United States
Enironmental Protection
Agency

Office of Research and
Development
Washington, DC 20460

EPA/600/R-93/140
May 1993

Behavior and Determination of Volatile Organic Compounds in Soil

A Literature Review

EPA 600/R-93/140
May 1993

BEHAVIOR AND DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN SOIL: A LITERATURE REVIEW

by

Marti Minnich
Lockheed Environmental Systems & Technologies Company
980 Kelly Johnson Drive
Las Vegas, Nevada 89119

Contract No 68-CO-0049

Work Assignment Manager

Brian Schumacher
Exposure Assessment Research Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89193-3478

ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89193-3478

Printed on Recycled Paper

NOTICE

The development of this document has been funded by the U.S. Environmental Protection Agency under Contract No. 68-C0-0049 to Lockheed Environmental Systems and Technologies Co. as part of an ongoing research effort in support of the Agency's Superfund and Hazardous Waste programs. It has been subject to the Agency's peer and administrative review, and has been approved for publication as an EPA document.

Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

EXECUTIVE SUMMARY

Accurate measurement of soil volatile organic compound (VOC) concentrations is crucial to site investigation, evaluation, and remediation efforts at Superfund sites contaminated by VOCs Soils that are contaminated with VOCs are potential reservoirs of long-term ground water contamination. This report summarizes literature pertaining to (1) the fate and transport of soil VOCs and, (2) the sampling and analysis of soil VOCs by SW-846 Methods 8240/8260 using purge-and-trap/gas chromatography/mass spectrometry (PT/GC/MS).

FATE AND TRANSPORT

Nonpolar VOCs are sorbed predominately by soil organic matter in moist or wet soil. Soil sorption exhibits an initial phase of fast uptake, followed by slow continued sorption or diffusion of VOCs into soil microsites. Resorption studies show a similar rapid resorption phase preceding an extended slow release phase. Soil water retains VOCs in proportion to compound-specific Henry’s Law constants. VOC vapors are adsorbed by soil minerals in dry soil and the quantities adsorbed are 2 to 4 orders of magnitude greater than sorption by wet soil. Contamination by nonaqueous-phase liquids (NAPLs) results in a residual saturation fraction, described as tiny portions of NAPL held by capillary forces in soil pores, which changes in composition over time by physiochemical weathering. The size of the residual NAPL fraction is related to the soil porosity.

Biodegradation of naturally occurring VOCs (such as petroleum products) readily occurs under aerobic conditions. Microorganisms also degrade halogenated aromatics (such as chlorobenzene) aerobically, but more slowly than the naturally occurring VOCs Halogenated aliphanes (such as chloroform and TCE) are degraded far more slowly than the other compounds, by microorganisms or abiotic processes, and mainly under anaerobic conditions. Degradation of halogenated aliphanes, however, has been observed in soils containing substantial amounts of biodegradable carbon compounds, presumably by co-metabolism.

VOCs move in soils by diffusion and advection. Vapor diffusion, density-driven NAPL vapor advection, and gravity-driven NAPL advection are the most important mechanisms for movement. The movement of two fluorocarbons by diffusion in deep sediments in Texas progressed approximately 44 m vertical in 40 years (time since manufactured). Movement of carbon tetrachloride (a dense solvent) 177 m to ground water at a site in Idaho (time of travel unknown) is believed to be caused by density-driven vapor advection. Movement of benzene, toluene, and xylene (solvents less dense than water) 24.4 m vertically in less than 7 years at a California site has been attributed to gravity-driven NAPL advection.

SAMPLING AND ANALYSIS

Substantial volatile and degradative losses of soil VOCs have been documented to occur from sample preservation and subsampling steps of SW-846 Methods 8240/8260. Soil samples stored cold (4°C) have maximum holding times of less than 3 days before the concentration falls below the 90% confidence limit of the initial value. Laboratory soil transfers create VOC losses that widely vary by compound and soil, but losses average approximately 60%.

Immersion of soil samples in methanol has been shown to reduce VOC losses during sample storage and preparation for analysis. Although the analytical sensitivity of methanol-preserved samples is less than that of soil/water samples analyzed by purge-and-trap (PT) preparation, soil-VOC concentrations in methanol-preserved samples were 1 to 3 orders of magnitude greater than soil-VOC concentrations in collocated samples analyzed by low level PT/GC/MS. This implies that much of the existing data of soil VOCs analyzed by SW-846 Method 8240 could be 1 to 3 orders of magnitude below values obtained in properly preserved samples or obtained by field analysis.

