PID/FID level indicative of a NAPL source and provides additional useful indicator criteria for identifying the presence of PHCs in soil (ITRC, 2014), as does Mass DEP (1996).

5.3 Soil Gas Monitoring

Soil gas monitoring probes installed into undisturbed soil or the intact soil in excavation sidewalls and floors is commonly used as a line of evidence to assess VI risks (U.S. EPA, 2015) and can be used to determine whether further excavation is needed. The probes need to be installed at a sufficient depth to pass a leak test to ensure they are truly sampling soil gas. The soil gas samples collected with this method can be analyzed with methods (such as TO-15 and TO-17) that have MDLs sufficiently low to directly assess VI potential. Soil gas samples can be analyzed in the field with a mobile laboratory/instrument or shipped for analysis in a fixed laboratory.

However, pausing excavation operations to sample and analyze soil gas may not be practicable. Leaving an excavation open for a long period may pose safety concerns and affect the excavation schedule and cost. Additionally, soil vapor concentrations measured in an excavation may not be representative of those that may arise when buildings are constructed. There are also complications in obtaining representative soil gas samples if the soils are wet; soils under buildings are likely to be drier than surrounding open areas subject to recharge. Furthermore, soil vapor concentration profiles in the absence of buildings may differ considerably from profiles that may develop after a building is constructed.

6 OPTIONS FOR ENHANCING SOIL EXCAVATION REMEDIES TO REDUCE VAPOR INTRUSION RISK

Soil excavation commonly is used to remediate VOCs and can be the most practical and cost-effective remedy where high concentrations of VOCs are present and accessible at shallow depths (~20 ft or less). A key parameter in designing an excavation remedy is the bulk soil concentration that can remain unexcavated, which is used to define the extent of excavation. For example, EPA has developed and published bulk soil screening levels for the groundwater, direct ingestion, outdoor air inhalation (of VOCs and fugitive dust), and dermal contact exposure pathways (e.g., U.S. EPA, 1996b; 2002a).

As previously described, however, bulk soil sampling and analysis is not sufficiently sensitive for most VOCs to adequately evaluate the protectiveness of an excavation remedy for indoor air exposures through the VI pathway. An alternative approach for soil may be to excavate as much source material (e.g., NAPL-containing soil) as possible and employ polishing remedies to bring the unexcavated soil concentrations down to levels that will not lead to a VI concern. The following examples of subsurface remediation technologies can be used to augment or polish soil excavation remedies (Suthersan, 1997; Nyer et al., 2001; Van Deuren et al., 2002):

- SVE (U.S. EPA, 2013) to remove VOCs from permeable soils above the water table, especially after NAPL is removed. If the soil permeability is too low for SVE, excavation to the extent possible may be the best option for contaminants that do not readily biodegrade (Suthersan, 1997; Nyer et al., 2001; Van Deuren et al., 2002);
- natural attenuation, bioventing, or both to aerobically biodegrade PHCs in place (U.S. EPA, 1994; 2012b; 2014c);
- enhanced degradation to anaerobically degrade chlorinated hydrocarbons in place (U.S. EPA, 2014b);
- backfill areas of soil excavation with low-permeability, fine-grained material or other material to create a barrier or decrease the effective mass flux rate from the unexcavated soil to the surface; and
- building mitigation systems such as active subslab depressurization or ventilation, or vapor barrier systems (U.S. EPA, 2008; 2014d).

PHC vapor concentrations in shallow aerobic (oxygenated) soils will biodegrade naturally after excavation of NAPL, especially if the soil surface is left open to the atmosphere for a few years prior to redevelopment (Trombetta, 2008). PHCs in somewhat deeper soils or soil below buildings or other low-permeability ground cover where oxygen may be limited may benefit from a bioventing system to bring additional oxygen to the subsurface.

Chlorinated hydrocarbons like TCE and PCE are more difficult to biodegrade naturally in the vadose zone because they usually require anaerobic (low oxygen) conditions that can be difficult to maintain above the water table. Biodegradation of chlorinated hydrocarbons often requires adding nutrients, catalysts, reducing agents, and other such supplements to maintain anaerobic conditions and enhance biodegradation.

