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Measuring and Interpreting VOCs in Soils: State of the Art and Research Needs

A Symposium Summary

Las Vegas, NV
January 12-14, 1993

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PREFACE

This document contains a summary of a national symposium which included platform and poster presentations, panel discussions, and working group sessions. An attempt has been made to summarize the information presented and discussed, and to highlight any apparent consensus among the Symposium participants. The summary was assembled based on information exchanged at the Symposium. This included information from the following sources: the abstracts and supporting papers submitted for the working proceedings distributed to the attendees at the Symposium, the presentations and panel discussions, and the discussions during the working group sessions. The summary was prepared and reviewed by members of the planning committee and is believed to represent a factual account of the Symposium proceedings. As far as possible, controversy and consensus regarding the state-of-the-art and -practice have been described as well as current research needs. Many details were necessarily omitted, however, and for in-depth treatment of any particular subject, the reader is directed to appropriate literature cited in the references or bibliography sections of this document.

Many individuals contributed significantly to the conduct of the Symposium. Gratefully acknowledged is the diligent work of the following members of the Symposium planning committee:

Bruce J. Bauman	American Petroleum Institute, Washington, D.C.
Ruth Z. Bleyler	U.S. Environmental Protection Agency, Washington, D. C.
David W. Bottrell	DOE Office of Technology Development, Washington, D.C.
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Martin Stutz	U.S. Army Environmental Center, Aberdeen Proving Ground, Maryland

These members were not only critical to establishing the content and organization of the Symposium, but were also active participants in it. Many presented papers, appeared on panels, led working group sessions, and/or wrote summaries of the Symposium. Their support and enthusiasm contributed to the success of this meeting. Appreciation is also extended to Dean Neptune, Neptune & Company, for chairing and summarizing a working group session.

Several individuals prepared summaries and critiques of the Symposium for consideration in preparing this Symposium summary and they are acknowledged for their contributions:

Dr. Neil Hutzler	Michigan Technological University, Houghton, Michigan
Dr. Thomas Spittler	U.S. Environmental Protection Agency, Lexington, Massachusetts
Fred Cornell	Environmental Liability Management, Inc., Princeton, New Jersey
David Goldblum	Consultant, San Antonio, Texas

The authors acknowledge all of the Symposium participants who contributed by attending and actively participating not only during the formal presentations, but during the late afternoon and evening working group sessions. Finally, Pat Eagan of the University of Wisconsin-Madison was responsible for the logistics. The Symposium ran smoothly and for this, everyone is extremely grateful.

1. INTRODUCTION

Volatile organic compounds (VOCs) encompass a broad class of chemicals that includes benzene, methylene chloride, and trichloroethylene, as well as many other solvents, petrochemicals, and agrochemicals. As a result of their widespread and intensive usage over the years, VOCs are the most prevalent chemicals at contaminated sites across the United States and abroad. The adverse effects of VOCs vary widely depending upon the compound or mixture in question, source concentrations, transport pathways, and human and environmental exposures. In a majority of cases, soil and ground water contaminated by one or more VOCs are the primary focus of major characterization, assessment, and remedial actions.

Substantial funds are being expended on VOC sampling and analysis, and significant site assessment decisions and remedial actions have occurred and are ongoing. For VOC contaminated sites, however, the conventional measurement and interpretation process may not adequately address sources of error that can severely hamper the overall effectiveness of site assessment and remedial action. Problems result from the unique properties and behavior of these compounds and the manner in which they may move in soil, a complicated system of solids, liquids, and gases. As a result, the effective characterization and assessment of contaminated soil is constrained by spatial and temporal variability and by sampling and analysis errors.

A symposium on "Measuring and Interpreting VOCs in Soil - State of the Art and Research Needs" was held in Las Vegas, Nevada on January 12-14, 1993 (Appendix A). The Symposium was attended by approximately 300 people, representing a wide variety of interests, backgrounds, and disciplines (Appendix B). The geologists, chemists, engineers, hydrologists, and environmental scientists that generate data on VOCs in soil were brought together with the risk assessors and engineers who need the data to evaluate risks and to design and implement cleanup technologies. During three days of formal presentations and working group sessions, the participants:

- Explored the foundation of the conventional VOC measurement and interpretation process,
- Examined results from research and practice that have advanced the understanding of this process,
- Discussed whether data from hazardous waste sites are adequate for addressing the multiphase distribution of VOCs in soil, and
- Attempted to develop a consensus on the state of the art, recommendations for current practice, and critical research needs.

At the beginning of the Symposium, each participant received a proceedings notebook that contained extended abstracts and supporting publications for platform and poster presentations describing:

- Behavior of soil VOCs and implications for measurement,
- Validity of conventional VOC measurements for risk assessment purposes,
- Soil sample collection and handling techniques,
- Sample analysis techniques for mobile and fixed-base laboratories,
- Utility of onsite screening techniques,
- In situ VOC measurement devices and methods,
- Conventional and alternative quality control strategies,
- Data analysis and interpretation for risk assessment and decision making, and
- Innovations in measurement techniques and assessment approaches.

A list of critical questions was prepared by the planning committee and provided to the participants to foster meaningful discussion during the Symposium (Appendix C). Some of the questions were addressed during a series of working group sessions and the results from those sessions are summarized

in Appendix D.

The purpose of this document is to summarize the key issues discussed and conclusions reached at the Symposium. The measurement and interpretation of soil VOCs are described herein in a comprehensive manner with due focus on whether the data being collected and reported are sufficient to meet the needs of the data user. As far as possible, controversy and consensus regarding the state-of-practice and -knowledge have been highlighted in this summary. Current research needs are also outlined. Many details were necessarily omitted. For in-depth treatment of any particular subject, the reader is directed to appropriate literature cited in the references or bibliography sections of this document.

2. SUMMARY AND CONCLUSIONS

During the Symposium many issues were raised and discussed related to measuring and interpreting VOCs in soils (Table 1, Appendix C and D). There was consensus that current practices were seriously flawed in many areas and that results of recent research and practice provided a sound basis for change.

Based on the presentations and discussions at the Symposium, the following conclusions were drawn.

2.1 State-of-the-Art and -Practice

Behavior and Measurement Process --

- The classification of VOCs is somewhat arbitrary and includes a variety of organic compounds that possess widely varying properties and behaviors in soils.

- VOCs in soil are unique due to their prevalence, multiphase behavior, and potential adverse public health and environmental effects. They often are the principal contaminants of concern and determine the need for and nature of remedial actions at a given site.

- Decision-making needs and adequacy are incorporated in the data quality objectives and data assessment process. The adequacy of data is largely dependent on the potential for and impact of making an erroneous decision. Errors in measurement and interpretation of VOCs in soils include (1) real spatial and temporal variations that are not adequately characterized due to the normally limited number of sample locations and observations, or (2) errors due to soil VOC sampling and analysis and data management. A comprehensive and robust model for allocating error among various process activities is currently unavailable.

- Design of sampling and analysis programs must be based on the question(s) to be answered and the potential decisions to be made within the context of decision support zones (i.e., volumes of soil). Naturally large spatial variability in soils can lead to wide variation in soil VOCs over short distances. To define this variability, high sampling densities and spatially disperse data are needed.

- Measurements of ancillary soil properties (e.g., water content, organic carbon content) can provide valuable complimentary insight into spatial variability and soil VOC behavior. This information can enhance decisions made regarding characterization, assessment, and remedial actions for soil VOCs.

Sampling and Analysis --

- Ground surface and in situ diagnostic tools provide a valuable method for examining soil regions and defining decision support zones. Measurements of VOCs in soil vapor have been widely used for diagnostic purposes. They are not as quantitative for total VOCs as bulk soil matrix measurements if the latter are properly done.

Table 1. Examples of relevant problem areas and issues discussed at the Symposium. [a]

Area	Some issues discussed
Perceived problem	• Purpose of VOC measurements, overall problem and significance, technical facets, and institutional facets.
Decision-making needs	• What are the questions to be answered, decision quality versus data quality, risk analysis requirements and use of field data.
Sampling designs	• Definition of decision support zones, reconciliation of diverse data and information sources, requirements and use of ancillary data.
Measurement techniques	• Diagnostic techniques to define regions of interest, sample acquisition methods, utility and methods of sample compositing, sample screening and infield analyses, sample containerization for off-site analyses, accuracy and precision of VOC analyses.
Data interpretation	• Role of formal data validation, treatment of values near the detection limit, statistical treatment of spatially and temporally disparate data, visualization methods.
Regulatory framework	• Requirements versus guidance, how practices can be changed.

[a] Refer to Appendix C for discussion questions and Appendix D for working group responses.

- Soil samples should be acquired with as little disruption as possible during collection and handling. The subsample for analysis should be removed from the bulk soil sample in an intact state and quickly transferred to the analysis vessel in a single step, either in the field or in the laboratory. This subsample transfer should be made as soon after collection as possible.

- The use of direct-push sampling technology can acquire intact bulk soil samples at depths of 30 m or more with less disruption and lower cost than conventional drilling and split-barrel sampling methods.

- Far greater emphasis must be placed on the use of field analytical methods for providing data for decision-making purposes. Field methods offer the potential of providing increased spatial and temporal information more rapidly and at reduced cost.

- Laboratory analytical results are not inherently superior to field analytical results. However, quantitative field analytical methods must be distinguished from qualitative field screening methods. There is need for an effective program that provides for timely evaluation and approval of field analytical methods.

- Field measurements of some, perhaps many, soil VOCs can be made with an accuracy equivalent to a fixed base laboratory by using available and affordable field gas chromatographs (GCs) with water immersion and headspace methods.

- Field analytical data can be used for significant decision-making, including quantitative risk assessment, as long as this intention is clearly incorporated into the data quality objectives process.

- Portable instruments, sensors, and test-kits are emerging, for on-site and in situ measurement, that provide adequate information more rapidly and at lower cost. In selecting an emerging field method, it is important to consider data quality objectives and the method accuracy, precision, and interferences.

- Soil samples collected by conventional practices (i.e., disrupted soil placed in

sealed containers and refrigerated at 4°C with subsequent laboratory subsampling and analysis) will normally yield VOC concentrations that are significantly different than the true in situ concentrations. Significant losses of VOCs (up to 90% or more) have been reported due to volatilization caused by sample disruption during field or laboratory subsampling, as well as due to leakage and/or transformation during pre-analytical holding. These losses have been observed for both halocarbons and petroleum hydrocarbons. These losses can be mitigated by sample collection and transfer with coring devices and through improved preservation methods.

- Improved preservation of soil VOCs beyond that afforded by low temperatures can be achieved by either onsite immersion of the sample in an organic solvent (methanol is commonly used) or containerization in a closed-vial analysis vessel. The former method is most appropriate for high concentrations of VOCs and offers potential for indefinite holding and high extraction efficiencies. It does suffer from field handling of a potentially hazardous material and dilution of 10- to 100-fold during analysis. The latter method is most applicable for low concentrations and offers low detection limits. Since dilution is precluded, however, samples with high VOC concentrations can swamp the analytical instrument.

- Compositing of soil samples seemingly can be employed to more cost-effectively establish, and to some degree, characterize decision support zones. Further work is required to assess the detection limit and matrix interference questions, however.

- Some VOCs may become physically entrapped in the microstructure of soils and be difficult to desorb and remove during conventional purge-and-trap extraction. This may result in underestimation of the concentration of soil VOCs in the soil matrix. Disruption of the soil macro- and microstructure may be required to recover these entrapped VOCs.

Data Assessment and Interpretation --

- Data assessment must answer questions regarding data quality, adequacy, and acceptability. This is normally done within a regulatory and contractual framework that focuses on laboratory analyses. Depending on the type of data and the depth of assessment, costs for validation can range from three to ten times the analytical costs. While validated laboratory analyses are costly, they can be of little value if sampling and handling yield substantial and significant bias, or if discrete samples do not represent the region of interest.

- Interpretation must reconcile and integrate the various elements of a soil VOC data set (e.g., field screening, on-site lab analysis, off-site lab analysis, physical site conditions, etc.). The emphasis on the analytical portion of the soil VOC measurement process has inappropriately focused on discrete values rather than on comprehensive data sets and information packages.

- Uncertainty exists with prediction of VOC concentrations at un-sampled locations. Due to normal subsurface heterogenieties combined with the complex behavior of VOCs, true soil concentrations at unobserved locations may deviate by one or two orders of magnitude from those predicted based on measurements at an adjacent but separate location. This situation further emphasizes the need for and value of diagnostic measurements (e.g., in situ soil gas) and field screening of spatially disperse samples (e.g., with field immunoassay tests).