To a large extent erratic recovery of same-day spikes and loss of analyte during storage has impeded the accurate assessment of soil-VOC measurement errors. Quality control samples or performance evaluation materials (PEMs) are not available for soil VOCs Recently, vapor fortification of small (2 to 3 g), dry soil samples (four compounds spiked onto two soils) has established low relative standard deviations among samples and storage of at least 3 weeks without measurable sample loss. The technique does not calculate spike recoveries but creates stable and reproducible concentrations of VOC-contaminated soils. It is limited to small aliquots of dry soil. Another option for PEMs might be samples immersed in methanol.

Current analytical methods that utilize PT techniques to remove soil VOCs are not sufficient to extract entrapped VOCs (also referred to as residual, nonequilibrium, or slowly desorbing VOCs).

Field (static) headspace techniques offer a rapid means of quantifying soil VOCs with some restrictions. First, the detection limit is not as low as can be achieved with a PT preconcentration step. After the compounds of interest are identified, however, options for detectors other than the mass spectrometer allow for extremely low detection limits. Second, in soils that are high in organic matter or soils that have a large fraction of slowly desorbing VOCs, PT extraction may be more thorough than soil headspace, thus necessitating laboratory corroboration of field data.

CONTENTS

FIGURES

TABLES

Number Page

ABBREVIATIONS AND ACRONYMS

ASTM	American Society of Testing and Materials
BET	Brunauer-Emmett-Teller
BTEX	benzene, toluene, ethylbenzene, and xylene(s)
BTX	benzene, toluene, and xylene(s)
CLP	Contract Laboratory Program, administered under the EPA Superfund Program
EDB	ethylene dibrornide, l,2-dibromoethane
EPA	U.S. Environmental Protection Agency
FID	flame ionization detector
GC	gas chromatography
HS	headspace
INEL	Idaho National Engineering Laboratory
LD	limited disruption
MHT	maximum holding time
MS	mass spectrometry
NAPL	nonaqueous-phase liquid
NOC	nonpolar, nonionic organic compound
PCB	polychlorinated biphenyl
PCE	perchloroethylene, tetrachloroethene
PEM	performance evaluation material
PID	photoionization detector
PT	purge and trap
PTFE	polytetrafluoroethylene, Teflon®
PVC	polyvinylchloride
QA/QC	quality assurance/quality control
RCRA	Resource Conservation and Recovery Act
RH	relative humidity
RSD	relative standard deviation
SFE	supercritical fluid extraction
SOW	Statement of Work, laboratory procedures for the CLP
TCLP	Toxicity Characteristic Leaching Procedure
TCE	trichloroethylene, trichloroethene
TPH	total petroleum hydrocarbons
VOA	volatile organics analysis
VOCs	volatile organic compounds

ACKNOWLEDGMENT

The author is grateful for the helpful conversations and reviews furnished by colleagues at Lockheed, especially Neal Amick, Roy Cameron, Patty Fitzpatrick, Tim Lewis, Cindy Mayer, Beth Moore, and Jim Pollard. Formal reviews were provided by Brian Schumacher, Robert Siegrist, Steve Ward, Jeff van Ee, Katrina Varner, and William Spencer, all of whom helped revise and clarify this document. Many thanks to the editors Domenic Fuccillo, Marianne Faber, and Bobbie Stephens who endured and managed to concentrate while reading this manuscript.

SECTION 1

INTRODUCTION

Volatile organic compounds (VOCs) are the most common and the most mobile subsurface contaminants encountered at Superfund and other hazardous waste sites. VOCs can be toxic, mutagenic, or carcinogenic. Soil VOCs are of concern primarily as a potential source of ground-water contamination. They may contribute to inhalation exposure, which can result when volatile emissions emanate from the soil surface. Soil VOCs also may be associated with ingestion exposure, which can occur when children play in contaminated soil or when the compounds are absorbed into the edible portion of agricultural plants. Accurate soil and sediment VOC determinations are needed to assess the extent of contamination to make decisions on appropriate cleanup activities, and to verify remediation efforts.

