

Volatile organic compounds in contaminated soils: The nature and validity of the measurement process*

Robert L. Siegrist

Environmental Sciences Division, Oak Ridge National Laboratory¹, P.O. Box 2008, Oak Ridge, TN 37831-6038 (USA)

Abstract

A wide variety of volatile organic compounds (VOCs) such as toluene and trichloroethene routinely appear as principal pollutants in contaminated sites. As part of the site assessment and environmental restoration process, quantitative determination of soil VOCs is required. While accurate and precise measurements are desired, the validity of the current process in which a discrete sample is collected and a 1 to 5 g subsample is analyzed for a suite of organic compounds of widely different properties is questionable. Research has demonstrated that the soil VOC measurement process is complex and current, commonly employed practices can lead to substantial measurement errors. For example, -100 to +25% bias can occur in measurements of some soil VOCs. Knowledge of VOC behavior in soils and the measurement process continues to expand and advances are being made in sampling and analysis techniques. Further research is needed to enable development of a valid soil VOC measurement process.

1. Introduction

Due to their widespread use throughout commerce and industry, volatile organic compounds (VOCs) are found in soil and ground water at contaminated sites throughout the U.S. and abroad (Table 1). VOCs are typically mobile and persistent in the environment and can be potentially toxic at trace concentrations. Measurements of soil VOCs are necessary to confirm the presence and magnitude of contamination; to assess site risks and the need for cleanup; to evaluate remedial technologies; and to verify the performance of a selected alternative. Decisions regarding these issues can have far-reaching technical, economic and legal impacts and ideally should be based on valid measurements. Yet, recent research has shown that the measurement process

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TABLE 1

Volatile organic compounds included within the Hazardous Substance List (HSL) in the USA and their occurrence at Superfund Sites

Compound	Properties ^a				Hazardous waste site rank and prevalence ^b
	Molecular weight (g/mol)	Boiling point (°C)	Vapor pressure (mm)	Aqueous solubility (mg/L)	
Chloromethane	51	-24	3800	4000	
Bromomethane	95	4.6	-	900	
Vinyl chloride	62	-13.9	2660 (25°C)	1100 (25°C)	23 [8%]
Chloroethane	64.5	12.4	1000	5740	
Methylene chloride	85	40	349	20000	18 [10%]
Acetone	58	56.2	270 (30°C)	Miscible	
Carbon disulfide	76.1	46.3	260	2300 (22°C)	
1,1-Dichloroethane	97.0	31.9	500		20 [9%]
1,1-Dichloroethane	99.0	57.3	180	5500	19 [10%]
<i>trans</i> -1,2-Dichloroethane	97.0	48	200 (14°C)	600	17 [12%]
Chloroform	119.4	62	160	8000	6 [20%]
1,2-Dichloroethane	99.0	83.5	61	8690	25 [7%]
2-Butanone	72.1	79.6	78	353000 (10°C)	
1,1,1-Trichloroethane	133.4	71-81	100	4400	8 [17%]
Carbon tetrachloride	153.8	76.7	90	800	27 [7%]
Vinyl acetate	86.1	73.0	83	25000	
Bromodichloromethane	163.8	90.0			
1,2-Dichloropropane	113.0	96.8	42	2700	
<i>trans</i> -1,3-Dichloropropane	111.0	112	34 (25°C)	2800	
Trichloroethene	131.5	86.7	60	1100 (25°C)	1 [35%]
Dibromochloromethane	208.3	116-122			
1,1,2-Trichloroethane	133.4	113.7	19	4500	
Benzene	78.1	80.1	76	1780	5 [23%]
<i>cis</i> -1,3-Dichloropropene	111.0	104.0	43 (25°C)	2700	
bromoform	252.8	149	5.6 (25°C)	3190 (30°C)	
4-Methyl-2-pentanone	100.2	116-119	6	17000	
2-Hexanone	100.2	128	2	35000	
Tetrachloroethene	165.8	121.4	14	150 (25°C)	9 [17%]
1,1,2,2-Tetrachloroethane	167.9	146.4	5	2900	
Toluene	92.1	110.8	22	515	3 [27%]
Chlorobenzene	112.6	132	8.8	500	26 [7%]
Ethylbenzene	106.2	136.2	7	152	15 [12%]
Styrene	104.1	145.2	5	300	
<i>m</i> -Xylene	106.2	139	6		14 [13%]
<i>o</i> -/ <i>p</i> -Xylene	106.2	144.4	5	175	14 [13%]

^aProperties are at 20°C unless another temperature is shown in parentheses.