- A serious shortcoming with the current process of characterizing soil regions for VOCs may be the limited number of samples often collected from which

inferences are made (e.g., one, 5-cm^3 sample per 50 m^3 of soil). While spatial correlations and geostatistical techniques can provide some measure of uncertainty, no statistical tool will overcome the lack of spatial information provided in a limited data set.

- Interpretation of soil VOC data is often fraught with difficulties due to inherent problems with the measurement process coupled with inadequate planning and communication across all involved disciplines. For example, a question often remains as to whether a given measurement method is appropriate to answer questions regarding the exposure pathways of concern.

Improving Past Practices --

- Despite recent advancements, serious deficiencies remain in practices commonly used for measurement and interpretation of soil VOCs. Changes are warranted and should be made within the context of total quality management. There is new knowledge to infuse into an existing process to improve its efficiency and effectiveness. In many cases, the information base is adequate to support change and there is flexibility in many regulatory programs to permit change.

- Modifications to conventional practices are being adopted as standard practices by standards-setting agencies and being mandated for use by some state regulatory agencies. An example is ASTM method 4547, standard practice for sampling waste and soils for volatile organics (includes limited disruption subsampling by coring and in-field immersion in methanol).

- Modifications to standard analytical methods are also being implemented. In the Third Update to EPA SW-846 a new procedure will be included for solid matrices that employs an automated purge-and-trap system which agitates the sample within the original collection vessel during the purge step (new SW-846 method 5035). This method enhances VOC preservation and recovery efficiency.

- There is great concern over the lack of a clear process for getting approval to use improved practices. This is of particular concern for individuals who must complete sampling and analysis projects, but are unable to use new methods.

- While erroneous conclusions may have been reached regarding soil VOC concentrations at a given site, it is uncertain what the adverse impacts may have been on decisions regarding the nature and extent of contamination, need for cleanup, and/or verification of cleanup achieved.

2.2 Research Needs

Despite a considerable body of research and experience in measuring and interpreting VOCs in soil systems, further research is necessary and appropriate in several areas as outlined below.

- The interactions of VOCs of differing properties with mineral and organic materials in soil need to be assessed in light of current and future methods of sampling and analysis. The potential for matrix diffusion and intraparticle entrapment and their effects on measurement accuracy need to be elucidated.

- There is a need to elucidate the spatial and temporal variability typically encountered with soil VOCs under different conditions. This information is needed to better understand the degree of accuracy and precision appropriate for assessing a given soil region.

- Continued research and development are needed to yield field screening and analytical methods of known and predictable performance for measuring

different VOCs in different soil media.

- Controlled laboratory and field experiments are needed to rigorously evaluate the stability of VOCs of widely differing properties as affected by containerization and preservation techniques. Methods to increase the stability of samples to long time frames would provide more accurate VOC data and also facilitate sequential analysis of samples and sample archiving.

- To help address spatial variability issues, technically viable methods of compositing soil samples for analysis of VOCs need to be developed. Issues of matrix interferences and detection limit constraints need to be resolved.

- There is a need for a comprehensive error model that defines the different error components for soil VOC measurements at a single point in space and time and for multiple measurements within a soil region of interest.

- QA/QC strategies and methods need to be analyzed to determine the most cost-effective process. Alternatives include use of performance evaluation materials and referee laboratories.

- The relative importance of accurate measurements of discrete samples must be evaluated in light of the great uncertainty and error potential within risk assessment and remedial action decision-making. This is important given that the uncertainty associated with risk assessment can be several orders of magnitude greater than that of the characterization process itself.

3. THE SOIL VOC PROBLEM

VOCs are the most prevalent contaminants at many hazardous waste sites in the U.S. and abroad (Table 2) (4, 31, 43, 51, 63). They are significant in that they are often mobile and persistent in soil environments and frequently contaminate extensive regions of soil and ground water. They may also contaminate ambient air and nearby surface waters. Inherent properties of the compounds vary widely as do their mobility in various media and their potential health effects (18, 29, 32, 33, 51, 61, 90).

An understanding of soil and how VOCs behave within it is important to understanding the degree and rate at which VOCs can migrate and lead to potentially harmful exposures to humans and the environment. While most investigators focus on measuring the highest concentration of VOCs that may be extracted from the soil in virtually any phase, it is most important in the risk assessment and remedial action process to understand the soil system and the phase distribution of VOCs. This enables better characterization of transport and fate processes and exposure pathways, and enhances evaluation of remediation options.

Soil is normally considered to be the fine-earth fraction of geologic material (e.g., < 2 mm) (3, 6, 8, 48, 61). It is a complex media comprised of solid, liquid, and gaseous phases which interact in a dynamic equilibrium. Soil is a heterogeneous material with properties varying at different spatial and temporal scales (Fig. 1 - 2, Table 3). At some hazardous waste sites, "soil" may actually be a poor description of the solid material being sampled. In the sampling of soil and soil-like material, particle size is important as is the composition, both of which may vary over a range of spatial scales.

Volatile organic compounds in soils are typically present in several phases (Fig. 1) (29, 32, 51, 61). The compounds may be adsorbed to or absorbed in the soil, and the compounds may exist in the interstitial spaces as liquids or vapors. The degree and rate at which the compounds partition within and migrate through soil depends on the properties of the compound and the soil system. A detailed discussion of these factors may be found in several excellent reviews (e.g., 29, 51, 61).

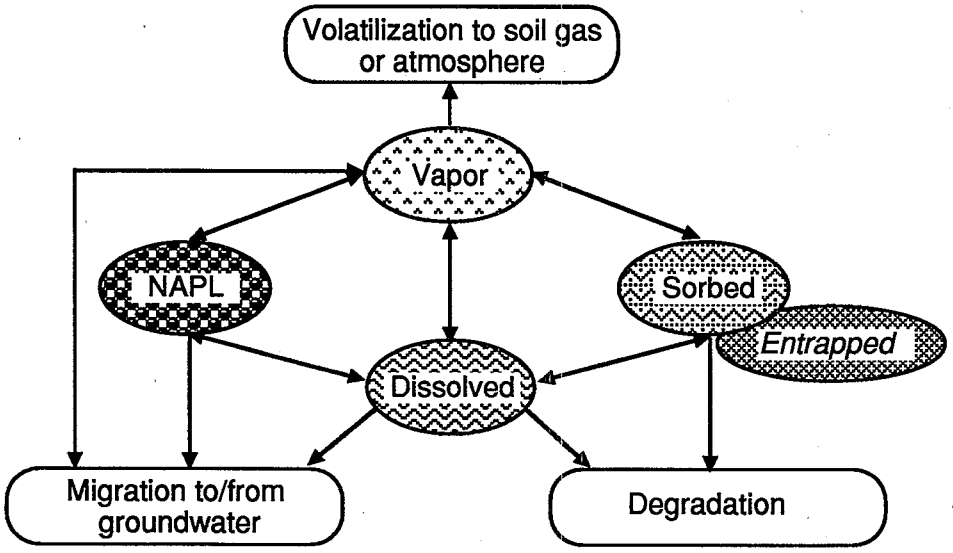

Fig. 1. Illustration of the partitioning and potential interphase transfers of VOCs in soils (after 51).

Soil VOCs pose significant challenges to the investigator who seeks to assess the risks they pose to human health and the environment. The accurate measurements necessary for assessment purposes are difficult to achieve since VOC concentrations in soils vary widely in space and time, and measurements are subject to considerable random and systematic error (3, 12, 15, 21, 25, 35, 37, 43, 44, 51, 52, 63). The goal of an investigator of a hazardous waste site is to obtain measurements of VOCs that are sufficient to meet the needs of the decision-makers, including those who must assess the risk to human health and the environment and those who select, design, and implement a remedial action.

Variability in the measurement of VOCs can be disturbingly large (e.g., 1 to 3 orders of magnitude) as a result of natural variability and measurement errors even when standard measurement techniques are employed (Fig. 2) (43, 51, 52, 63). The distribution of VOCs in soil can be quite variable as a function of time and space (6, 9, 18, 44, 48, 51, 68, 89).

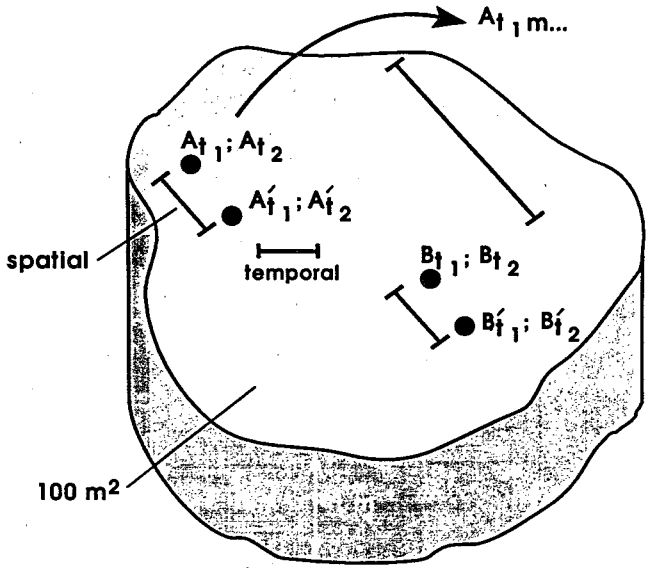

Fig. 2. Illustration of spatial and temporal variability and measurement error potential within contaminated soil regions (64).

Table 2. Some volatile organic compounds included within the Target Compound List (TCL) in the USA and their occurrence at Superfund Sites (after 63).

Compound	Properties [a]				Occurrence rank and frequency [b]
	Molecular weight	Boiling point	Vapor pressure	Aqueous solubility	
	g/mol	°C	mm	mg/L	
Vinyl Chloride	62	-13.9	2660 (25°C)	1100 (25°C)	23 [8%]
Methylene Chloride	85	40	349	20000	18 [10%]
Acetone	58	56.2	270 (30°C)	Miscible	
1,1-Dichloroethene	97.0	31.9	500		20 [9%]
1,1-Dichloroethane	99.0	57.3	180	5500	19 [10%]
trans-1,2-Dichloroethene	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%]
Trichloroethylene	131.5	86.7	60	1100 (25°C)	1 [35%]
Benzene	78.1	80.1	76	1780	5 [23%]
2-Hexanone	100.2	128	2	35000	
Tetrachloroethylene	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	
m-Xylene	106.2	139	6		14 [13%]
o-/p-Xylene	106.2	144.4	5	175	"

[a] Properties are at 20°C unless another temperature is shown in ( ).

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

Table 3. Typical distributions of soil properties important to VOC behavior (68).

Soil property	Distribution	Average [a]	Std. dev. [a]
Total volumetric porosity (v/v)	Normal	0.373	0.09
Volumetric water content (v/v)	Log-normal	0.048	2.
Fractional organic carbon content (wt./wt.)	Log-normal	0.028	3.17

[a] Geometric mean and standard deviation are given for log-normal distributions.

As a result, closely spaced samples can yield dramatically different VOC concentrations. Measurement variability and bias can also be large. A common problem is negative bias due to large losses of the VOCs before the sample is analyzed, and incomplete extraction of the VOCs from soils at the time of analysis (43, 50, 51, 63, 71). Positive bias may also be present where compounds are created as a result of biological and chemical transformation processes, or where compounds are mistakenly reported as a result of interferences or gross errors in the analytical phase. Negative bias can greatly influence the risk assessment process by underestimating the potential risks to human health and the environment.

Measurements are made to support decisions and the various sources of variability and error may or may not adversely affect a given decision or subsequent action (Fig. 3). An investigator may take precautions to minimize the bias and variability in the measurement process. But typically an accurate assessment of bias and variability is lacking because of difficulties in accurately measuring VOCs in soils. Often, an investigator is unaware of the bias and variability that may be tolerated in a risk assessment process. Consequently, an investigator may try to obtain what is thought to be the best available VOC data by concentrating time and money on the analytical phase. Frequently, the bias and variability in the analytical phase of the measurement process, is only a small part of the uncertainty and error associated with characterization of VOCs in soil regions (12, 15, 52, 44, 63).

A benchmark that is used to evaluate acceptable levels of contaminants in soil is frequently referred to as an "action level". Concentrations of VOCs in soil that are reported above the action level are presumed to be unacceptable, and a variety of actions may be triggered. Generic "action levels" for VOCs in soil have been difficult to establish because site-specific factors and various soil types can greatly influence the risks that might be created from soil that is contaminated at a particular concentration. Even if action levels are prescribed, an equally important parameter often is not. This is the volume or mass of soil within which the concentration of contaminant is sampled, measured, or is of concern. A reported action level without a corresponding soil volume, can be virtually meaningless in characterizing a region of interest.