In some cases, polishing techniques may not be needed if sufficient VOC mass is removed and the remaining mass can be shown to yield vapor concentrations that decline over time sufficiently that long-term VI risks become acceptable. This approach entails estimating the VOC mass remaining (e.g., through soil concentration profiling) and evaluating (e.g., through modeling or monitoring) the expected decrease in mass transport rates that occurs when only limited source material is available.

7 SUMMARY AND CONCLUSIONS

This EIP discusses the benefits and limitations of bulk soil sampling for assessing VI risks from contaminated soil and describes alternatives for monitoring and enhancing soil remedies at sites where soil excavation is being considered or used as part of the remedy for VOC-contaminated soils. Topics discussed include how VOCs may be distributed among the solid, liquid, and gaseous phases in bulk soil; how to calculate bulk soil concentrations corresponding to soil vapor screening levels; how those bulk soil concentrations compare with typical laboratory detection limits for bulk soil analysis; and the usefulness of those bulk soil concentrations for assessing VI risks.

Bulk soil concentrations corresponding to VI screening levels for soil gas were calculated using equilibrium partitioning relationships and compared with typical bulk soil analysis MDLs. This evaluation indicates that bulk soil sampling is useful for identifying source areas with high concentrations of VOCs, such as where NAPL is present, and for estimating the total VOC mass that may be present in soils at a site. However, available analysis methods are not sufficiently sensitive to detect VOCs in bulk soil concentrations corresponding to typical VI screening levels. Other challenges with bulk soil sampling and analysis include the potential for low bias (underestimation) of VOC levels due to loss during sampling and analysis and the difficulty characterizing the heterogeneity in VOC concentration distributions in the bulk soil mass of interest.

Soil excavation can be an appropriate part of a VOC contamination remedy, particularly if focused on shallow accessible source materials with relatively high concentrations of VOCs that are readily measured with bulk soil samples. But because of the limitations described above, soil excavation alone is not likely to be cost effective for soil with relatively modest VOC concentrations that may pose a VI risk but cannot be detected with current bulk soil analysis methods.

Remedies to augment soil excavation in such cases include SVE, bioventing, and natural attenuation (for PHCs); enhanced/accelerated bioattenuation (for chlorinated hydrocarbons); building structure mitigation; and backfilling excavated areas with low-permeability barrier materials that will reduce the concentrations reaching the surface. Improved understanding (e.g., through modeling or monitoring) of the role mass flux plays in VI will help with the assessment of how much source mass needs to be excavated and what additional activities may be needed to manage post-excavation VI risk.

8 ACRONYMNS AND ABBREVIATIONS

EIP	Engineering Issue Paper
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
HLC	Henry’s Law Constant
ITRC	Interstate Technology & Regulatory Council
MDL	Method Detection Limit
NAPL	Nonaqueous Phase Liquid
PCE	Perchloroethylene
PHC	Petroleum Hydrocarbon
PID	Photoionization Detector

SVE	Soil Vapor Extraction
TCE	Trichloroethylene
VI	Vapor Intrusion
VISL	Vapor Intrusion Screening Level
VOC	Volatile Organic Compound

9 ACKNOWLEDGMENTS

This Engineering Issue Paper was prepared for the EPA Office of Research and Development (ORD), National Risk Management Research Laboratory (NRMRL), Engineering Technical Support Center (ETSC) by RTI International under Contract No. EP-C-11-036. Doug Grosse served as the EPA Task Order Manager and technical lead. Robert Truesdale directed the project for RTI. Additional authors were Dr. Helen Dawson of Geosyntec Consultants (lead author), Dr. Todd McAlary of Geosyntec, Chris Lutes of CH2MHILL, and Dan Carr of Sanborn|Head Associates. Helpful direction and comments were received from Dr. Henry Schuver of the EPA Office of Resource Conservation and Recovery, Hal White of the Office of Underground Storage Tanks, and Rich Kapuscinski of the Office of Superfund Remediation and Technology Innovation. Dr. Dave Mickunas of EPA's Environmental Response Team and Dr. Blayne Hartman of Hartman Environmental Geosciences peer reviewed this paper. The authors express their gratitude for all of these reviews.