^bRank (highest=1) and prevalence (% of sites) based on a total of 466 different substances found at the 888 Superfund sites (as of October 1986).

for many soil VOCs remains poorly understood and is error prone. Despite the uncertainty and error potential of the current process, the assumption is often implicitly made that soil VOC data are of sufficient quality for the intended purpose. This paper provides an overview of VOC contaminated soils and the current measurement process and discusses its validity and need for improvement.

2. VOC Contaminated soils

There is no precise definition of a VOC. Rather, compounds appear to have been grouped into a class known as VOCs based on their amenability to extraction, separation and detection by a coordinated and compatible analytical procedure (e.g. water extraction, purge and trap concentration, gas chromatographic separation, flame ionization detection) e.g. [1]. In the USA, there are 35 organic compounds included in the Hazardous Substance List (HSL) for volatile organic compounds (Table 1). While all are considered VOCs, their inherent physicochemical properties vary over several orders of magnitude.

VOCs can be released to an otherwise "clean" soil system by various chemical handling and waste management practices. Examples include surface oil and solvent spills, leaks from underground fuel storage tanks and leachates from landfills, waste oil land farms and septic tank drainfields. Once in the soil system, migration of VOCs through soil can occur in both the liquid and the vapor phases [2,3]. Behavior of VOCs in soils is complex and not yet completely understood. Of particular importance to the measurement process is the fact that VOCs co-exist in multiple phases as described below.

VOCs present in an aqueous solution in soil tend to distribute between the vapor, liquid and solid phases according to the following equilibrium relationships [2-5],

$$C_T = aC_v\rho_b + \theta C_L/\rho_b + C_s \quad (1)$$

where C_T denotes the VOC concentration per unit weight of dry soil ($\mu\text{g/g}$), C_v the soil vapor phase concentration ($\mu\text{g/cm}^3$), C_L the soil solution concentration ($\mu\text{g/cm}^3$), C_s the soil sorbed concentration ($\mu\text{g/g}$), ρ_b the soil bulk density (g/cm^3), θ the soil water content (cm^3/cm^3), and a is the soil air content (cm^3/cm^3).

Equilibrium sorption of organic compounds from aqueous solutions onto soils is often described by a Freundlich isotherm:

$$C_s = KC_L^{1/n} \quad (2)$$

where K is the partition coefficient (mL/g) and n is an empirical constant. For many situations with dilute aqueous solutions of VOCs, $n = 1$, and the partition coefficient, K , is often referred to as a distribution coefficient, K_D . In soil systems, K_D has been shown to be strongly correlated with the fractional soil

organic matter content, f_{OM} , and the organic matter/water partition coefficient, K_{OM} :

$$K_D = f_{OM} K_{OM} \quad (3)$$

The soil organic matter/water partition coefficient, K_{OM} , has been related to the water solubility, S_w , or the octanol/water partition coefficient, K_{OW} , both of which are interrelated [3-5]:

$$\text{Log}(K_{OM}) = a_1 \text{Log}(S_w V) + b_1 \quad (4)$$

$$\text{Log}(K_{OM}) = a_2 \text{Log}(K_{OW}) + b_2 \quad (5)$$

$$\text{Log}(K_{OM}) = a_3 \text{Log}(S_w) + b_3 \quad (6)$$

where K_{OM} is the organic matter/water partition coefficient (mL/g), K_{OW} is the octanol/water partition coefficient (mL/g), and S_w is the water solubility (mol/L), V is the molar volume (L/mol), and a, b are empirical constants.

In unsaturated soils VOCs also partition from the liquid phase into the vapor phase according to Henry's law:

$$C_V = K_H C_L \quad (7)$$

where C_V is the soil vapor-phase concentration ($\mu\text{g}/\text{mL}$), K_H is Henry's law constant (dimensionless), and C_L is the soil solution phase concentration ($\mu\text{g}/\text{mL}$).