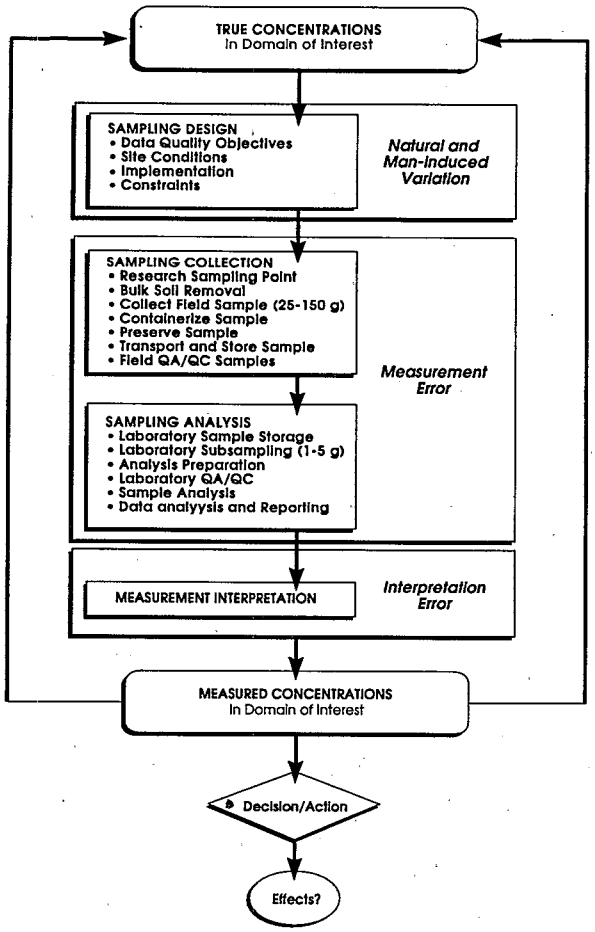

Fig. 3. Illustration of a conventional measurement process for VOCs (after 62 - 64).

The volume of material being sampled is often referred to as the "support". The volume of material being analyzed is always significantly smaller than the volume of material being sampled. These small sample volumes are typically used to make inferences about the characteristics of larger volumes of material at a site. These larger volumes are increasingly being described in terms of units, e.g., "decision unit", "exposure unit", and/or "distribution unit". Like most contaminants being sampled and measured in soils, VOCs must be carefully measured and reported with significant attention devoted to the "support" and the "units" of soil being assessed throughout the measurement process.

Analytical methods measure the concentration of a contaminant in a soil sample that may be as small as 1 to 5 grams. This sample may come from a soil core that is supposed to represent the volume of soil in a "decision unit" or "exposure unit" that may be 100 m^3 or more in size. Homogenization and compositing of samples are means for increasing the "representativeness" of the sample, but these processes have so far been especially difficult to employ in VOC sampling. Due to analyte losses, they may lead to samples that are actually less representative of actual site characteristics. For example, reducing the particle size of a soil core sample by grinding so that any subsample is comparable to another may dramatically alter the concentration and phase of the VOC contaminants in that subsample relative to actual site conditions. Data from soil samples that are treated in this way may be input into risk assessment, transport and fate, or treatability models and yield very misleading results.

For characterizing larger spatial scales, compositing or statistical "averaging" of samples may be required due to resource limitations. However, with soil VOCs, simple compositing or averaging may obfuscate the identification of important small-scale features such as "hot spots." Reported concentrations for an area may be significantly less than the concentration of contaminants in hot spots. Important features, such as stringers and layers of soil contaminated with VOCs, may also be completely missed or misrepresented.

4. DECISION-MAKING NEEDS AND INFORMATION ADEQUACY

All too often the basic questions to be answered by a sampling and analysis program have been poorly stated and defined. Sampling efforts are frequently developed to define the extent of contamination at a site and to determine whether the contamination exceeds an action level (3, 6, 12, 28, 48, 68). Resources are often allocated to the sampling effort with little thought being given to acceptable error rates and margins for error in the site characterization effort. Important volumes, e.g. support, exposure units, and decision units, are often not defined. Tradeoffs between the collection of more data to better define the nature and extent of contamination, versus remediating portions of the site, are often made poorly or not made at all.

Defining exactly what data is needed and how good the data must be for various purposes (e.g., risk assessment, engineering design, process monitoring and control) is frequently done too late in the characterization and monitoring process. The necessary and appropriate scientific and technical disciplines (e.g., analytical chemists, toxicologists, statisticians, quality assurance specialists, engineers, lawyers) are frequently not assembled into a team at the beginning of the project to help define basic questions. Instead, they are independently consulted at various stages of the process and often at stages where they have little ability to review the basic questions and determine whether those questions will be addressed efficiently and economically.

Increasing attention is being paid to the development of data quality objectives (DQOs) at an early stage in a site characterization effort (28, 77, 85). All too often, however, DQOs are narrowly developed and focused on the analytical phase of the process. Precision, accuracy, representativeness, completeness, and

comparability are addressed with emphasis on the analytical phase. Little effort is devoted to an analysis of the number, type and quality of data that will be required to meet the needs of the decision-maker in answering basic questions.

Exposures to contaminants at hazardous waste sites depend on contaminant sources, transport pathways, and activity patterns (86). A person or species may spend part, or all, of its life at a point where direct exposure to a contaminant can occur. In other cases, the contaminant in the soil must be capable of migrating to a point where it can come into contact with the person or species. VOCs can move through the environment in many ways, including transport as nonaqueous liquids, aqueous constituents, vapors, or particle-sorbed compounds.

The exposure pathways of concern contribute significantly to the decision-making needs and must be considered in establishing the measurement process. For example, if the exposure pathway of concern was the migration of vapors through the subsurface because the vapors might enter basements, manholes, and underground utility corridors, then sample collection and analytical methods that assess the amount of VOCs that are present, or may develop, in the interstitial spaces of the soil would be most appropriate. Similarly, if the exposure pathway of concern was contamination of groundwater used for drinking water, then methods using a aqueous extractant to determine the soil VOCs that would leach into ground water over time would be appropriate. To assess the risk from soil ingestion, bulk soil samples could be collected and extraction done with a technique designed to mimic the desorption that occurs during and following ingestion. In contrast, for some modeling purposes, total soil VOCs must be quantified using bulk sample collection and more aggressive extraction techniques, possibly using an organic solvent or supercritical fluid. In each exposure scenario some consideration must be given to the volatile organics of concern and the soil morphology and chemistry. The goal is to select a measurement process that is most appropriate to answer basic questions regarding exposure pathways for VOCs.

No measurements of soil VOCs are made without some prior knowledge of the site. This knowledge is used formally, or informally, to determine locations where samples are collected. Each source of data carries with it the potential for bias and variability. The quality of the data influences in varying degrees the basic decisions that are made about the site. It is likely that no single data point and single observation will determine the degree to which resources are spent to further investigate a site and to remediate the contamination. If this were the case, the quality assurance/quality control (QA/QC) program for the site investigation would have to be quite rigorous. It would not be enough to ensure that the analytical portion of the study were producing data of high accuracy and precision, without ensuring that the samples were properly collected. In reality, critical decisions on hazardous waste sites are usually made with a minimum number of data from different sources with the goal being to have a preponderance of information that leads to a high quality decision.

There are several ways to reduce the risk of making an incorrect decision in characterizing soil VOC contamination at a hazardous waste site. One way is to divide the site up into smaller areas where a risk of making an incorrect decision in a given area will not be catastrophic overall. Another is to obtain more discrete data. Another is to obtain less, but more "representative" data. This may involve compositing of samples if the basic objective for the study allows this. Another way is to improve the quality of the data.

A major source of bias and variability in VOC measurements in discrete samples is the loss of volatiles from sample collection to analysis. Soil matrix effects can also be a factor. Field screening methods that can generate data at relatively low cost and with minimal delays may be superior to more conventional laboratory measurements even if the analytical methods are judged to produce more representative, more accurate, and more precise data. Research has shown that large bias and variability occurs before a sample is analyzed and this error can overwhelm the

error present in many currently prescribed laboratory methods (35, 37, 43, 47, 65, 75). Loss of volatiles begins from the time a sample is collected to the time it is analyzed. The losses may be from biological degradation, chemical transformation, or outright losses of the sample. A sample that is analyzed soon and with little disruption is more likely to be representative of actual site conditions.

Decision-making needs and information adequacy must be considered within the overall perspective of the characterization and assessment process. It can be argued that due to a high degree of uncertainty present in exposure scenarios and health effects (i.e., orders of magnitude) coupled with potentially great spatial variability, striving for accurate and precise quantitation of VOCs in discrete soil samples is unfounded and unnecessary (12, 15, 44, 49, 68). If one were to generalize, the relative uncertainty and error in the characterization and assessment process could be ranked from high to low as follows:

exposure/health effects >>>

spatial variability > >

sampling and handling > >

analysis.

Depending on the decision to be made, an investigator should place appropriate emphasis on the sampling design, soil VOC measurement methods, or data interpretation process.

5. SAMPLING DESIGN

A major objective of sampling design is to yield measurements that satisfy the DQOs established (20, 21, 28, 77). This normally involves measuring concentrations of VOCs in regions of interest that are representative of the true concentrations present (Fig. 3). To accomplish this, the design process must address the phase distribution of soil VOCs, real spatial and temporal variability, and measurement variability and error. Many decisions must be made, including determining a measurement strategy (e.g., in situ soil gas survey, collection/analysis of discrete samples from a 3-dimensional grid), the number and placement of sample locations, the frequency of sampling, and the analyses to be completed. If done properly, decision-making based on the data generated will not be flawed by the measurement process. For example, if VOC concentrations truly exist that would pose unreasonable risks to human health and the environment, they would be measured and a correct decision made.

Data from individual sample locations are frequently clustered to make decisions on areas of a site (e.g., decision support zones). A "remediation unit" can be described as the smallest unit of soil to be treated or remediated if the measured concentration within the unit exceeds a particular level. An "exposure unit" is a portion of a site where present or future exposures of humans or species would exceed acceptable levels of risk.

Error (i.e., measured concentrations ≠ true concentrations) is a fundamental part of the measurement process. The sampling design should ideally provide for an estimate of the uncertainty and error in the measurements made (20, 21). A key question is what are the sources of error and how much error can be tolerated in the measurement process while still allowing for reasonably correct decisions.

The assessment of error in the measurement of VOCs in soils is complicated. Few soil standards exist. Standard analytical methods often do not provide consistent, accurate results when known concentrations of VOCs are introduced into soils, and the soils are subsequently measured. The concentration and nature of the compound, matrix effects, and the chosen analytical technique contribute to the bias and variability. How, then, can a sampling design enable an assessment of bias and variability in soil VOCs at a given site?

Methods have been proposed for QA/QC programs that can provide quantitative assessments of error at various stages of the sample collection and measurement process (42, 89). A comprehensive approach,

developed primarily for conservative contaminants such as metals in soil, may be adapted to VOCs in soil. In this approach emphasis is placed on the identification of batches and the placement of a variety of QA/QC samples in the batches during an investigation to assess and track the errors. QA/QC samples, such as collocated samples and split samples, can be used to provide estimates of analytical precision, but estimates of sampling bias are more complicated.

The assessment of bias requires soil samples with known concentrations of contaminants. Making representative "evaluation samples" is difficult for metals in soil and even more so for VOCs in soils. Controlled spiking of soil with VOCs to yield representative partitioning within the soil matrix is difficult and highly variable, as is the subsequent recovery of the VOCs. Changes in VOC concentrations can occur at the time the soil is spiked and continue until the time the sample is analyzed. The use of surrogate spikes may not provide a true measure of VOC recovery in the purge phase because they are only introduced to the soil with the internal standards immediately prior to analysis.

Advocates of the use of organic solvents, such as methanol, to preserve and extract VOCs in soil, offer a technique that allows evaluation samples to be readily created. Double- and single-blind QA/QC samples can be created by spiking VOCs into the methanol solution in a sample vial, rather than trying to spike the soil itself.

There are many considerations in assessing the impact of errors in the measurement of VOCs in soil. If the measured concentration of VOCs is clearly above a concentration of concern (or action level), then it is unlikely that good estimates of error will be required, especially if a negative bias is a common error. The VOC data will support needed action. However, if the measured VOC concentrations are near an action level and the consequences from making a wrong decision are great, then the importance increases for a rigorous QA/QC program to assess the error and variability in the data. A QA/QC program that attempts to assess errors throughout the entire sample collection and measurement process becomes more important.