As the technology and science advances, interested parties should further consult the body of literature and experience that constitutes the state of the art for vapor intrusion and soil excavation monitoring. For additional information, interested parties may also contact EPA ORD/NRMRL/ETSC:

Dr. John McKernan, Director
U.S. EPA Engineering Technical Support Center
26 W. Martin Luther King Drive, Mail Code-190
Cincinnati, OH 45268
513-569-7415

10 REFERENCES

Boulding, J.R., and M.J. Barcelona. 1991. Chapter 8, Geochemical variability of the natural and contaminated subsurface environment, in *Seminar Publication: Site Characterization for Subsurface Remediation*. EPA/625/4-91/026. November. Available at http://www.epa.gov/OUST/cat/sitchasu.pdf.

Brusseau, M.L. 1994. Chapter 7, Sorption and transport of organic chemicals, in *Handbook of Vadose Zone Characterization and Monitoring*. L.G. Wilson, L.G. Everett, and S.J. Cullen, editors. CRC Press, Boca Raton, FL.

Carr, D.B., L.C. Levy, and A.H. Horneman. 2010. Vertical profiling to better understand vadose zone processes related to vapor intrusion. Short Paper from 2010 AWMA Vapor Intrusion Conference. Available at http://www.clu-in.org/download/contaminantfocus/vi/vadose%20zone%20profiling%20to%20better.pdf.

Chiou, C.T., and T.D. Shoup. 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanisms and capacity. *Environmental Science and Technology* 19(12):1196–1200.

Feenstra, S. 2003. Spatial variability of non-aqueous phase liquid chemicals in soil-implications for source zone mass estimates. *Environmental & Engineering Geoscience* 9(1):19–23.

Feenstra, S., D.M. Mackay, and J.A. Cherry. 1991. A method for assessing residual NAPL based on organic chemical concentrations in soil samples. *Ground Water Monitoring Review* 11(2):128–136.

Fitzgerald, J. 1993. Chapter 4, Onsite analytical screening of gasoline contaminated media using a jar headspace procedure, in *Principles and Practices for Petroleum Contaminated Soils*. E.J. Calabrese and P.T. Kostecki, editors, Lewis Publishers, Boca Raton, FL.

Hewitt, A.D., C. Ramsey, and S. Bigl. 2008. Multi-increment TCE vadose-zone investigation. *Remediation Journal* 19(1):125–140.

Indiana Department of Environmental Management. 2012. *Sampling Soil and Waste for Volatile Organic Compounds (VOCs)*. Technical Guidance Document. Indianapolis. Available at http://www.in.gov/idem/files/land_soil_sampling_and_waste_for_vocs.pdf.

ITRC (Interstate Technology & Regulatory Council). 2012. *Technical and Regulatory Guidance: Incremental Sampling Methodology*. Section 5.4.2. February. Available at http://www.itrcweb.org/ism-1/pdfs/ISM-1_021512_Final.pdf.

ITRC (Interstate Technology & Regulatory Council). 2014. *Petroleum Vapor Intrusion: Fundamentals of Screening, Investigation, and Management*. October. Available at http://www.itrcweb.org/PetroleumVI-Guidance.

Maskarinec, M.P., C.K. Bayne, L.H. Johnson, S.K. Holladay, and R.A. Jenkins. 1989. *Stability of Volatile Organics in Environmental Water Samples: Storage and Preservation*. Oak Ridge National Laboratory Final Report ORNL/TM-11300. Oak Ridge, TN. August. Available at http://www.dtic.mil/docs/citations/ADA412461.

Mass DEP (Massachusetts Department of Environmental Protection). 1996. *Commonwealth of Massachusetts Underground Storage Tank Closure Assessment Manual*. DEP Policy #WSC-402-96. Office of Environmental Affairs. Boston, MA. http://www.mass.gov/eea/docs/dep/cleanup/laws/96-402.pdf.

Nyer, E.K., P.L. Palmer, E.P. Carman, G. Boettcher, J. Bedessem, D.F. Kidd, F. Lenzo, G.J. Rorech, and T.L. Crossman (eds.). 2001. *In-situ Treatment Technology*, 2nd ed.. Lewis Publishers, Boca Raton, FL.