Data provided in Table 2 and Fig. 1 illustrate how several common VOCs partition under equilibrium conditions as described by the above relationships. It is important to recognize that these relationships describe the equilibrium behavior of dilute aqueous solutions in soils. Releases of concentrated VOC

TABLE 2

Equilibrium phase distributions for 100 ppm of selected VOCs in a sandy soil^a

Compound	Vapor pressure (mmHg) at 20°C	Partition coefficients			Total soil VOCs C_T ($\mu\text{g}/\text{g}$)	Soil phase distribution		
		K_H (-)	K_{OM} (mL/g)	K_D (mL/g)		Liquid W_L (wt.%)	Solid W_s (wt.%)	Vapor W_v (wt.%)
Methylene chloride	349	0.060	4.96	0.036	100	69	26	5
1,1,1-Trichloroethane	100	0.415	27.1	0.197	100	28	56	16
1,2-Dichloroethane	61	0.050	4.92	0.036	100	69	26	5
Trichloroethylene	60	0.232	27.4	0.199	100	30	61	9
Toluene	22	0.164	39.6	0.288	100	24	71	5
Chlorobenzene	8.8	0.105	63.6	0.463	100	17	81	2

^aCalculated based on equations presented in text for an unsaturated sandy soil matrix (temperature: 10°C, dry bulk density: 165 g/cm³, water content: 0.16 cm³/cm³, air content: 0.22 cm³/cm³, organic carbon content: 0.42 wt.%).

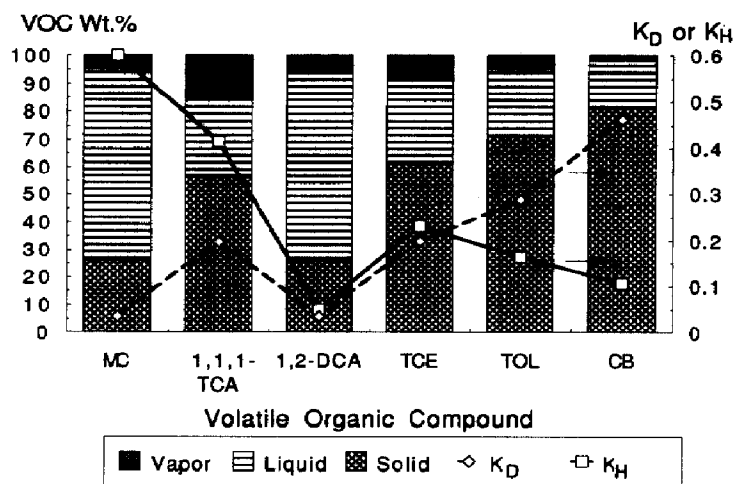


Fig. 1. Equilibrium distribution of selected volatile organic compounds in a sandy soil (based on the data given in Table 2).

solutions can yield non-aqueous phase liquids which complicates VOC behavior. Moreover, non-equilibrium conditions may intermittently occur and VOC behavior will depart from that under equilibrium conditions. Nonequilibrium conditions can be caused by variable VOC inputs (e.g. rainfall-induced leaching), VOC outputs (e.g. volatilization, biodegradation, abiotic transformation), and system conditions (e.g. diurnal variations in temperature and pressure, changes in soil moisture/vapor volumes).

3. Soil VOC measurements

The current soil VOC measurement process involves three major elements (i.e. design, collection and analysis) which include a series of potential activities as illustrated in Fig. 2 and described below.

3.1 Sampling design

When sampling VOC contaminated sites, soil samples are collected according to various statistical designs (e.g. random, systematic, judgmental) under a wide variety of site conditions (e.g. weather conditions, safety hazards, obstructions). Sampling designs must account for these conditions as well as the wide variability in natural soil properties which affect contaminant transport and fate [6–10]. Natural spatial variability can be particularly great including short-range (e.g. < 1 m) and long-range variability. It is common for soil properties to vary up to several hundred percent (coefficient of variation), although 10 to 100 percent may be typical for many situations [7,8]. This natural variability is exacerbated by unknown or uncertain anthropogenic impacts and complex VOC transport and fate processes.