OBJECTIVE AND SCOPE

At the request of the U.S. EPA a literature review was conducted to present and assess literature research results pertaining to the problems and inconsistencies observed in the sampling and analysis of soil VOCs by SW-846 Methods 8240/8260. SW-846 Methods 8240/8260 are the primary soil-VOC laboratory methods, intended to provide the most definitive compound identification and the lowest detection limits. These methods entail a purge-and-trap (PT) preparation/extraction step SW-846 Method 5030 and gas chromatography/mass spectrometry (GC/MS) analysis procedures (USEPA, 1986, 1990). SW-846 Method 8240 uses a packed GC column and Method 8260 uses a capillary GC column. Field sampling procedures are largely unspecified. The results and discussion presented here are intended to be used by the U.S. EPA to evaluate problems with the current SW-846 methods and to be the basis for future potential research needed that will increase the precision and accuracy of soil vadose zone VOC measurements.

The scope of this project included vadose zone soil and sediments only, even though the SW-846 methods are designed to be applied to any solid matrix samples. Literature on vapor-phase and other field measurement techniques was included insofar as data comparisons with laboratory purge-and-trap (PT) techniques were given or when data were supplied that help define the representativeness, precision, and accuracy of the total soil-VOC measurements.

The term “soil” in this report refers generally to any unconsolidated surficial geologic sediments and associated organic matter, 2 mm or less in size, irrespective of pedogenic processes. This definition derives from common usage in the fields of engineering (Holtz and Kovacs, 1981) Geologists and soil scientists would consider this definition to represent “soils and sediments.”

The literature search for this project was conducted in three modes: (1) tree-searching, starting with an initial body of literature obtained from Lockheed researchers, (2) scanning Current Contents: Agriculture, Biology, and Environmental Sciences (Institute for Scientific Information, Inc., Philadelphia, PA) from 1990 through mid-1992 for relevant titles, and (3) personal communications with researchers currently studying soil-VOC measurement procedures. On-line data bases were searched by using different strategies and key words. On-line searches provided some, but not sufficient, references to support this project. Literature was collected for this review through mid-1992, with the exception of the inclusion of abstracts from the January 1993 National Symposium on “Measuring and Interpreting VOCs in Soils State of the Art and Research Needs.”

BACKGROUND

Definition of a Soil VOC

For soil and water samples, the prevailing definition of VOCs is associated with the PT/GC/MS analytical methods (USEPA, 1986, 1990, Lesage and Jackson, 1992). These are broad-based methods, i.e. designed to measure as many compounds as possible with a single procedure, comprised of compounds that are relatively insoluble in water and that have boiling points below 200°C (USEPA, 1986, 1990) or below 150°C (Lesage and Jackson, 1992). The PT preparation technique promotes low detection limits (parts-per-billion range) and the MS detector provides positive compound identification. Volatile compounds that contain polar functional groups (such as low molecular weight ketones, alcohols, aldehydes, nitriles, and ethers) are generally soluble in water, do not purge well, and produce broad, tailing GC peaks that give poor quantitative estimates and are often difficult to identify by MS (Swallow, 1992). Some polar compounds are included in SW-846 Methods 8240/8260 (USEPA, 1986, 1990), but the recovery of polar compounds is often less than 20% (Swallow, 1992). New preparation methods for some of the nonconventional analytes (water soluble analytes such as alcohols, ketones, ethers, and esters) are included in the Third Update to SW-846 (Lesnik, 1993). These methods are Azeotropic Distillation (SW-846 Method 5031) and Closed System Vacuum Distillation with Cryogenic Condensation (SW-846 Method 5032).

While the efficiency of broad-based methods is positive, the use of broad-based methods as definitions has tended to induce an obtuse view promoting the likeness of VOCs and the aggregate similarities of compound behavior in soil (Siegrist, 1993). In fact, the physicochemical properties of various VOCs vary over orders of magnitude. Differences in vapor pressure, water volubility, and octanol water partition coefficient impart even larger differences in air-water partitioning and soil sorption coefficients. Additionally, divergent appraisals of a compound's physiochemical parameters are the rule, as several plausible measurement and estimation techniques exist. The reader is referred to Lewis et al. (1991), Devitt et al. (1987), or recent handbooks (Howard, 1990; Lyman et al., 1990) for listings that describe the physiochemical properties of VOCs

Occurrence and Ranking of VOCs

The presence of VOCs in ground water is well documented A study of 479 waste disposal sites throughout the United States (Plumb, 1991) reported that VOCs accounted for 84% of all the detectable events in the composite data set of the Resource Conservation and Recovery Act (RCRA) Appendix IX organic constituents (52 FR 25942, July 9, 1987). VOCs were also the most prevalent subsets when organic compounds found in ground water were ranked by number of sites and regions (Plumb, 1991).