Payne, F.C., J.A. Quinnan, and S.T. Potter. 2008. *Remediation Hydraulics*. CRC Press, Boca Raton, FL.

Rorech, G.J. 2001. Chapter 3, Vapor Extraction and Bioventing, in *In Situ Treatment Technology*, 2nd ed., E.K. Nyer et al., editors. Lewis Publishers, Boca Raton, FL.

South Dakota Department of Environment and Natural Resources. 2003. *Standard Operating Procedure: One: Field Screening*. Version 2.0. March. Available at https://denr.sd.gov/des/gw/Spills/Handbook/SOP1.pdf.

Suthersan, S.S. 1997. *Remediation Engineering: Design Concepts*. CRC Press, Boca Raton, FL.

Thomas, R.G. 1990. Chapter 16, Volatilization from Soil, in *Handbook of Chemical Property Estimation Methods: Environmental Behavior of Organic Compounds*. Lyman, W.J., W.F. Reehal, and D.H. Rosenblatt, editors. American Chemical Society, Washington, DC.

Trombetta, M. 2008. Monitored natural attenuation and risk-based corrective action at underground storage tanks sites. Montana Department of Environmental Quality. Presented at Petroleum Tank Release Fund Subcommittee Meeting. June. Available at http://leg.mt.gov/content/Committees/Interim/2007_2008/environmental_quality_council/subcommittees/petro_fund/Materials/6_4_Trombetta_DEQ_presentation.ppt.

U.S. EPA (United States Environmental Protection Agency). 1993. *Behavior and Determination of Volatile Organic Compounds in Soil - A Literature Review*. EPA/600/R-93/140. Environmental Monitoring Systems Laboratory, Office of Research and Development, Las Vegas, NV. March. Available at http://www.epa.gov/esd/cmb/pdf/voclr.pdf.

U.S. EPA (United States Environmental Protection Agency). 1994. Bioventing. Office of Solid Waste and Emergency Response, Washington, DC. Available at http://www.epa.gov/oust/cat/biovent.htm. Last updated December 20, 2012.

U.S. EPA (United States Environmental Protection Agency). 1996a. *Method 5035: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples.* SW-846 Method 5035. Office of Solid Waste and Emergency Response, Washington, DC. December. Available at http://www.epa.gov/osw/hazard/testmethods/sw846/pdfs/5035.pdf.

U.S. EPA (United States Environmental Protection Agency). 1996b. *Soil Screening Guidance: Technical Background Document.* EPA/540/R-95/128. Office of Solid Waste and Emergency Response, Washington, DC. July. Available at http://www.epa.gov/superfund/health/conmedia/soil/toc.htm.

U.S. EPA (United States Environmental Protection Agency). 1997. Chapter VI, Field methods for the analysis of petroleum hydrocarbons, in *Expedited Site Assessment Tools for Underground Storage Tank Sites: A Guide for Regulators.* Office of Underground Storage Tanks, Washington, DC. March. Available at http://www.epa.gov/oust/pubs/esa-ch6.pdf.

U.S. EPA (United States Environmental Protection Agency). 2002a. *Supplemental Guidance for Developing Soil Screening Levels for Superfund Sites.* OSWER 9355.4-24. Office of Solid Waste and Emergency Response, Washington, DC. December. Available at http://www.epa.gov/superfund/health/conmedia/soil/.

U.S. EPA (United States Environmental Protection Agency). 2002b. Draft Guidance for Evaluating the Vapor Intrusion to Indoor Air Pathway from Groundwater and Soils (Subsurface Vapor Intrusion Guidance). EPA 530-D-02-004. Office of Solid Waste and Emergency Response, Washington, DC. November. Available at http://www.epa.gov/epawaste/hazard/correctiveaction/eis/vapor.htm.

U.S. EPA (United States Environmental Protection Agency). 2002c. Appendix A: The Collection and Preservation of Aqueous and Solid Samples for Volatile Organic Compound Analysis, in *Method 5035A: Closed-System Purge and Trap and Extraction for Volatile Organics in Soil and Waste Samples.* SW-846 Method 5035A. Office of Solid Waste and Emergency Response, Washington, DC. July. Available at http://www.epa.gov/osw/hazard/testmethods/pdfs/5035a_r1.pdf.