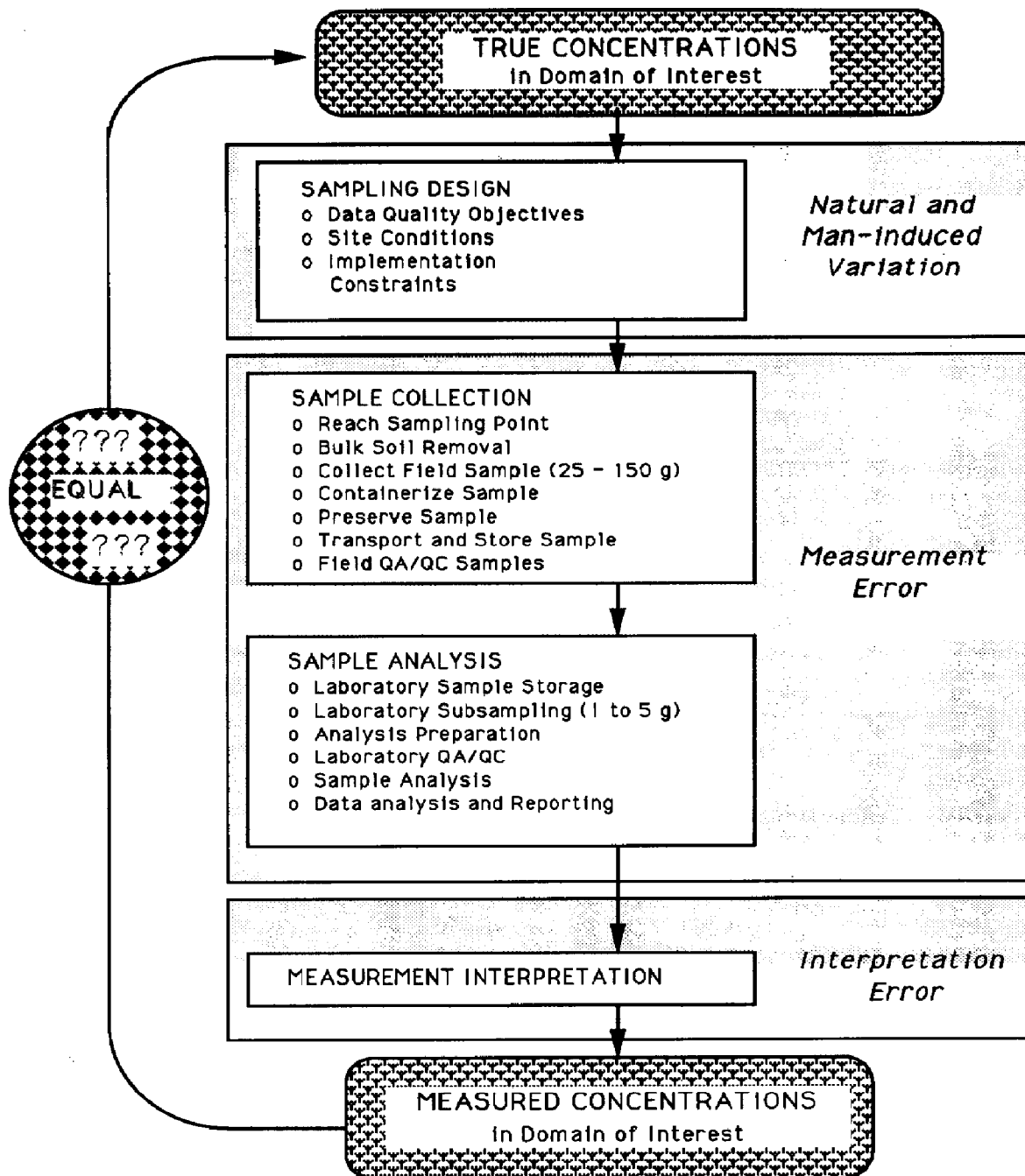


Fig. 2. Measurement process for volatile organic compound in contaminated soil and potential error components.

During the planning phase of a soil measurement program, the objectives and scope of the effort should be specified along with the requisite type, quantity and quality of data to be generated. Data quality objectives (DQOs) should

include the desired data accuracy, precision, representativeness, completeness and comparability [9]. A principal goal of this process is to provide an understanding of the nature and magnitude of any measurement errors and the validity of the measurements made. Sound data interpretation and hypothesis testing require that measurements be valid and measurement errors be small. Measurement error variance should normally be less than 10% of the total variance between measurements of different populations while measurement bias should be negligible [7,8].

Real variability associated with spatial heterogeneities and/or anthropogenic effects can often lead to data deficiencies and frustrate data interpretation and decision-making. While this variability can be addressed by statistical techniques (e.g. stratified sampling, increasing sample numbers and replication), time and budget constraints often preclude collection and analysis of a statistically requisite numbers of samples. As a result, the soil VOC database for a given problem is often small and the VOC concentration detected in each soil sample takes on greater decision-making importance. Measurement error caused by deficiencies in measurement techniques are of great concern since they can be elusive and difficult to control. Deficiencies in current measurement techniques along with potential improvements are outlined below.