Sampling designs should enable the integration of VOC analytical results with general geologic and meteorological information. This is important to better understand the VOC occurrence, transport, and fate and to put the VOC sample data into proper perspective. Samples corresponding to those used for VOC analysis should be analyzed for other important properties (e.g., texture, water content, organic carbon content). This information will help answer important questions. For example, were the samples collected in a soil horizon that is important to characterize for the assessment of potential exposure pathways? Did the rain, wind, or temperature affect the sampling program and the collection of the samples? Clearly, a number of factors need to be assessed in conjunction with the assessment of the data from the VOC analytical phase.

Sampling designs need to include far greater emphasis on collection of spatially disperse sample data of "acceptable quality" to enhance the overall characterization within a site and its decision support zones. This can be best accomplished using on-site, real-time methods taking advantage of new technologies such as hydraulic probes, in situ detectors, and field analytical instruments. While simple screening procedures (e.g., hand-held photoionization detectors for headspace measurements) have been used to provide qualitative information, advancements in sample acquisition equipment and field analytics need to be incorporated in quantitative decision making. It must be recognized that meaningful data can be achieved with improved field instruments and procedures (e.g., field-portable gas chromatographs). Continuing development of chemical and immunoassay test kits will likely provide attractive advantages for field analysis of VOCs.

The sampling design must ensure that the data generated will be useful with respect to answering the basic questions that were identified in the early DQO stages of the site investigation. For example, does the bias

and variability in the VOC data significantly affect the basic assumptions and models that are being developed to estimate the risk to human health and the environments? Do the assumptions made in the risk assessment process and the evaluation of remediation measures warrant the collection of more data, or better data? These questions are best addressed by a team approach where all parties involved in the investigation are willing to accept the fact that uncertainties in the data may be great. Specific actions then can be taken to further resolve the basic questions that were identified early in the site investigation process.

6. SAMPLING AND ANALYSIS

Measurements of soil VOCs can be made with varying degrees of quantitation certainty and specificity (13, 26, 30, 31, 42, 46, 54, 58, 69, 70, 74, 79). The VOC measurement process is illustrated in Fig. 3 while the current soil VOC sampling and analysis paradigm is depicted in Fig. 4. The current soil VOC paradigm emphasizes the character and quality of discrete data points by employing bulk soil sampling for laboratory analyses and data validation. This paradigm is believed to be flawed by some and in need of change (e.g., 63, 64). Questions can be raised regarding the reasonableness of the current practice of collecting a 1 to 5 g subsample from a discrete location, analyzing it off-site for a suite of VOCs of widely different properties, scrutinizing the data point to determine its "quality", and using only the "quality" data for making inferences about large soil regions (e.g., 50 to 100 m^3 or more).

Measurement of soil VOCs often involves quantitation of a large number of organic compounds with widely differing properties (see Table 3). The basis for this is not clear and quantifying a lengthy list of compounds can compromise effective measurement of the most prevalent and important ones. Evidence is growing that quantification of a selected number of compounds can yield adequate information about the risk posed by a site and the need for action (58).

It may be appropriate to reconsider and refine the definition and categorization of VOCs. The current categorization of VOCs was developed based on analytical considerations. Contaminant properties and sampling considerations suggest that multiple categories of VOCs 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, trichloroethylene (TCE) would likely be grouped in a separate category from ethylbenzene, based on TCE's higher mobility, persistence, and adverse health effects. Such a re-categorization would be conducive to field screening and onsite analytical methods, since it would facilitate development and use of methods targeted at one or a few analytes.

When making soil VOC measurements at a given site, there is always need to define boundaries for decision support zones. For example, boundaries can be used to separate clearly contaminated areas from clearly clean areas. The use of diagnostic tools, like in situ and ground surface soil vapor surveys, represent a reasonable approach to boundary definition. These techniques provide for identification and cursory evaluation of areas of potential contamination, but are limited for quantitation of total soil VOCs (4). While some argue for the quantitative and definitive use of soil gas surveys in lieu of bulk soil sampling and analysis, evidence supporting this application has not been generated.

Sample acquisition from surface and near-surface soil regions is normally done with hand-held sampling tools and utensils (e.g., shovels and hand-augers, sampling spoons and spatulas) (43). Sample acquisition at depth (e.g., > 2 m) is often accomplished using a backhoe or drilling equipment. Once the bulk sample is acquired from the subsurface, it is either containerized in the sampling device (e.g., sleeve within a split-barrel sampler) or subsampled and then containerized in a relatively small vial or jar (e.g., 40-mL glass vial) (43, 76).

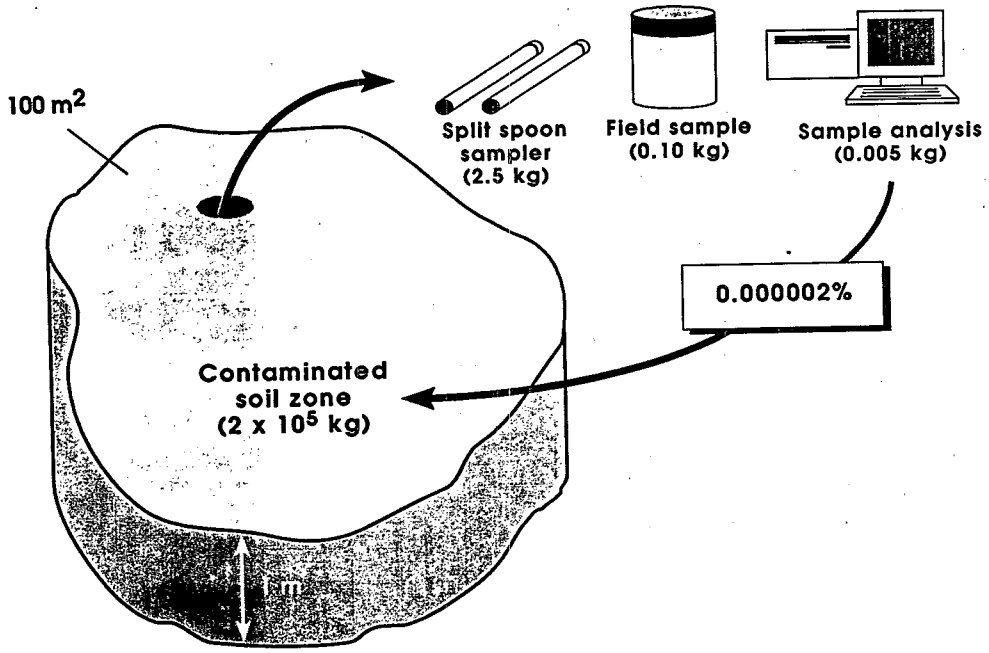

Fig. 4. Representation of a current paradigm for soil VOC measurement and interpretation (64).

The impact of sample acquisition on the concentrations and phase distribution of VOCs is not well understood. A number of investigators have described the impact of subsampling on true soil VOC concentrations. Losses of up to 90% or more have been recorded (30, 43, 62 - 65). Given these observations, there is concern that the sample acquisition process (e.g., coring) may alter the distribution of VOCs in a decision support unit. Minimizing disturbance of the subsurface should minimize acquisition-induced changes in VOC concentrations and distributions.

Hydraulic-powered probes (e.g., cone penetrometers) are new methods for sampling the subsurface in a less disruptive manner (5, 73, 74). These commercially available pieces of equipment are being increasingly utilized to acquire discrete samples from depths up to 30 m or more. The performance of these probe techniques is highly dependent on the nature of the subsurface materials (e.g., sand, clay, gravel, boulders). In general, these sampling techniques facilitate collection of samples more rapidly, at lower cost, and with less disruption. The addition of sensors to the probe devices will enable the collection of real-time information regarding VOCs in the subsurface.

Once the bulk sample is acquired, one or more subsamples are normally collected and containerized. These samples are then subjected to on-site analyses by qualitative or quantitative methods (13, 26, 30, 31, 42, 46, 54, 58, 69, 70, 74, 79). In many cases, samples are preserved for holding prior to off-site analyses which typically don't occur until near the end of the 40CFR-mandated 14-day holding time (76).

Questions were raised at the Symposium regarding the changes in soil VOCs caused by sample collection and handling. Research conducted during the past five years has consistently demonstrated that conventional

practices for sample collection, containerization, and pre-analytical handling can result in significant losses of VOCs (i.e., 90% or more) (Fig. 5 - 9) (3, 30, 35, 37, 43, 47, 51, 62 - 65, 67). The rate and extent of change varies with VOC and soil matrix properties, with seemingly higher rates of change with the more volatile compounds. While the mechanisms of change are not clearly understood, a major cause is speculated to be volatilization losses of analyte as a result of disruption during sample collection, storage, and laboratory subsampling.

Recent research and practice have revealed alternative methods which can improve VOC measurement accuracy by an order of magnitude or more for the more volatile/low solubility compounds (e.g., TCE) (43, 51, 65, 73, 75). Selected methods are highlighted below.

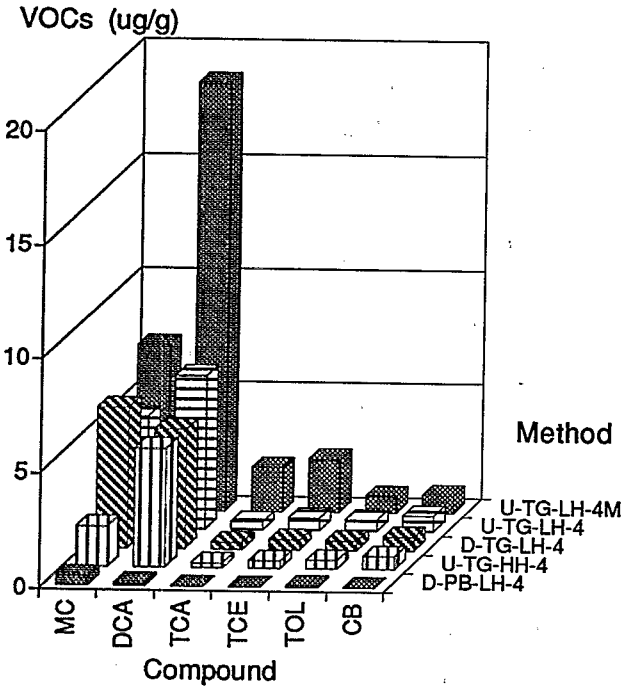

Fig. 5. VOC concentrations in samples of sandy soil as affected by sample collection and handling methods (65). (Note: Method attributes: D = disturbed soil; U = undisturbed soil; PB = plastic bag; TG = Teflon-sealed glass; LH = low container headspace; HH = high container headspace; 4 = 4°C holding; 4M = methanol immersion at 4°C)

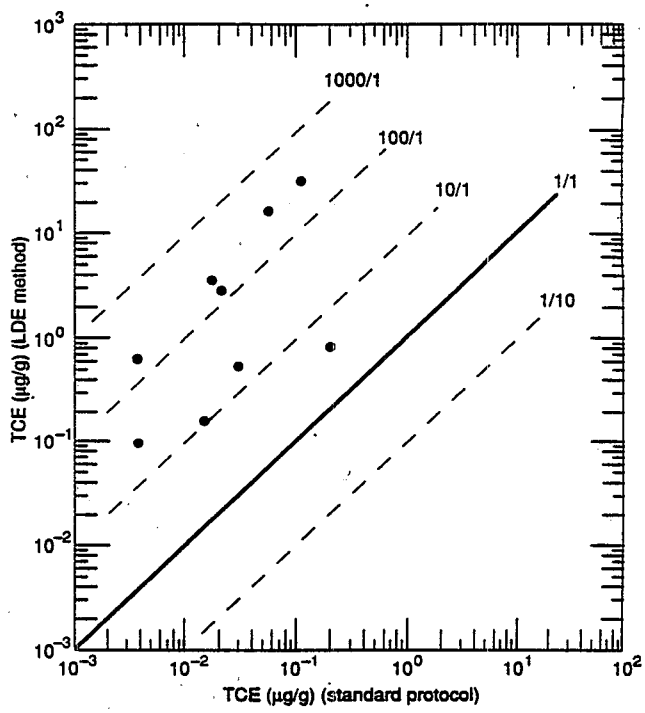

Fig. 6. TCE concentrations measured by purge-and-trap GC/MS in collocated field samples as collected by standard versus modified methods (30, 31). (Note: Standard = packing of a vial and lab subsampling; modified = micro-core subsampling and methanol immersion. LDE = limited disruption extraction)

One method involves collection of largely undisturbed soil cores in sleeve-lined, split-barrel samplers (2). 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 one subsampling step (i.e., field subsampling) and maintains an intact soil volume until analysis is imminent at which time a 1 to 5 g subsample is taken. This approach, however, 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, a known cause of VOC loss (Fig. 5 - 6). The soil from the micro-cores

(e.g., 3 to 10 mL) can be extruded directly into a 40-mL glass vial designed for analysis without further soil sample transfers. Analyses can be done by headspace techniques (30, 31, 46, 74) or by direct connection to a purge-and-trap instrument (64). 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 or a methanol solution) contained in a Teflon-sealed glass vial or jar (Fig. 5 - 7) (2, 65, 75). The methanol acts to inhibit volatilization and biodegradation while enhancing extraction efficiency. This 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 detection limits by a factor of 10 to 100 and requires field handling and transportation of potentially hazardous chemicals. An alternative solvent (e.g., acidified water) could mitigate this problem.