The Priority List of Hazardous Substances is revised annually as mandated by the Comprehensive Environmental Response, Compensation, and Liability Act as amended by the Superfund Amendments and Reauthorization Act. Two agencies, the U.S. Department of Health Services and the U.S. Environmental Protection Agency (EPA), are required to produce a list of substances most commonly found at facilities on the National Priorities List and which, at the discretion of these agencies, pose the most significant potential threat to human health (see 52 FR 12866, April 17, 1987). The 1991 list (56 FR 52169, October 17, 1991) ranked substances with a formula that included three factors (1) frequency of detection in all media at sites on the National Priority List, (2) toxicity, and (3) potential for human exposure.

Table 1 lists the volatile chemicals of concern, as ranked on the Revised Priority List of Hazardous Substances (56 FR 52169, October 17, 1991). The list includes all compounds that appear in EPA methods for analysis of volatile organics in soil (SW-846 Methods 8240/8260; USEPA, 1990) and compounds that could be termed "nonconventional" VOCs (Lesnik, 1993). For comparison, the compounds are also ranked by frequency of detection in ground water as the only criteria

TABLE 1. VOCs ON THE REVISED PRIORITY HAZARDOUS SUBSTANCES LIST (HSL)*.

HSL Rank	Ground-water Frequency Rank^{+}	Contaminant	SW-846 Analysis Methods**
4	15	vinyl chloride (chloroethene)	A
5	11	benzene	A
8	5	chloroform (trichloromethane)	A
10	2	trichloroethylene (trichloroethene, TCE)	A
22	3	tetrachloroethylene (perchloroethylene, PCE)	A
33	16	carbon tctrachloride (tetrachloromethane)	A
35	9	toluene (methyl benzene)	A
36	38	hexachlorobutadiene	B
44	76	dibromochloropropane (DBCP)	A,C
49	161	l,2-dibromoethane (ethylene dibromide, EDB)	A,C
52	1	methylene chloride (dichloromethane)	A
59	NL	methane	D
60	18	naphthalene	B
61	10	1.2 dichloroethane	A
62	98	2-hexanone (methyl butyl ketone)	A,E
63	7	1,1-dicholroethane	A
64	8	1,1,1-trichloroethane	A
65	14	chlorobenzene	A
66	12	ethyl benzene	A
68	NL	total xylene	A
80	6	1,1-dicholoroethane	A
96	4	1,2-dichloroethane, trans	A

(continued)

TABLE 1. VOCs ON THE REVISED PRIORITY HAZARDOUS SUBSTANCES LIST (HSL)*.

HSL Rank	Ground-water Frequency Rank^{+}	Contaminant	SW-846 Analysis Methods**
99	21	acetone (2-propanone)	A,E
101	95	acrolein (propenal)	A,F
111	NL	1,2-dibromo-3-chloropropane (DBCP)	A,C
120	36	1,1,2,2-tetrachloroethane	A
126	22	1,2-dichlorobenzene	B
129	102	carbon disulfide	A
131	NL	trichloroethane	A
132	19	1,1,2-trichloroethane	A
137	26	2-butanone (methyl ethyl ketone)	A,E
138	25	1,4-dichlorobenzene	B
139	20	chloroethane	A
145	27	1,2,4-trichlorobenzene	B
150	NL	hexane	D
175	NL	dichlorobenzene	B
182	69	chlorodibromomethane	A
183	NL	bromodichloroethane	D
187	43	1,3-dichlorobenzene	B
189	NL	1,2-dichloroethane	A
190	75	chloromcthane (methyl chloride)	A
191	NL	ethyl ether	E
194	82	bromoform (tribromomethane)	A
197	42	o-xylene	A
201	NL	dichloroethane	A

(continued)

TABLE 1. VOCs ON THE REVISED PRIORITY HAZARDOUS SUBSTANCES LIST (HSL)*.