3.2 Sample collection and analysis

The first step in the sample collection process involves a variety of classical methods used to expose the soil volume to be sampled (e.g. a shovel, hand auger, drilling rig, backhoe). Samples are routinely collected from undisturbed in-place soils at the surface, shallow subsurface or at great depth as well as from disturbed soil stockpiles. Various implements and devices are used to remove a subsample of soil for containerization and analysis. The balance of the sample collection and analysis process varies as described in the following sections.

3.2.1 VOC Screening

To reduce analytical costs and to provide real-time data, soil samples are routinely screened onsite to determine if there is VOC contamination [11-14]. Based on screening data, a selected number of soil samples are subjected to more rigorous, confirmatory laboratory analyses. Soil sample screening methods are not yet standardized and various methods are utilized. A common procedure involves the use of headspace techniques. For this purpose, soil samples are collected using spatulas and spoons, trowels or coring devices and simply placed in a container and sealed. Containers have included glass canning jars, plastic bags, or Teflon-sealed glass jars, all which are partially filled with soil. In some cases a volume of water is added as an extraction agent. After a short equilibration period, sometimes with heating, the VOCs in the container headspace are measured. Qualitative vapor analyses are widely made in the field

using simple hand-held detectors (e.g. photoionization or flame ionization), although the use of gas chromatographs is increasing.

While relatively simple, these soil headspace measurements are subject to error and misinterpretation [11–14]. Not only are there problems associated with major VOCs losses during sample collection and handling, but making inferences about total soil VOC concentrations from vapor concentrations measured by hand-held detectors alone is tenuous [11]. This is illustrated in Fig. 3 where an example correlation curve for soil VOCs as measured by headspace screening techniques with two different photoionization detectors versus total VOC analyses by purge and trap extraction and laboratory gas chromatography is shown. Poor correlation between field headspace measurements and laboratory analyses may be due to unfavorable site conditions (e.g. minimal vapor filled porosity or nonequilibrium conditions during vapor measurement) or the limitations of the VOC detectors often used. Photoionization and flame ionization detectors intended to measure soil VOCs can respond to and/or be affected by environmental conditions and other relatively common naturally occurring organics [11,12,14]. For example, photoionization detectors are extremely sensitive to water vapor, which can yield both negative and positive bias. In addition, they have decreased sensitivity to VOCs when high concentrations of methane are present [14]. Finally, some of these detectors can respond to natural organics, including methane, ethylenes and alcohols.

Efforts to improve on common headspace screening methods have focused on control of measurement conditions and the use field-portable gas chromatographs as well as the use of infield extractions and test-kit chemical analyses. For example, a simple field screening method has been developed which uses a water extraction followed by headspace screening in a reclosable plastic bag. Total hydrocarbons in the headspace are measured with a handheld detector.

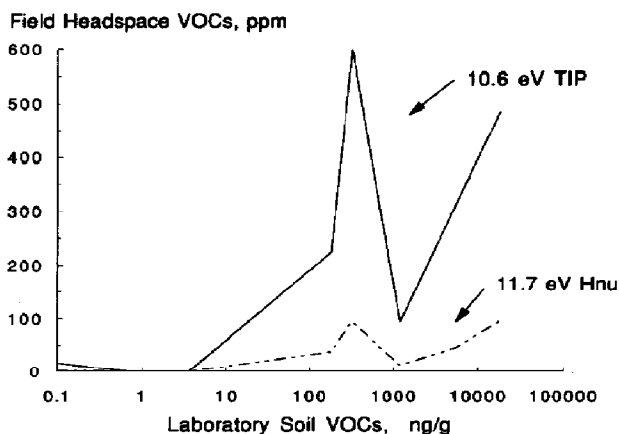


Fig. 3. Volatile organic compound concentrations as determined by field headspace screening techniques and laboratory gas chromatography. (Sandy soil contaminated principally by methylene chloride, ethylbenzene, xylenes and toluene.)

Another recently developed screening technique consists of a chemical test kit involving a solvent extraction and chemical reaction with the presence of aromatic hydrocarbons determined colorimetrically. Preliminary evaluations of these screening techniques have indicated good correlation between field screening data and laboratory analyses [12,13].