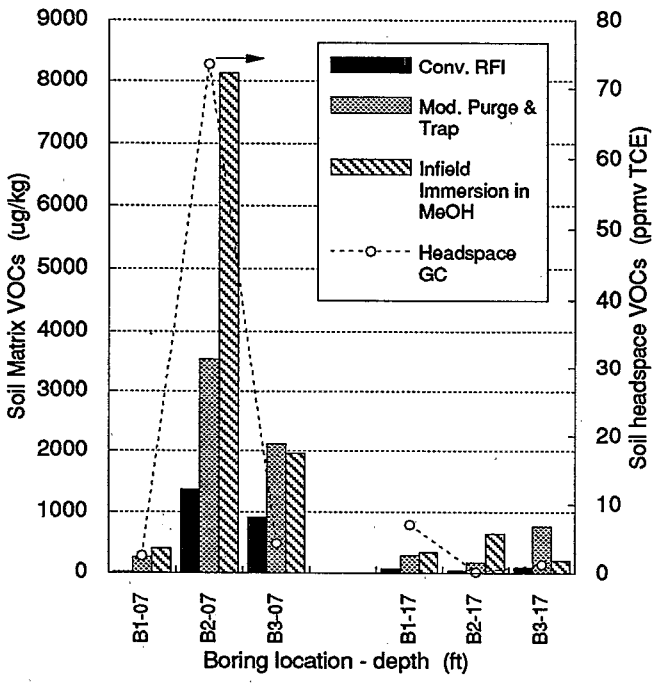

Fig. 7. VOC concentrations in collocated field samples from a silt and clay deposit as a function of sample collection and handling methods (63). (Note: Principal VOCs = TCE and methylene chloride. RFI = conventional RCRA packed vial and lab subsampling; Mod. Purge & Trap = micro-core subsampling and on-site transfer to a purge vessel; Infield immersion in methanol = micro-core subsampling and on-site transfer to a sample vial containing methanol; and Headspace GC = micro-core subsampling and on-site transfer to a sample vial containing distilled water. Analyses by GC/MS except the Headspace analysis done by GC.)

Minimizing pre-analytical holding time and variability of conditions is critical to help reduce measurement error (35, 37, 47). Soil samples must either be analyzed upon collection (e.g., field laboratory) or more rigorously preserved than that provided by simple 4°C refrigeration (e.g., infield solvent immersion or closed-vial,) (Fig. 8 - 9). Improved and expanded use of onsite analytical instruments and techniques has been demonstrated to provide VOC quantitation equivalent to standard fixed-base laboratory methods (Fig. 10) (30, 31, 46). Sample analysis techniques are emerging that focus on robust methodologies that provide reasonable accuracy and precision for soil VOCs. These are in contrast to methods that enable ever lower detection limits. Simplified, but effective, field instruments and procedures are rapidly becoming available (1, 4, 17, 26, 31, 46, 58, 59, 60, 70). Continued development and standardization of field instruments and methods was deemed necessary to stimulate their widespread and appropriate use.

Sequential analysis of samples has been demonstrated as a cost-effective strategy for measuring contamination in ground water and drinking water matrices (58). This approach relies on compositing, a sampling strategy that has not been commonly employed with soil VOCs due to concerns over compound losses and detection limit increases. While composited samples seemingly could be collected using methanol solutions, this method has not been fully developed or tested yet (63).

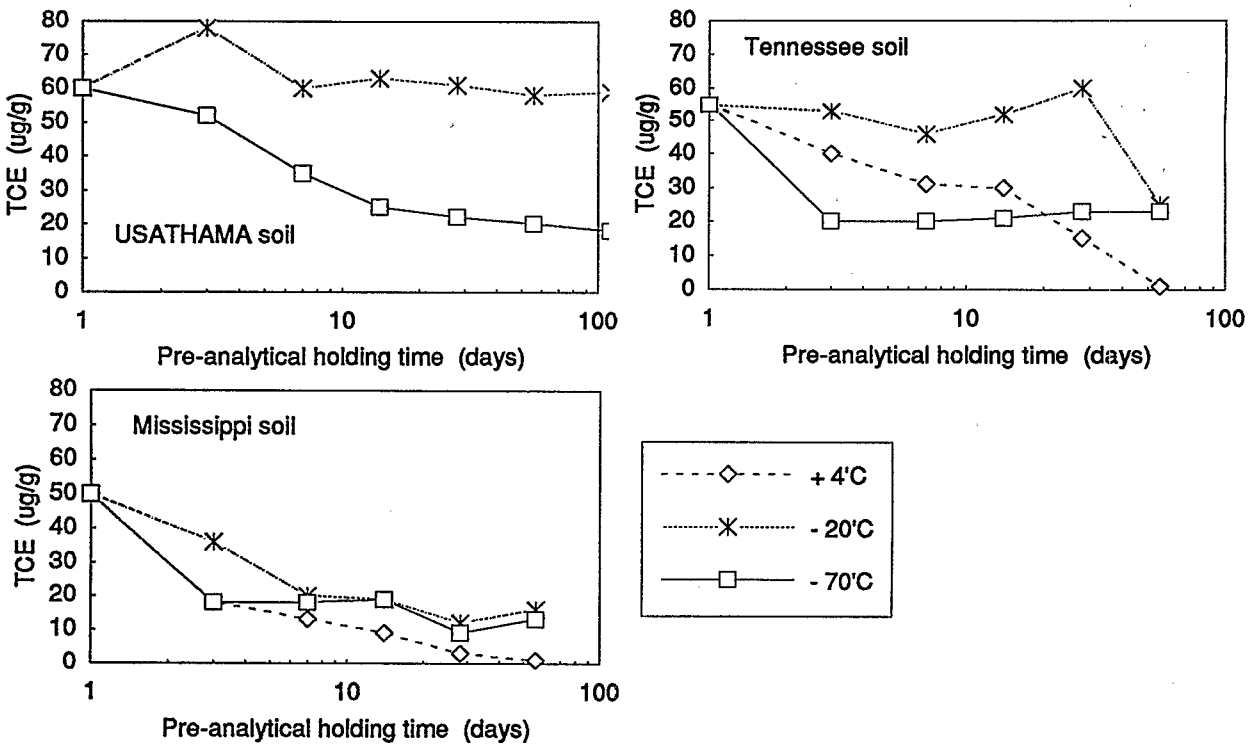

Fig. 8. Changes in concentrations of TCE in different soil media as affected by storage temperature and holding time (after 35, 47).

Soil VOC data vary widely in space and time; an accurate measure at one location and time may provide only limited insight into concentrations at an adjacent location or time. Soil VOC data are log-normally distributed and it may be reasonable to reduce expectations for measurement accuracy in discrete samples to account for this fact. It could be argued that soil VOCs should be assessed on a log-scale in much the same way soil bacteria or soil pH are.

7. DATA INTERPRETATION

Data assessment and interpretation must be done carefully and include review of not only sample collection, handling, and analysis procedures, but also information about the physical conditions at the site, source of contamination and rate of release, and exposure pathways. VOC measurements made years ago are probably more suspect than recent data due to recent improvements in practices.

The current emphasis of data validation is primarily on method adherence and does not adequately address sample/analyte-specific variability. For example, quality control acceptance limits are set to correspond to generally achievable windows by a reasonable laboratory under normal operation (e.g., surrogate, matrix spike, and matrix spike duplicate recoveries). In addition, laboratory analysis is the only component of the whole range of error sources that is considered. Depending on the type of data and the depth of the assessment, costs for validation can range from three to ten times the analytical costs. These extremely high costs and the inadequacy of current practices make the development and implementation of an effective data interpretation process a high priority need. Both improving the quality and changing the perspective of "data

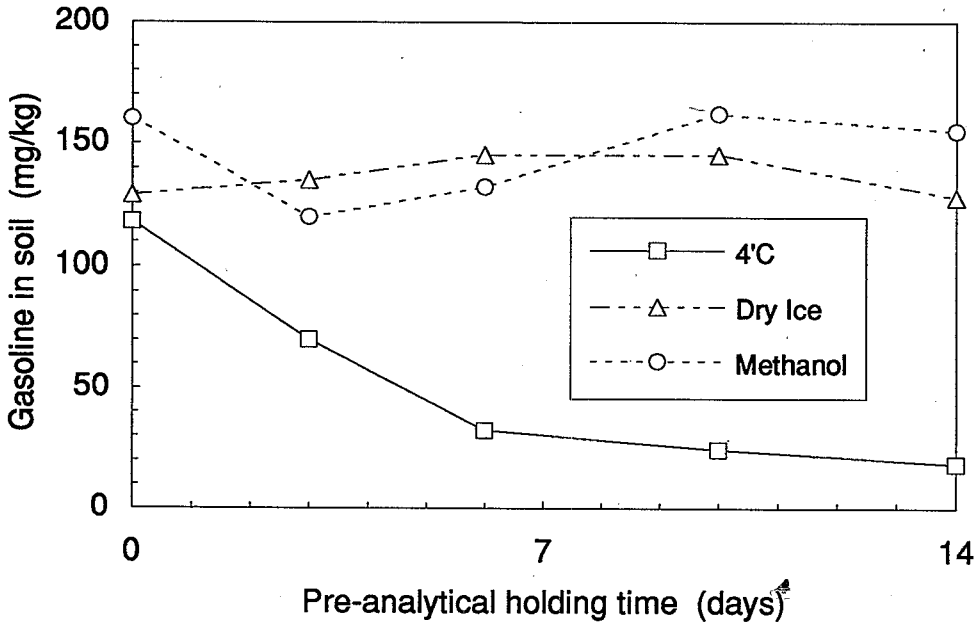

Fig. 9. Average changes in gasoline concentrations in fine-grained sand as a function of preservation methods (after 37).

validation" were ultimate goals this Symposium was directed to meeting.

Alternatives to current data validation practices are being conceived and evaluated. Examples include the use of performance evaluation materials (42) and laboratory splits employing referee laboratories (39).

Interpretation must reconcile and integrate the various elements of a soil VOC data set (e.g., field screening, on-site lab analysis, off-site lab analysis, meteorological data, etc.). The emphasis on the analytical portion of the measurement process has inappropriately focused on discrete values rather than on comprehensive data sets and information packages. The ultimate data collection goal is an appropriate decision, not the perception of highly documented laboratory results. Alternatives to current data validation practices, and efforts to develop and implement these processes, are advocated to provide optimized quality assurance in a more time and cost efficient manner.

Detection limits and their impact on sample analysis and interpretation are significant. There appears to be an implicit assumption made that lower detection limits are always better. Drinking water maximum contaminant levels (MCL's) have dictated low detection limits in ground water samples and may have led to a perceived need for similar low limits in soil. However, lowering detection limits may have adverse consequences. For example, field portable instruments may provide accurate, timely, and cost-efficient analyses, but their use may be limited because they are unable to reach a low enough detection limit. GC's with appropriate detectors are emerging that can be used in the field and achieve equal or lower detection limits than laboratory GC/MS's. In many applications, however, achieving lower detection limits may require more sophisticated off-site laboratory equipment. Due to the greater time and higher cost of these off-site analyses, fewer samples may be collected. As a result, spatial knowledge may be sacrificed and decision-making impaired.

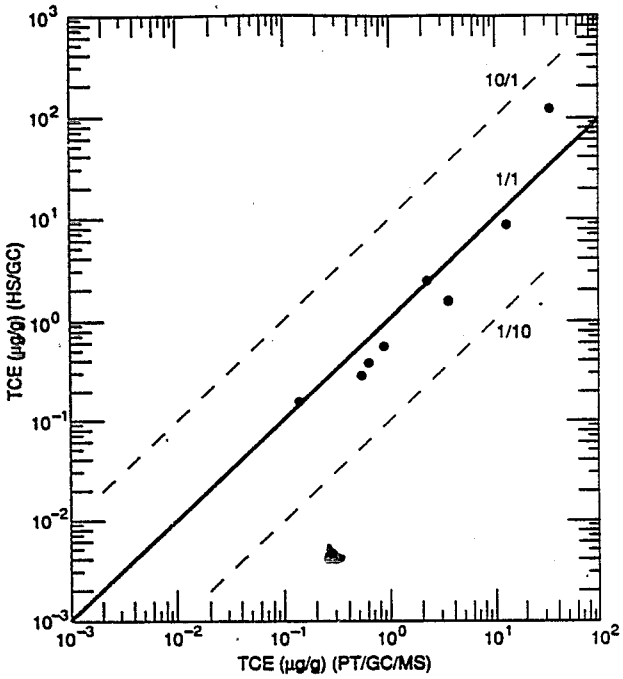

Fig. 10. Concentrations of TCE in soil as determined by aqueous extraction headspace/gas chromatography (HS/GC) versus purge-and-trap gas chromatography/ mass spectrometry (PT/GC/MS) per EPA SW-846, Method 8240 (30, 31).