HSL Rank	Ground-water Frequency Rank+	Contaminant	SW-846 Analysis Methods**
209	67	methyl isobutyl ketone (4-methyl 2-pentanone)	A,E
211	NL	trichlorofluoroethane	D
212	153	pentachloroethane	A,G
228	NL	formaldehyde	D
229	96	1,3-dichloropropane, cis	A
234	68	styrene (vinyl benzene)	A
235	24	trichlorofluoromethane	A
237	29	1,2-dichloropropane	A
247	NL	m-xylene	A
249	NL	p-xylcne	A
250	NL	isopropanol	D
253	NL	1,2-dichloroethane, cis	A
254	NL	dichloroethane	A
259	NL	1,3-butadiene	D
262	NL	isopropyl ether	D
264	NL	bromodichloromethane	A

Abbreviation: HSL = Hazardous Substances List; NL = not listed
* 56 FR 52169, October 17, 1991
+Frequency of detection in disposal site ground water (Plumb, 1991).
** SW-846 methods of analysis:
A - Methods 8240/8260
B - Methods 8260 and 8250/8270
C - Method 8011
D - No SW-846 method
E - Method 8015
F - Method 8030
G - Method 8240 notes poor chromatographic behavior for direct injection and it is inappropriate to use purge and trap for this analyte

(Plumb, 1991). Within the context of organic and inorganic hazardous substances in all media, four VOCs are included in the uppermost ten priority substances (56 FR 52169, October 17, 1991). On the basis of potential ground- water contaminants, VOCs comprise the entire list of the top ten organic substances occurring in ground water (Plumb, 1991).

Statement of the Problem

Soil VOCs are particularly difficult to describe because they occur in several phases (gas, aqueous solution, sorbed, and nonaqueous-phase liquid [NAPL]) within heterogeneous media that often must be drilled to obtain samples. VOC collection and quantification are confounded by the relative mobility of the vapor phase. The vapor fraction at the time of sampling will depend primarily on the physiochemical properties of the compound; total concentration of the compound temperature; soil organic matter content; soil water potentiat; and the amount, character, and distribution of soil pores. Estimates of the phase distribution of VOCs in soil are generally based on equilibrium calculations. The distributions, however, are simplifications of complex media and are difficult to verify because of the practical limitations of studying multiphasic, multicomponent soil systems.

Difficulties in measuring soil VOCs occur in sampling, storage, subsampling, and analysis steps. First, mixed and variable sources of contamination superimposed on a naturally heterogeneous medium aggravate sampling difficulties for all soil contaminants, including VOCs however, for VOCs rapid sample collection without any homogenization steps or compositing is generally necessary to minimize volatilization losses. This requirement imposes short-range variability that greatly aggravates the problem of representing field VOC concentrations. Second, storage of” samples prior to analysis has been associated with large losses of VOCs Rapid and severe loss of soil VOCs occurs during storage in sealed vials at 4 °C (Jenkins et al., 1993 King, 1993). Third, the current laboratory subsampling step causes losses averaging 60% (Maskarinec et al., 1988). Finally, laboratory analytical procedures contribute to large data variances. No adequate performance evaluation materials exist to assist in quality assurance/quality control (QA/QC) of soil volatiles analyses (Zarrabi et al., 1991). Analytical accuracy as measured by matrix spike recovery is generally 40% to 120%; however, the recoveries reported are achieved only when the matrix spike is purged seconds to minutes after addition of the spike. The use of PT sparging to extract volatiles from soils may be inadequate when the compounds have been in contact with a particular soil for months or years (Sawhney et al., 1988; Pignatello, 1990a; Pavlostathis and Jaglal, 1991).

Considered together, the difficulties mean that data obtained by following SW-846 Methods 8240/8260 are prone to poor field representativeness and a large negative bias.

A symposium was held in January 1993 in Las Vegas, NV, on “Measuring and Interpreting VOCs in Soils State of the Art and Research Needs.” The symposium served as a national forum for soil-VOC data users and generators of that data to (1) explore the foundation of the conventional VOC measurement and interpretation process, (2) examine results from research and practice that have advanced the understanding of this process, and (3) attempt to develop consensus on current practices, recommendations for alternative procedures, and critical research needs. Many abstracts from that symposium have been included in this review. When available, the symposium proceedings will offer additional perspective and insight beyond the scope of this literature review.