U.S. EPA (United States Environmental Protection Agency). 2004. *Site Characterization Technologies for DNAPL Investigations.* EPA 542-R-04-017. Office of Solid Waste and Emergency Response, Washington, DC. Available at http://nepis.epa.gov/Exe/ZyPURL.cgi?Dockey=30005YOX.txt.

U.S. EPA (United States Environmental Protection Agency). 2008. *Engineering Issue: Indoor Air Vapor Intrusion Mitigation Approaches.* Office of Research and Development, Cincinnati, OH. October. Available at http://www.clu-in.org/download/char/600r08115.pdf.

U.S. EPA (United States Environmental Protection Agency). 2012a. *Conceptual Model Scenarios for the Vapor Intrusion Pathway.* EPA 530-R-10-003. Office of Solid Waste and Emergency Response, Washington, DC. February. Available at http://www.epa.gov/oswer/vaporintrusion/documents/vi-cms-v11final-2-24-2012.pdf.

U.S. EPA (United States Environmental Protection Agency). 2012b. *Petroleum Hydrocarbons and Chlorinated Hydrocarbons Differ in Their Potential for Vapor Intrusion*. Office of Underground Storage Tanks, Washington, DC. March. Available at http://www.epa.gov/oust/cat/pvi/pvicvi.pdf.

U.S. EPA (United States Environmental Protection Agency). 2013. *Contaminated Site Clean-Up Information: Soil Vapor Extraction*. Office of Superfund Remediation and Technology Innovation, Washington, DC. Available at http://www.clu-in.org/techfocus/default.focus/sec/Soil_Vapor_Extraction/cat/Overview/. Last updated November 25, 2013.

U.S. EPA (United States Environmental Protection Agency). 2014a. *Regional Screening Table User's Guide*. Available at http://www.epa.gov/reg3hwmd/risk/human/rb-concentration_table/usersguide.htm. Last updated October 21, 2014.

U.S. EPA (United States Environmental Protection Agency). 2014b. *Remediation Technologies: Bioremediation*. Office of Superfund Remediation and Technology Innovation, Washington, DC. Available at http://www.clu-in.org/techfocus/default.focus/sec/Bioremediation/cat/Anaerobic_Bioremediation_(Direct. Last updated February 24, 2014.

U.S. EPA (United States Environmental Protection Agency). 2014c. *Remediation Technologies: Natural Attenuation*. Office of Superfund Remediation and Technology Innovation, Washington, DC. Available at http://www.clu-in.org/techfocus/default.focus/sec/Natural_Attenuation/cat/Overview/. Last updated April 17, 2014.

U.S. EPA (United States Environmental Protection Agency). 2014d. *Remediation Technologies: Vapor Intrusion Mitigation*. Office of Superfund Remediation and Technology Innovation, Washington, DC. Available at http://www.clu-in.org/issues/default.focus/sec/Vapor_Intrusion/cat/Mitigation/. Last updated June 14, 2014.

U.S. EPA (United States Environmental Protection Agency). 2014e. *Vapor Intrusion Screening Level (VISL) Calculator User's Guide*. Office of Solid Waste and Emergency Response, Washington, DC. May. Available at http://www.epa.gov/oswer/vaporintrusion/documents/VISL-UsersGuide.pdf.

U.S. EPA (United States Environmental Protection Agency). 2015. *OSWER Technical Guide for Assessing and Mitigating the Vapor Intrusion Pathway from Subsurface Vapor Sources to Indoor Air*. OSWER Publication 9200.2-154. Office of Solid Waste and Emergency Response, Washington, DC. May. Available at http://www.epa.gov/oswer/vaporintrusion/documents/OSWER-Vapor-Intrusion-Technical-Guide-Final.pdf

Van Deuren, J., T. Lloyd, S. Chhetry, R. Liou, and J. Peck. 2002. *Remediation Technologies Screening Matrix and Reference Guide*, 4th Ed. Federal Remediation Technologies Roundtable. Available at http://www.frtr.gov/matrix2/section1/toc.html.

United States
Environmental Protection
Agency

Office of Research and Development
National Risk Management
Research Laboratory
Cincinnati, OH 45268

EPA/600/R-14-277
December 2014
www.epa.gov