Another issue related to detection limits, is the treatment of data near or below the detection limit. This subject was touched on during the Symposium, but not fully resolved. There is a growing body of work on the subject and it is mentioned here only as an issue to be dealt with.

Spatially and temporally disparate data can be analyzed using a variety of statistical tools (21, 28, 52). Spatial correlations and geostatistical techniques enable regions of interest to be characterized with some measure of uncertainty. While different statistical tools can provide different results, most important to the successful application of the tool is having an adequate spatial dataset. No statistical tool will overcome the lack of spatial information provided in a limited data set (Fig. 11). A most serious short-coming within the current process of characterizing subsurface regions for VOCs may be the limited number of samples often collected from which inferences are made (e.g., one, 5-cm^3 sample per 50 m^3 of soil region). While often based on justifiable constraints, a limited number of samples can leave great uncertainty in data interpretation, even if analyses of the discrete samples were accurate and precise. The unique properties of VOCs in a soil system may complicate this problem (e.g., multiphase behavior and dynamic equilibrium).

A variety of 3-dimensional visualization tools are becoming available to graphically communicate information about subsurface regions. Application to soil VOCs has been done in several cases (46, 52). While these visualization tools offer great benefit, they rely on spatial continuity of the dataset and relatively intense sampling densities.

8. REGULATORY FRAMEWORK

Several key questions were raised and discussed regarding institutional and regulatory issues. There appeared to be some confusion as to what flexibility is available to those designing and implementing sampling and analysis plans with regard to VOC measurement. For example, there is a perception that SW-846 methods are mandatory and only acceptable as written in a promulgated version. However, in only a limited set of specific cases is use of SW-846 required by Federal regulation. SW-846 was developed as a guidance document setting forth acceptable but not required methods. It seems that many methods were originally developed using the best available information at the time, even though it may have been somewhat limited (41). Rather than serving as guidance with provisions for modification and change, many methods have been "codified" and mandated, with modification prohibited. This has evolved from an interest in using standard methods, which has in turn resulted in the simple adoption of guidance methods as standards.

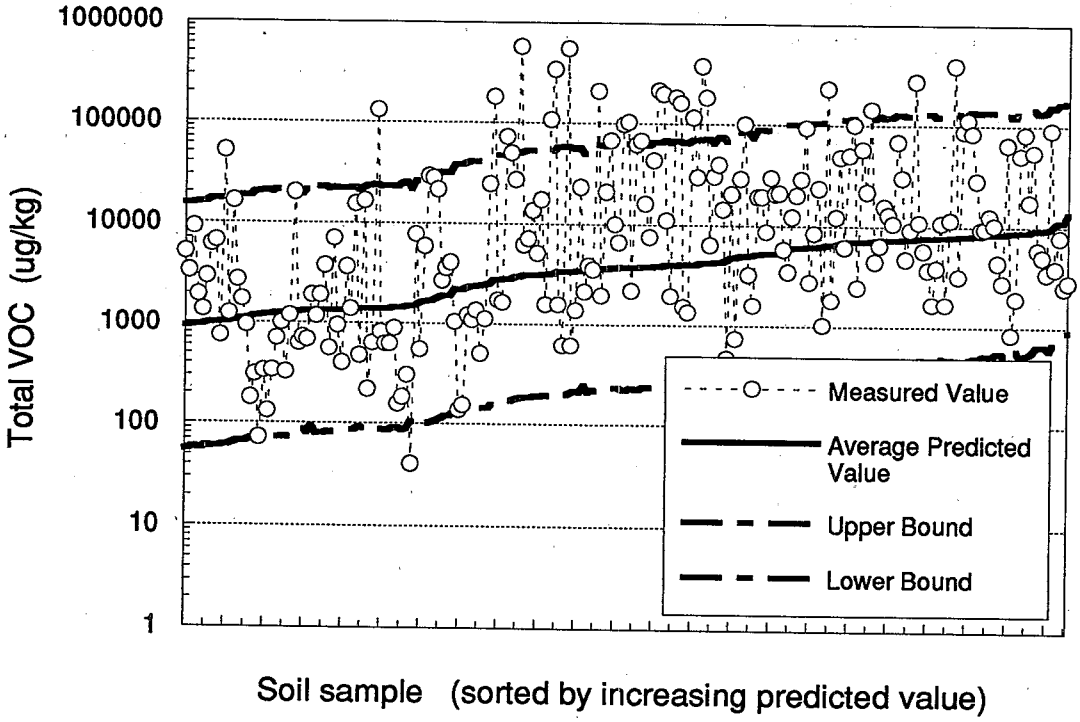

Fig. 11. Measured VOC concentrations for a sub-region of a contaminated site compared to the predicted concentrations based on a 3-dimensional kriging model for the entire site (52).

For example, a number of States have adopted SW-846 methods as mandatory standard methods.

Sampling and analysis plans are written to ensure quality control and legal defensibility of the data. There is a desire to use "standard methods" rather than best practices which are based on recent research and experience. As a result of this situation, there is great inertia to maintain the status quo and the so-called standard methods, even when the evidence dictates change.

Efforts have been made to "standardize" methods based on the results of recent research and practice. For example, ASTM adopted method D 4547, "Standard Practice for Sampling Waste and Soils for Volatile Organics" in August 1991 (2, 72). This method incorporates new knowledge regarding the adverse effects of sample disruption and holding in small containers without preservatives. The method prescribes collection of samples in metal rings (e.g., sleeves inserted in the sampling barrel of a split-spoon sampler, D 3550) or subsampling in the field using coring cylinders. For field subsamples, containerization is described for either a jar containing methanol, or a dry container with an adapter for direct connection to an analytical instrument (72).

States are also promulgating standardized methods based on new research. For example, the state of Wisconsin now requires the use of infield immersion in methanol for samples contaminated with petroleum hydrocarbons.

There is also continued work within EPA. Several modifications to current analytical methods are planned for the Third update of SW-846 (41). One of the methods is specifically written for VOCs in solid

matrices. This method prescribes an automated purge-and -trap system which agitates the sample within the original collection vessel during a 40°C purge step (new SW-846 method 5035). This method enhances VOC preservation (due to minimizing sample disruption and handling) and increases recovery efficiency due to the agitation.

Widespread use of new methods by practicing professionals requires their adoption and approval for use by regulating agencies. This adoption of methods by state or Federal agencies often hinges on activities by other standards-setting groups, like ASTM or groups within EPA or DOE. While current methods may be judged deficient in some respects, changes usually can be made only after extensive methods development and testing. To some extent this is justified, since adequate information is required so a deficient method is not replaced by another method which has different but equally detrimental deficiencies. An example for soil VOCs could include a new method of containerizing and preserving a sample that provides dramatically improved VOC stability but causes major problems with accurate and precise analysis. This example illustrates one of the difficulties in development and adoption of new soil VOC methods. That is, methods are typically for individual fragments of the measurement process (e.g., sample collection or analysis). Yet improving one fragment of the process may have little positive, and perhaps a negative impact on the overall process.

Advancements will continue to occur and improvements will be made in current practices on a local and national level. However, to facilitate more timely changes on a widespread basis, the requirements and process for change must be defined. A strategy or protocol should be adopted and widely disseminated that clearly describes the requirements for deviation from purported standard methods, either on a site specific or general application basis.

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APPENDIX A: SYMPOSIUM PROGRAM

Day 1 - Tuesday, January 12, 1993

Session 1: Opening Session

Session Chairs: Bob Siegrist, Oak Ridge National Laboratory
Jeff van Ee, U.S. Environmental Protection Agency

8:30 Welcome and Introduction
Wayne Marchant, Director, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV

8:40 Symposium Organization and Purpose
Bob Siegrist, Oak Ridge National Laboratory
Jeff van Ee, U.S. EPA Environmental Monitoring Systems Lab

9:00 *Keynote Remarks*
Dave Bennett, Chief, Toxics Integration Branch, Hazardous Sites Evaluation Branch, U.S. EPA Office of Emergency and Remedial Response
Joan Fisk, Chairperson, Interagency Steering Committee for Quality Assurance for Environmental Measurements, Los Alamos National Laboratory - on Intergovernmental Personnel Act assignment from U.S. EPA Office of Solid Waste and Emergency Response

Session 2: VOC Measurement Needs, Issues, and Concerns

Session Chairs: Jeff van Ee, U.S. Environmental Protection Agency
Pat Eagan, University of Wisconsin-Madison

9:30 *VOC measurement in soils: the nature and validity of the process*
Bob Siegrist, Environmental Sciences Division, Oak Ridge National Laboratory, Oak Ridge, TN

10:00 *Effect of VOC measurement uncertainty on the risk assessment process*
Jeff Wong, Office of the Science Advisor, Toxics Substances Control, California EPA, Sacramento, CA

10:50 Panel Discussion and Open Microphone
Diane Easley, Environmental Scientist, U.S. EPA Region 7, Kansas City, KS
Dan Stralka, Toxics Integration Coordinator, Region 9, U.S. EPA
Barry Lesnik, U.S. EPA Office of Solid Waste, Washington, DC
Charles Van Sciver, Chief, Environmental Measurements Section, Department of Environmental Protection, Trenton, NJ
Allen W. Verstuyft, Chevron Research and Technology Company, Richmond, CA
David Lincoln, Director of Risk Assessment, CH2M-Hill, Bellevue, WA
Ely Triegel, President, Triegel & Associates, Inc., Pittsburgh, PA
James Bentley, Vice President, Enseco Laboratories, Sacramento, CA
Al Tardiff, Program Manager, DOE Office of Technology Development, Washington, DC

Session 3: Soil VOC Measurements and Decision Making

Session Chairs: Ruth Bleyler, U.S. Environmental Protection Agency
Duane Geuder, U.S. Environmental Protection Agency

1:00 *Measurement needs and uncertainty in the risk assessment process*
David Lincoln, CH2M-Hill, Bellevue, WA

1:30 *Processes controlling the transport and fate of VOCs in soils*
Neil Hutzler, Michigan Technological University, Houghton, MI

2:00 *Soil sampling strategies and the decision making process*
Evan Englund, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV

2:30 *Data quality objectives and statistical treatment of soil VOC data*
Alfred Haeberer, Quality Assurance Management Staff, U.S. EPA Office of Research and Development, Washington, DC

3:30 *Sampling and analyses for soil VOCs*
Michael Barcelona, Western Michigan University, Kalamazoo, MI

4:00 *Field screening and soil gas measurement techniques for VOCs*
Thomas Spittler, Region I Laboratory, U.S. Environmental Protection Agency, Lexington, MA

4:30 Special Interest Group Sessions (Concurrent)
1. Facilitator = Ruth Bleyler and Duane Geuder
2. Facilitator = Dave Bottrell and Martin Stutz
3. Facilitator = Dean Neptune and Joan Fisk

5:30 *Poster Session*

Day 2 - Wednesday, January 13, 1993

Session 4: Soil VOC Behavior and Measurement Implications

Session Chairs: Bruce Bauman, American Petroleum Institute
Martin Stutz, U.S. Army Environmental Center

8:00 *Review of VOC sorption behavior in soils*
Marti Minnich, Lockheed Environmental Systems and Technology, Las Vegas, Nevada

8:20 *The persistence of several volatile organic compounds in a low organic carbon calcareous soil from southern Nevada*
Spencer Steinberg* and David Kreamer, *Department of Chemistry, University of Nevada, Las Vegas, NV

8:40 *Standard model for volatilization of chemicals from soil at Superfund sites*
Janine Dinan, U.S. EPA Office of Emergency and Remedial Response, Washington, DC

9:00 *VOC contamination in ground water: sources of variability and comparison of soil, well and hydropunch results*
Michael Barcelona*, Allan Wehrmann, Jane Denne, and Dannette Shaw, *Western Michigan University, Kalamazoo, MI