3.2.2 VOC Quantitation

For quantitative determination of total soil VOCs, collection, containerization and analysis of soil samples is required [1]. While analytical procedures have been specified by regulatory agencies, sample collection and handling has been largely ignored. There are currently no standardized collection and handling procedures, but only general guidance. This is exemplified in Test Methods for Evaluating Solid Wastes. (U.S. EPA SW-846) in which the following guidance is given: collect a soil sample in an unspecified manner and deposit it in a 4 oz (120 mL) widemouth glass container with Teflon liner; minimize sample agitation during collection and minimize free air space in the container; cool the sample to 4°C and analyze it within 14 days; for high level soils (individual VOCs > 1 mg/kg), extract the soil in the laboratory with methanol [1].

In practice, soil VOC measurements have been accomplished by various means. Materials and methods for collecting and containerizing the soil have historically been similar to those used for basic sampling of soil and geologic materials. Typically, a small soil sample (ca. 25 to 150 g) is collected using spatulas and spoons, trowels or coring devices and containerized in 40-mL glass vials or 125-mL glass jars, both of which are sealed with a Teflon-lined cap. Analyses of the containerized soil samples are normally accomplished by laboratory subsampling of 1 to 5 g from the field sample and immersing the sample in water or methanol. The soil/liquid sample undergoes purge and trap extraction followed by gas chromatography employing various detectors (e.g. flame ionization, electron capture, mass spectrometer). Laboratory analyses are normally conducted offsite at a remote facility, while in comparatively few situations are analyses conducted onsite in a mobile laboratory.

Quantification of some soil VOCs has been shown to be subject to substantial measurement errors when samples are collected and analyzed by commonly used methods [15–19]. Measurement error variances for some soil VOCs (i.e. coefficient of variation) of 10 to 100% can reasonably be expected. Of greater concern is the measurement error bias which can be in the range of –100% to +25% [16]. The potential for substantial negative measurement bias associated with sampling methods is clearly indicated Fig. 4. Negative bias in VOC measurements (i.e. measured value < true value) can be caused by diverse factors including: (1) volatilization losses during soil surface exposure and sample removal from the soil profile, (2) volatilization losses from the sample container during preanalytical holding, (3) chemical and biochemical trans-

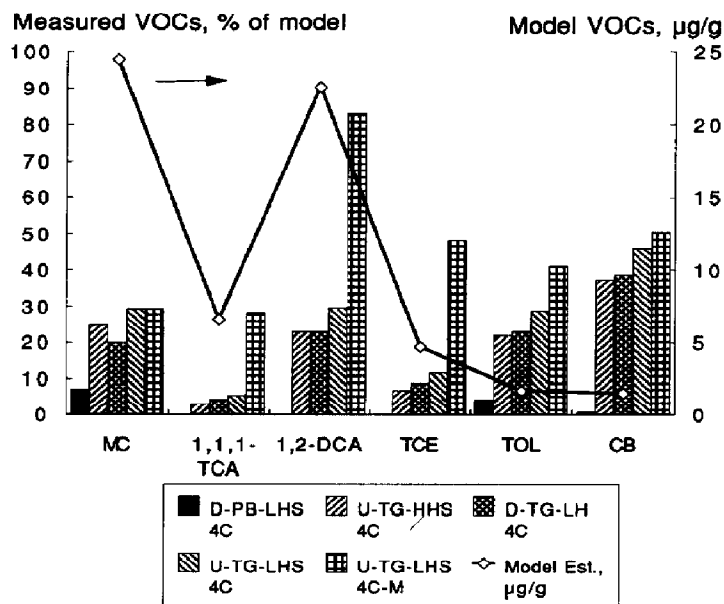


Fig. 4. VOC concentrations in soil samples as a function of sampling methods as determined in a laboratory experiment with a sandy soil [15]. Sampling method attributes: D=disturbed soil, U=undisturbed soil, PB=plastic bag, TG=teflon-sealed glass, LHS=low container headspace, HHS=high container headspace, 4C=4°C holding, and 4C-M=methanol immersion plus 4°C.

formations during pre-analytical holding, and (4) volatilization losses during subsampling for analyses. Susceptibility to negative bias appears to be correlated with increasing K_H and decreasing K_D [15].