SECTION 2

INTERPHASE TRANSFERS

Soil VOCs can exist in four distinct phases aqueous, gaseous, sorbed, and NAPL. This section provides a review of studies on the equilibrium distribution of soil VOCs among phases aqueous-sorbed, vapor-sorbed, aqueous-vapor, and NAPL-aqueous/vapor distributions. Studies of kinetically slow or nonequilibrium distributions of sorbed VOCs are presented in a separate subsection.

AQUEOUS-SORBED DISTRIBUTION

Most VOCs analyzed by SW-846 Methods 8240/8260 are relatively nonpolar, nonionic organic contaminants (NOCs) that partition into soil organic matter because of the hydrophobic nature of the compounds. Here the term “partition” is used to describe a model in which the sorbed material permeates or dissolves (absorbs) into an organic phase (Chiou, 1989). “Adsorption” refers to the condensation of vapor or solute on the surfaces of a solid by physical forces or chemical bonding. The term “sorption” is used to denote uptake of a vapor or solute without reference to a specific mechanism (Chiou, 1989). These terms are not consistent in the literature. “Partition” or “distribution” coefficients may be used more generally to denote the equilibrium ratios of a compound between any two phases, viz., air-water, soil-water, or soil-air. The term “sorption coefficient” carries the implicit assumption of a reversible process at equilibrium, that is, a state in which sorption and resorption are occurring at the same rate.

The sorption of NOCs in saturated porous media, as measured in the laboratory, can be predicted within an order of magnitude based on properties of the pollutant, using either the water volubility or the octanol-water partition coefficient (K_{ow}) and the weight fraction of soil organic carbon (Chiou et al., 1979; Karickhoff, 1984; and Karickhoff et al., 1979). Sorption is described by a linear equation of the form $S = K_dC$, where S is the NOC concentration in soil, K_d (also denoted as K_p) is the sorption coefficient, and C is the equilibrium NOC concentration in solution. The sorption coefficient, K_d, can be normalized by dividing it by the fractional organic carbon content of soil, f_{oc} to give the relatively invariable organic carbon partitioning coefficient, Koc($K_d/f_{oc} = K_{oc}$) This linear partitioning is bounded at the low end by some minimal value of soil organic matter (e.g., organic carbon fraction exceeding 0.1%; Schwarzenbach and Westall, 1981) and bounded at the high end by some fraction of sorbate (NOC) volubility

(Piwoni and Banerjee, 1989). Brusseau and Rao (1989) place the upper boundary in terms of the sorbate activity coefficient; a concentration threshold of 0.056 M is established, below which the sorbate activity coefficient is constant and linear isotherms are likely.

The order-of-magnitude error in estimates of sorption based on K_{oc} occurs because there are inherent limitations to the empirical correlations. Figure 1 shows the 95% confidence limits for K_{oc} as estimated by an empirical correlation with the K_{oW} for a diverse set of 34 NOCs, including pesticides, polycyclic aromatic compounds, and 7 VOCs (Hassett et al., 1983). Graphical depiction of the log-log correlation demonstrates the approximate 6 orders of magnitude over which the relationship was generated and the order of magnitude error for any particular K_{oc} value within the 95% confidence limits of the correlation. The situation is similar for the other empirical correlations with K_{ow} or water volubility (Hassett and Banwart, 1989).

Other reasons for differences between estimated and measured K_d values generally fall into two categories the contribution of soil mineral matter, or differences in the chemical nature of organic matter. Mingelgrin and Gerstl (1983) reviewed the literature on soil sorption of nonionic compounds and discussed the many limitations of K_{oc} estimates. They cited work by some researchers which showed that removal of organic matter from soils and sediments had relatively little effect on, or actually increased, sorption of nonionic compounds. In part, this phenomenon may be an artifact caused by the difficulty in measuring small quantities of organic matter and small values of sorbate uptake (Rutherford et al., 1992)

Garbarini and Lion (1986) studied sorption of toluene and TCE by several organic sorbents (viz., whole soil; humic acid, fulvic acid, and humin extracts of soil; tannic acid, lignin, zein, cellulose; ethyl ether extracted soil, and the resulting extracts, which contained soil fats-waxes-resins). They found widely varying affinities for the chemicals that could not be explained by the organic carbon content of the sorbent. Lignin followed by zein had the highest sorption coefficients of all sorbents studied. On an organic carbon basis (K_{oc}, however, the fats-waxes-resins sorbed the largest amount. Observations on the relative degree of decomposition, the direct or indirect effects of the inorganic matrix, and the contribution of relatively hydrophilic oxygen-containing functional groups in organic matter were explored by multivariate regression analyses. Results showed that using the oxygen and carbon content of a sorbent yielded more accurate predictions of the sorption coefficient than did carbon content alone.