9:20 *Statistical simulation and 3-dimensional visualization for analysis and interpretation of soil VOC datasets*
Toby Mitchell*, Olivia West, R.L. Siegrist, *Eng. Physics & Math Division, Oak Ridge National Laboratory, Oak Ridge, TN

9:40 Open microphone

Session 5: Sample Collection and Handling for Soil VOCs

Session Chair: Dave Bottrell, U.S. Department of Energy

10:20 *Comparison of collection and handling practices for the analysis of volatile organic compounds in soils*
Alan Hewitt, U.S. Army Cold Regions Research Laboratory, Hanover, NH

10:40 *Experimental determination of maximum pre-analytical holding times for volatile organics in selected soils*
Roger Jenkins, Chuck Bayne, Mike Maskarinec, L.H. Johnson, S.K. Holladay, and B.A. Tomkins, Oak Ridge National Laboratory, Oak Ridge, TN

11:00 *Evaluation of sample holding times and preservation methods for gasoline in fine-grained sand*
Paul King, P&D Environmental, Oakland, CA

11:20 *Development of an ASTM standard for sampling soils for VOCs*
Ely Triegle, Triegle & Associates, Inc., Pittsburgh, PA

11:40 Open Microphone

Session 6: Measurements of Soil VOCs by In Situ & Onsite Techniques

Session Chair: Roger Jenkins, Oak Ridge National Laboratory

1:00 *Soils, synthetics, and screening: may the odds be with you*
R. Rajagopal, University of Iowa, Iowa City, IA

1:30 *Geoprobe soil sampling and field VOC analyses by gas chromatography*
Hunt Chapman and Jeff Tuttle, Envirosurv, Inc., Arlington, VA

1:50 *An evaluation of four field screening techniques for measurement of BETX*
E.N. Amick and J.E. Pollard, Lockheed Engineering & Sciences Co., Las Vegas, NV

2:10 *Application of field VOC data in quantitative risk assessment at CERCLA sites*
Ruth Kramel and Anthony Armstrong, Health and Safety Research Division, Oak Ridge National Laboratory, Oak Ridge, TN

2:30 *Site investigations: the role of field screening & analytical tools*
Fred Cornell, Environmental Management, Inc., Princeton, NJ

2:50 *Advances in on site and in situ VOC measurement techniques*
Eric Koglin, U.S. EPA Environmental Monitoring Systems Laboratory, Las Vegas, NV

Session 7: Laboratory Sample Analyses for Soil VOCs

Session Chair: Barry Lesnik, U.S. Environmental Protection Agency

3:30 *Laboratory analyses and quality assurance for soil VOCs*
Jim Bentley, Enseco Labs, Sacramento, CA

3:50 *Interlaboratory study of analytical methods for petroleum hydrocarbons*
Roger Claff*, Dianna Kocurek, Jeff Lowry and Jerry Parr, *American Petroleum Institute, Washington, DC

4:10 *Modifications to EPA procedures for soil VOC analyses*
Barry Lesnik, U.S. EPA Office of Solid Waste, Washington, DC

4:30 Open microphone

5:00 Special Interest Group Sessions (Concurrent)
1. Facilitator = Ruth Bleyler and Duane Geuder
2. Facilitator = Dave Bottrell and Martin Stutz
3. Facilitator = Dean Neptune and Joan Fisk

5:30 *Poster session*

Day 3 - Thursday, January 14, 1993
Session 8: State of the Art and Research Needs

Session Chairs: Bob Siegrist, Oak Ridge National Laboratory
Jeff van Ee, U.S. Environmental Protection Agency

8:00 Special Interest Group Session Presentations
1. Facilitator = Ruth Bleyler and Duane Geuder
2. Facilitator = Dave Bottrell and Martin Stutz
3. Facilitator = Dean Neptune and Joan Fisk

10:00 Panel Commentary
Diane Easley, Environmental Scientist, U.S. EPA Region 7, Kansas City, KS
Dan Stralka, Toxics Integration Coordinator, Region 9, U.S. EPA
Barry Lesnik, U.S. EPA Office of Solid Waste, Cincinnati, OH
Charles Van Sciver, Chief, Environmental Measurements Section, New Jersey Department of Environmental Protection, Trenton, NJ
Allen W. Verstuyft, Chevron Research and Technology Company, Richmond, CA
David Lincoln, Director of Risk Assessment, CH2M-Hill, Bellevue, WA
Ely Triegel, President, Triegel & Associates, Inc., Pittsburgh, PA
James Bentley, Vice President, Enseco Laboratories, Sacramento, CA
Al Tardiff, Program Manager, DOE Office of Technology Development, Washington, DC

11:30 Open Microphone

12:00 Closing Remarks and Symposium Adjournment

Poster Session --

Purge-and-trap GC/MS method modifications
Steve Ward, Harry Reid Center for Environ. Studies, University of Nevada, Las Vegas, NV

Slow desorption dynamics for volatile organic compounds from five ion-exchanged smectites
Jerry Fairly* and Spencer Steinberg, *Department of Geoscience and the Water Resources Management Program, University of Nevada, Las Vegas, NV

Experimental determination of non steady-state diffusion of o-xylene from a sandy soil
B. Lindhardt and T.H. Christiansen, Technical University of Denmark, Department of Environmental Engineering, Lyngby, Denmark

Performance of a new soil sampling tool for use with methanol preservation of samples containing volatile organic compounds
David E. Turriff, En Chem, Inc., 1795 Industrial Drive, Green Bay, WI

Preanalytical holding times: advanced data treatment
Chuck Bayne*, Denise Schmoyer, Roger Jenkins, *Computing and Telecommunications Division, Oak Ridge National Laboratory, Oak Ridge, TN

Active soil gas sampling - collection by air withdrawal
Samuel Johnson and T.V. Prasael, The Advent Group, Inc., Brentwood, TN

Field identification and quantitation of volatile organics in soils utilizing fourier transform infrared (FTIR) spectroscopy
J. Demirgian*, M. Clapper-Gowdy, G. Robitaille, *Analytical Chemistry Division, Argonne National Laboratory, Argonne, IL

The inadequacy of commonly used risk assessment guidance for determining whether solvent-contaminated soils can affect ground water at arid sites
Nic Korte*, Pete Kearl, T.A. Gleason, and J.S. Beale, *Environmental Sciences Division, Oak Ridge National Laboratory, Grand Junction, CO

Referee analyses - a better approach than data validation
Nic Korte* and David Brown, Environmental Sciences Division, Oak Ridge National Laboratory, Grand Junction, CO

Vapor fortification: a method to prepare quality assurance soils for the analysis of volatile organic compounds
Allan Hewitt, U.S. Army Cold Regions Research and Engineering Lab, Hanover, NH
Field observations of variability of soil gas measurements
Jon Fancher, Westinghouse Hanford Co., Richland, WA
Estimation of potential VOC emissions during trial excavation activities via flux chamber and fourier transform infrared open path transform
Michelle Simon, U.S. EPA Risk Reduction Eng. Lab, Cincinnati, OH
The effect of barometric pumping on the migration of volatile organic compounds from the vadose zone into the atmosphere
Robert Pirkle*, Douglas Wyatt, Van Price, and Brian Looney, *Microseeps, Pittsburgh, PA
Use of risk assessment ground water model in installation restoration program site decisions
David Goldblum*, John Clegg, John D. Erving, Sverdrup Environmental, San Antonio, TX
A fiber optic chemical sensor for the measurement of TCE
Marcus Butler, Stanley Klainer*, Kisholov Gosvami and Jonahtan Tussey, *FiberChem, Inc., Las Vegas, NV
Biodegradation of high concentrations of TCE and effects on aquifer permeability
Martin A. Rowland, New Orleans, LA
Field analysis of VOC's by photoacoustic detection
John McClelland, R.W. Jones, and S. Ochiai, Ames Laboratory, Iowa State University, Ames, IA
Evaluation of headspace method for volatile constituents in soils and sediments
Brian Looney, C.A. Eddy, W.R. Sims, Westinghouse Savannah River Company, Aiken, SC
On-site analysis of VOCs in soils by transportable GC/MS
Jeff Christensen and Dave Quinn, Viking Instruments, Reston, VA
Measuring the flux of chlorinated, volatile organic compounds from the soil surface
Paul Daley* and Stan Martins, *Environmental Restoration Division, Lawrence Livermore National Laboratory, Livermore, CA

APPENDIX B: LIST OF ATTENDEES

Attendee	Affiliation	Location
Bruce Bauman	American Petroleum Institute	Washington, D.C.
Ruth Bleyler	U.S. Environmental Protection Agency	Washington, D.C.
David Bottrell	U.S. Department of Energy	Washington, D.C.
Patrick Eagan	University of Wisconsin	Madison, WI
Joan F. Fisk	Los Alamos National Laboratory	Los Alamos, NM
Duane Geuder	U.S. Environmental Protection Agency	Washington, D.C.
Roger A. Jenkins	Oak Ridge National Laboratory	Oak Ridge, TN
Eric Koglin	U.S. Environmental Protection Agency	Las Vegas, NV
Mike Maskarinec	Oak Ridge National Laboratory	Oak Ridge, TN
Robert L. Siegrist	Oak Ridge National Laboratory	Oak Ridge, TN
Martin H. Stutz	U.S. Army Environmental Center	Aberdeen, MD
Jeff van Ee	U.S. Environmental Protection Agency	Las Vegas, NV
Joseph S. Arena	U.S. Environmental Protection Agency	Philadelphia, PA
J.W. Atwater	University of British Columbia	Vancouver, BC
Jim Barnaby	Analytical Technologies, Inc.	Fort Collins, CO
Susan W. Bass	Compu-Chem Laboratories	Res. Triangle Park, NC
Charles. K. Bayne	Oak Ridge National Laboratory	Oak Ridge, TN
Dan Bergman	Pyrite Cannon Group	Riverside, CA
Bernie B. Bernard	O.I. Analytical	College Station, TX
Charles Bidondo	Shoshone Bannock Tribes	Fort Hall, ID
Peter Biltoft	Lawrence Livermore National Lab	Livermore, CA
Gary Bloom	Martin Marietta Energy Systems	Knoxville, TN
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APPENDIX C: DISCUSSION QUESTIONS FOR THE WORKING GROUPS

Questions were developed in three areas by the planning committee, including sampling and analysis planning (denoted as "P"), sample collection, handling, and analysis (denoted as "H"), and data assessment (denoted as "A"). These questions were provided to the Symposium participants and used as a framework for discussion during the Symposium and the working group sessions.

C.1 Questions Regarding Sampling and Analysis Planning

Questions regarding sampling and analysis planning (denoted as "P") were framed around the following: During up front planning for data collection of VOCs in soil, what considerations are important to obtain the right kind of data for the various uses of that data, including risk assessment, remedial action design and implementation, clean-up goal achievement, waste management, and monitoring?

1. What is unique about measuring VOCs in soil that makes this Symposium important? Can we use this measurement data as an indicator of other problems such as potential aquifer contamination through use of a model? What exposure pathways are of greatest concern with VOCs in soil (e.g., for risk assessment)?

2. Are there any situations where VOCs may present more of a problem than other contaminants (e.g., sites with certain contamination release characteristics, physical conditions, or exposure scenarios)?

3. What techniques will ensure collecting and measuring representative samples for various data uses: (1) risk assessment, (2) remedial action design and implementation, (3) clean-up goal achievement, (4) waste management, (5) monitoring?

4. What effect does spatial and temporal variation in phase distribution across a site have on obtaining a representative set of samples? What technique can accurately describe and predict the spatial distribution of VOCs across a site (e.g., kriging)?

5. Can existing fate and transport models accurately describe and predict the behavior of VOCs in soil to account for all phases (e.g., non-aqueous, aqueous, vapor, sorbed)?

6. How can field analysis or screening be used to optimize the collection of VOC in soil data? Are there any quantitative field analysis methods available that can be used for risk assessment and other decision making? [also in "H"]

7. What additional information is needed to maximize the use of VOCs in soil data to allow more informed decision making (e.g., site meteorology and geology, soil particle size distribution, water content, pH, organic carbon, etc.)? [also in "H" and "A"]

8. Are performance evaluation materials to quantify sampling and analysis error necessary? Appropriate? Feasible? Available? How should error be expressed? [also in "H"]

C.2 Questions Regarding Sample Collection, Handling, and Analysis

Questions regarding sample collection, handling, and analysis (denoted "H") were framed around the following: How can the information necessary to support environmental decisions be most efficiently produced; i.e., execution of the sampling and analysis plan such that it meets the user

needs as determined by the data review process?