Improvements in the measurement process, particularly to mitigate measurement bias, can be made by more rigorous sample collection and handling practices [6,10,15–18]. Recent research and practice has revealed alternative methods which can improve VOC measurement accuracy by 50 to 90% for the more volatile/low solubility compounds (e.g. trichloroethene). The advantages and disadvantages of several are highlighted below. One method involves collection of undisturbed soil cores in sleeve-lined, split-barrel samplers [19]. The relatively undisturbed soil cores are sealed within the sleeves onsite and then transported to a laboratory for controlled subsampling and transfer to an analysis vessel. This method eliminates field subsampling and containerization and maintains the 1 to 5 g subsample used for analysis in continuity with a bulk soil volume until analysis is imminent. However, this approach requires shipment of larger quantities of material, subsampling by someone unfamiliar with the site and a small subsample (i.e. 1 to 5 g) is still analyzed. Another method involves onsite subsampling with a micro-coring device to minimize soil disturbance [18]. The soil from the micro-cores (e.g. 5 to 10 mL) can be extruded into a 40-mL glass vial with an O-ring sealed cap that is designed to attach directly to a purge and trap instrument. This approach eliminates laboratory subsampling, maintains low detection limits and does not requiring field handling of chemicals. However, the sample volume analyzed is quite

small (1 to 5 g) and compositing of soil samples is precluded. Yet another method involves immediate onsite immersion of a soil sample in an organic solvent (e.g. methanol) contained in a Teflon-sealed glass vial or jar [15–17]. The methanol approach has the advantage of increasing the sample size analyzed (thereby attenuating short-range spatial variability) and also enables sample compositing. However, the methanol addition can increase the detection limits by a factor of 10 to 100 and requires field handling and transportation of hazardous chemicals. An alternative solvent could mitigate this latter problem. Finally, minimizing pre-analytical holding time and variability of conditions may also help reduce measurement error. Improved and expanded use of onsite analytical instruments and techniques may provide great benefits, but their contribution to the measurement process and measurement error reduction is yet to be determined.

4. Discussion

Much uncertainty remains regarding the behavior of soil VOCs and their measurement, and questions exist regarding the validity of the common soil VOC measurement process. The costs associated with soil VOC measurements can be great (e.g. \$150 to \$300 per sample) and seemingly not commensurate with the overall quality of the data generated (e.g. –100 to +25% error variance). Moreover, far-reaching decisions are being made based on data of questionable quality. To improve the current situation, efforts to assess current practices and promulgate standard methods for VOC sampling are ongoing. An ASTM technical committee has had a draft standard under review and consideration for several years and several states and the U.S. EPA have been working toward development of standard methods in support of their regulatory programs. While commendable, these efforts have not been supported by a fundamental understanding of individual VOC behavior in soils and the necessary and appropriate features of a valid measurement process. Moreover, no efforts are being made to develop an integrated measurement process which encompasses the sampling and analysis elements. Yet, this is needed for VOCs where the measurement is subject to sampling and analysis interactions. Further research and development is clearly needed.

Despite the lack of complete understanding, several comments can be made regarding the soil VOC measurement process. First, it seems appropriate to reconsider and refine the categorization of VOCs. The current class of VOCs was developed based on analytical considerations, yet sampling considerations would suggest that multiple classes may be appropriate. This categorization should be based on the environmental behavior of each soil VOC as well as its environmental and public health significance. For example, trichloroethene would likely be grouped in a separate category from ethylbenzene. For quali-

tative VOC screening, great care must be exercised in data interpretation and inference about total soil VOC concentrations. If a valid correlation curve is not developed for the application of interest, the screening data may have limited utility. With a correlation curve, meaningful data can be achieved with improved procedures, particularly when field-portable gas chromatographs are used. Recently developed chemical test kits provide attractive advantages for field screening of some VOCs. For quantitative VOC measurements, data interpretation must be done carefully and include review of sample collection, handling and analysis procedures. VOC measurements made years ago are probably more suspect than recent data due to recent improvements in sampling practices. Where accurate and precise measurements are required for VOCs with high volatility and low solubilities (e.g. trichloroethene), more rigorous sample collection and handling practices should be considered. Greater consideration should also be given to sample compositing employing infield solvent immersion. This would permit cheaper, more accurate measurements of site average VOC concentrations, a characteristic used in deterministic modeling and decision making. Finally, sampling designs should include field quality control samples to characterize measurement error variance and bias associated with field activities.