1. How should soil samples for VOC analyses be collected, handled, and prepared? Does sample acquisition affect the integrity of the sample (e.g., probing versus drilling/tube sampling)? Are cores encased in sleeves preferred over transfer to a sample container (e.g., 40-mL VOA vial)? Are special preservation techniques required for soil samples which are to be held prior to analysis (e.g., solvent immersion)?

2. Many alternatives to current technologies have been described and documented in the presentations at the Symposium. What is preventing their acceptance and use?

3. How can field analysis/screening be used to optimize collection efforts? Are there any quantitative field methods appropriate to support environmental decisions (e.g., risk assessment, waste management)?

4. One mechanism to foster acceptance of advances in technology is by designation of alternatives to current practices during the planning process (e.g., effective use of field data). Is this practical and is it done? How can it be encouraged?

5. What fraction of VOCs present in soil are measured by different analytical methods? Do current analytical methods for VOCs in soil accurately characterize potential problem situations (e.g., tightly sorbed VOCs, VOCs in soil matrix micropores, non-aqueous phase VOCs)?

6. What additional information is needed to maximize the use of VOC in soil data to allow more informed decision making (e.g., site meteorology and geology, soil particle size distribution, water content, pH, organic carbon, etc.)? [also in "P" and "A"]

7. Are performance evaluation materials to quantify sampling and analysis error necessary? Appropriate? Feasible? Available? How should error be expressed? [also in "P"]

8. Can samples for soil VOCs be composited? What are the advantages and limitations for risk assessment, remedial action design, or waste management? What methods can be used to create a valid composite?

C.3 Questions Regarding Data Assessment

Questions regarding data assessment (denoted as "A") were developed in the following framework: How can the data assessment process for soil VOCs (herein, meaning the entire process including review of the data for technical quality and integrity, assimilation with other needed data, statistical analysis treatment of the data, and the determination that the data is suitable for the decision to be made) and the communication of its product be improved to save time and resources, and provide products for more efficient use by the users (e.g., risk assessors, engineers designing remedial strategies, waste management personnel, etc.)?

1. How can the data assessment process be streamlined?

2. How can data collection and analyses results be best interpreted and communicated for more efficient use for the various uses of the VOCs in soil data? What communication is needed for (1) risk assessment, (2) remedial action design and implementation, (3) clean-up goal achievement, (4) waste management, (5) monitoring?

3. How are data quality parameters (e.g., precision, accuracy, detection levels) best defined/determined for VOCs in soil?

4. How can field analytical data be assessed for adequate quality for various intended uses? - e.g., placing of wells, identifying hot spots, risk assessment, performance verification? - or when is it necessary to perform data assessment in real time on field analysis of VOCs in soils [related to question 3 in "H" group]?

5. What additional information is needed to maximize the use of VOC in soil data to allow more informed decision making (e.g., site meteorology and geology, soil morphology, water content, pH, organic carbon, etc.)? [also in "P" and "A"]

6. How can performance evaluation materials be used to assess the quality of VOCs in soil data and the appropriateness of the analytical method used? [related to question 7 in "H" group]?

7. How does a decision maker reconcile data sets comprised of different measurements (e.g., soil gas results, on-site soil sample analyses, off-site laboratory analyses, etc.)? Should data quality be viewed less on a discrete sample/analyte basis and more on a region of interest basis?

8. What statistical tools should be used for treatment of VOCs in soil data? Should the data be analyzed after log transformation? Should the data be reported and decision making done on a log-scale (like pH)? Other?

APPENDIX D: DISCUSSIONS IN THE WORKING GROUP SESSIONS

Working group discussions were held at the end of the first and second day of the Symposium. Symposium participants were free to participate in one of three groups, each led by two pre-assigned facilitators. Participants could move from one group to another and were encouraged to interact freely and openly regarding all relevant issues. In some cases, the facilitators within a group set the focus for the group and only some issues were discussed in detail.

During each group session, remarks were recorded as they were made, using marking pens and flip charts. While the facilitators were responsible for recording the information exchanged, it was done in a fashion to avoid any censorship or bias in the reporting as given below. The information presented and so recorded is provided below.

D.1 Responses and Remarks of Working Group 1

Remarks made by participants involved in Working Group 1 discussions were recorded by the facilitators, Ruth Bleyler and Duane Geuder. A summary of the key remarks is given below.

What is Unique About VOCs in Soils?

- They change over time
- "volatility"
- Most complicated medium is soil
- Samples are poorly preserved
- Can be locally homogenous in real world
- Present sampling procedures result in non-reproducible results
- Samples change in situ (e.g ., due to climate)

Additional Comments

- Know geology - use multi-disciplinary approach
- Take extra samples to store for litigation or other contingencies
- Spend money on sampling; we can accept imperfect analysis
- Recognize error level in data; demonstrate how bad present methods are and what their effect is on risk assessment and risk management decisions with a "white paper"
- Validity of sampling error is unimportant compared to administrative (regulatory) problem

Issues

The discussion did not deal only with VOCs as a unique problem, but became generic at times. The overriding issues seemed to be how to influence the bureaucracy to allow for improvement in technology to be transferred into full use. The scientists seem to know what to do, but they are constrained by a system they can't control. There was a definite consensus that VOCs in soil are being underestimated with our present methodologies and therefore, risks are not being adequately addressed.

1. Sample Integrity: Holding times, Handling/Preservation, Containers
   - Present practice: 14 days holding, no preservation
   - Recommendations/Comments:
     - Write into QA plans
     - Do instant analysis

- o Preserve instantly (e.g., methanol in field)
- o Publish, promulgate appropriate methods
- o Need EPA acceptance and more research

2. Dealing with Precedents
   - Present practice: lawyers insist
   - Recommendations:
     - o If put in workplan, it should be acceptable

3. Acceptability of New Methods
   - Present practice: Encounter resistance from contractors, regulators, lawyers, QA people
   - Recommendation/Comments:
     - o Need bench tests, pilot tests, and EPA approval
     - o Appropriate methodology depends on level of contamination; i.e., purge and trap may be good for high levels

4. Mechanism for Disseminating New Technologies
   - Present practice: DOE has system in place called TIE (Technical Information Exchange), EPA has Field Methods Compendium
   - Recommendations/Comments:
     - o Need informal exchange mechanism
     - o "Advertise", "sell" at EPA et al.
     - o Educate, consolidate
     - o Need policy memo(s) from EPA encouraging or allowing use of new technologies

5. Adequacy of Sample Design (includes sub-issues such as number of samples taken, compositing, and filtering)
   - Present Practice: should be part of DQO process, but use of DQOs is inadequate
   - Recommendation/Comments:
     - o Identify the questions to be answered; will sample collection and analysis meet the intended use of the data?
     - o Generally, need to take more samples to increase representativeness
     - o Get local regulators to accept Sampling and Analysis Plans (SAPs)
     - o Use field methods to increase sample numbers and representativeness
     - o Involve data user in scoping/planning (i.e., risk assessor)

6. Limited Resources
   - Recommendations/Comments:
     - o Use field methods to generate more data for same cost
     - o Need to balance cost with sample collection and analysis

7. Data Collection Usable to User
   - Present Practice: Guidance's are available for DQ0s and Data Useability (*Guidance for Data Useability in Risk Assessment* in final, 1992; *Guidance for Data Useability in Site Assessment*, and ...*Removal* are drafts)
   - Recommendations/Comments:
     - o Know acceptable uncertainty for risk vs. remediation, removal, etc.
     - o Train field samplers
     - o Use multi-disciplinary approach in site planning, etc.
     - o Samplers need familiarity with what data will be used for
     - o User can assist in sample collection (biologist sometimes used to assist in sample

collection for ecological assessment)

8. Uncertainties
   - Recommendations/Comments:
     - o First step is to have "reliable analysis"
     - o Report bias, conditions, "pedigree"
     - o Use complimentary methods (i.e., field with fixed lab confirmatory)
     - o Increase number of samples
     - o Provide field oversight audits

9. Performance Evaluation Samples
   - Present Practice: problems with development
   - Recommendations/Comments:
     - o Can contribute to quantification of uncertainty/error
     - o Not certain what they assure
     - o Needs research and methodology development

10. Mixed Waste
    - Present practice: interaction with radionuclides
    - Recommendations
      - o Need methods development

D.2 Responses and Remarks of Working Group 2

Remarks made by participants involved in Working Group 2 discussions were recorded by the facilitators, Martin Stutz and Dave Bottrell. A summary of the information exchanged is given in Table D.1.

D.3 Responses and Remarks of Working Group 3

Remarks made by participants involved in Working Group 3 discussions were recorded by the facilitators, Joan Fisk and Dean Neptune. The issue that the group chose to focus on was sampling and analysis planning and data assessment (e.g., modification of discussion question number 6 (See Appendix C)). A summary of the information exchanged is given below.

1. "How can field analysis or screening be used to optimize the collection of VOCs in soil data? How can we gain acceptance of the use of field analyses for VOCs in soil data?"
   - What do we want to use the data for?
     - o Identification of the site problem
     - o Definition of the magnitude of the problem
     - o Assurance that risk has been adequately reduced.
   - Present Practices
     - o Only "CLP Quality" data can be used for decision making
     - o There is a perception that field methods are inferior
     - o The is a perception that only the "best" quality data may be used in risk assessment
   - Comments
     - o Marketing field methods is necessary
     - o Field methods performance is not documented
   - o There must be flexibility built into the data collection process concerning analytical methods/number of samples

Table D.1. Remarks made and recorded during discussions in Working Group 2.

Issues	Present practices	Comments	Recommendations
Extreme data variability (Vapor phase transport)	All VOC treated the same Presumption of no loss in sampling/transport		Little formal DQO Define problem No automatic answers
Types of data - Lab - Field measurement - Soil gas	SW-846, 8240		No efficient integration of historical and current soil studies
Sample composting - Integrity - Utility	Don't attempt without regulator acceptance	Dependent upon procedures to prevent loss from handling, e.g., methanol preservation	Develop guidance when appropriate and when not, e.g., detection limits
Dissemination of methods/ alternatives	"Miss or miss"	Need mechanism for distribution	Individual Responsibility, local organization
Guidance as "Leading Edge"	"Guidance" taken as "Law"	Need to convince public	EDUCATE, EDUCATE
Current sampling sampling and holding times requirements are not" Correct"	Gross under estimate of VOCs	Need to identify and establish procedures that preserve samples and "Take Better" (more representative) samples	
Mechanism to implement change	None / slow	Need "Driving Force"	Involvement of external organizations, e.g., API, CMA, etc

e.g., Any combination of method (A) at $Z/sample with B #'s of samples that equal X data performance is OK

- Recommendations
  - o Develop a compendium of field methods
  - o There must be flexibility built in by incorporation of performance criteria
  - o Sampling methods must be included with documentation of the procedure and methods performance
  - o Appropriate QA/QC must be built in to assure adequacy and provide a measure of the quality (user defined)
  - o An effective tech transfer process must be developed
  - o It must be a multi-agency effort
    THIS METHOD COMPENDIUM WITH PERFORMANCE DATA MUST BE A PRIORITY! (How can we leverage this issue to include support by the various Agencies?)

2. Data Assessment
The data assessment process must be streamlined and results of assessment transferred to <u>multiple</u> users for more efficient use of the data.

- Present Practices
  - o "Functional guidelines: approach - prescriptive
  - o "DQOs" limited to CLP contract requirements
  - o Generic definition of what is "good enough"
  - o Perception that all criteria are absolute
  - o Perception that all samples and analytes must be evaluated
- Comments
  - o Data assessment must be related to DQOs
  - o There must be a process that starts with input from the DOS and continues with evaluation of the output against DOS
  - o Timeliness of data availability to the users is crucial!
- Recommendations
  - o There must be a standardized electronic deliverable
  - o Automated review must be implemented to allow streamlining
  - o Consider review of a subset of the data set
  - o Permutations of above
  - o Allow DQOs to drive QC limits
  - o Labs must be more involved with users and informed on DQOs to enable more flexibility in analytical process to meet clients needs (> communication!)
  - o Must streamline <u>whole</u> decision making process - not just data assessment (e.g., a process approach)
  - o Concurrent data processing
  - o Statistician finds anomalies and tries to understand them rather than limiting the data
  - o Must define "stopping points"
  - o Must define what we are assessing, e.g.,
    - contract compliance
    - attainment of DQOs
    - meeting of QC limits
    - integrity
  - o Must identify what information must be collected for adequate assessment
  - o Must define data quality identifiers needed for each analytical batch, e.g.,
    - precision
    - bias
    - data "pedigree"
    - site information

APPENDIX E: BIBLIOGRAPHY

A selected number of references concerning VOCs in soil are contained in this Appendix. This bibliography has been assembled based on references contained in the abstracts and publications submitted for the Symposium proceedings notebook and from several other published sources.

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