References

- 1 U.S. EPA, Test Methods For Evaluating Solid Waste. SW-846. 3rd. edn. Vol. 1B: Laboratory manual, Physical/Chemical Methods, Chap. 4 - Organic Analytes. Office of Solid Waste and Emergency Response, Washington, DC, 20460, 1986.
- 2 B.L. Sawhney and K. Brown (Eds.), Reactions and movement of organic chemicals in soils. In: B.L. Sawhney and K. Brown (Eds.), Reactions and Movement of Organic Chemicals in Soils, Soil Science Society of American, Madison, WI, 1989, pp. 271-304.
- 3 S.C. Hern and S.M. Melancon (Eds.), Vadose Zone Modeling of Organic Pollutants, Lewis Publ., Chelsea, MI, 1986, 295 pp.
- 4 C.T. Chiou, Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. In: B.L. Sawhney and K. Brown (Eds.), Reactions and Movement of Organic Chemicals in Soils, Soil Science Society of America, Madison, WI, 1989, pp. 1-29.
- 5 P. Kjeldsen and T. Larsen, Sorption af organiske stoffer i jord og grundvand, Laboratoriet for Teknisk Hygiejne, Danmarks Tekniske Hojskole, Lyngby, 1988, 85 pp. (Danish).
- 6 M.J. Barcelona, In: L.H. Keith (Ed.), Principles of Environmental Sampling, American Chemical Society, Washington, DC, pp. 3-23.
- 7 C.A. Black, D.D. Evans, J.L. White, L.E. Ensminger and F.E. Clark, Methods of Soil Analysis, American Society of Agronomy, Inc., Madison, WI, 1965, pp. 1-72.
- 8 B.J. Mason, Preparation of soil sampling protocol: Techniques and strategies, EPA-600/4-83-020, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, 1983.
- 9 D.S. Barth, B.J. Mason, T.H. Starks and K.W. Brown, Soil sampling quality assurance user's guide, EPA 600/8-89/046, U.S. EPA Environmental Monitoring Systems Lab, Las Vegas, NV, 1989.

- 10 J.J. van Ee, L.J. Blume and T.J. Starks, A rationale for the assessment of errors in the sampling of soils, EPA/600/4-90/013, U.S. Environmental Protection Agency, Environmental Monitoring Systems Lab., Las Vegas, NV, 1990.
- 11 P.G. Smith and S.L. Jensen, Assessing the validity of field screening of soil samples for preliminary determination of hydrocarbon contamination, In: Proc. Superfund '87, Washington, DC, Hazardous Materials Control Institute, Silver Spring, MD, 20910, 1987, pp. 101-103.
- 12 G.A. Robbins, R.D. Bristol and V.D. Roe, A field screening method for gasoline contamination using a polyethylene bag sampling system, *Ground Water Monit. Rev.*, 19(4) (1989) 87-97.
- 13 K.A. Roy, Analytic technique measures aromatics in soil and water, *Hazmat World*, December (1990) 52-54.
- 14 J.E. Nyquist, T.H. Wilson, L.A. Norman and R.B. Gammage, Decreased sensitivity of photoionization detector total organic vapor detectors in the presence of methane, *Am. Ind. Hyg. Assoc. J.*, 51(6) (1990) 326-330.
- 15 R.L. Siegrist and P.D. Jensen, Evaluation of sampling method effects on volatile organic compound measurements in contaminated soils, *Environ. Sci. Technol.*, 24(9) 1990) 1387-1392.
- 16 R.L. Siegrist, Measurement error potential and control when quantifying volatile hydrocarbon concentrations in soils, In: *Hydrocarbon Contaminated Soils*, Lewis Publ., Chelsea, MI, pp. 205-215.
- 17 M.J. Urban, J.S. Smith, E.K. Schulz and R.K. Dickinson, In: *Fifth Annual Waste Testing and Quality Assurance Symp.*, U.S. Environmental Protection Agency, Washington, DC, 1989, pp. II-87-II-101.
- 18 T.E. Lewis, A.B. Crockett, R.L. Siegrist and K. Zarrabi, Soil sampling and analysis for volatile organic compounds, U.S. Environmental Protection Agency, EPA/540/4-91/001, pp. 1-24.
- 19 R.D. Flotard, M.T. Homsher, J.S. Wolff and J.M. Moore, Volatile organic analytical methods — performance and quality control considerations, In: C.L. Perket (Ed.), *Quality Control in Remedial Site Investigations: Hazardous and Industrial Solid Waste Testing*, Vol. 5, ASTM STP 925, ASTM, Philadelphia, PA, pp. 185-197.