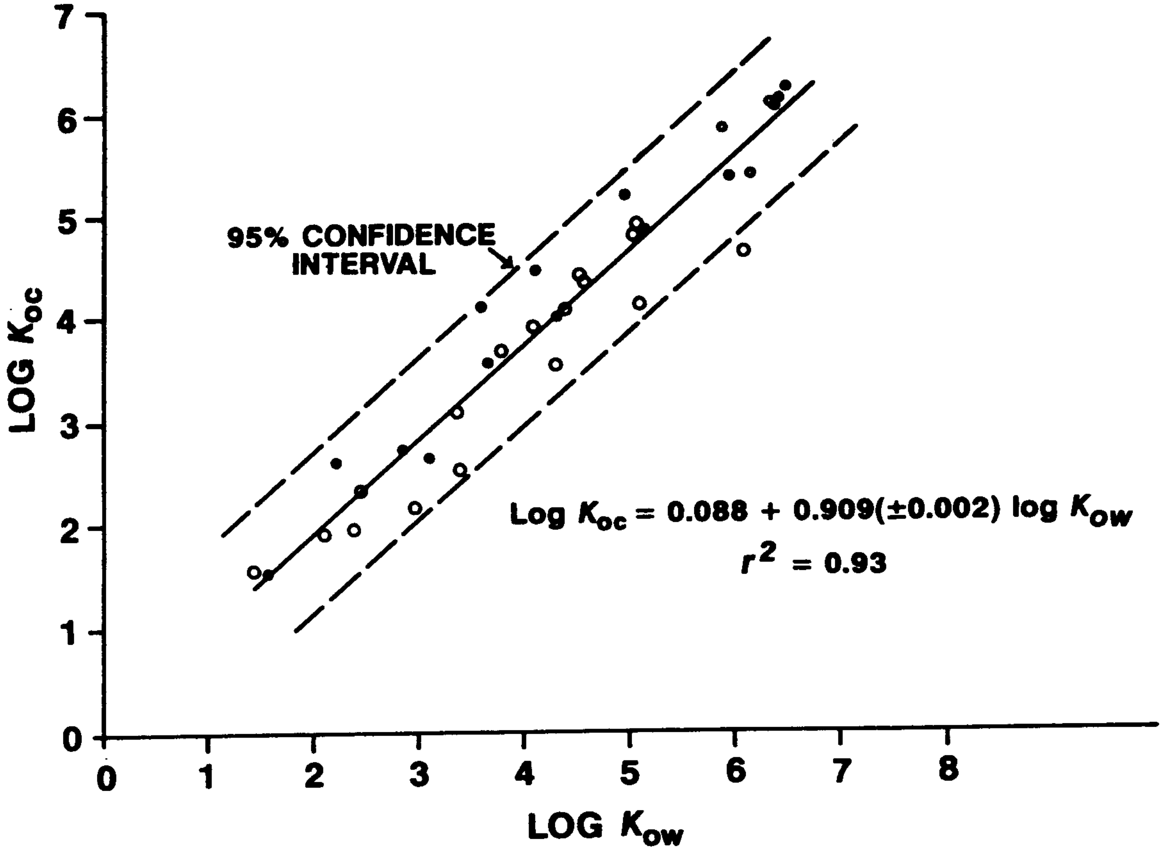

Figure 1. Log K_{oc} - Log K_{ow} relationship (after Hasset and Banwart, 1989.)

Similarly, Rutherford et al. (1992) found that peat sorbs relatively more NOCs than does cellulose. They propose that differences correlate with the polar to nonpolar group ratio [(O+N)/C]of the organic matter. They suggest, however, that variability in soil organic C content of organic matter falls within 53% to 63% for most soils. On the basis of this assumption, and confining the prediction to soils that contain at least 0.2% organic matter (or approximately 0.l% organic carbon), the variation in partitioning coefficients attributable to the nature of the organic matter is within a factor of 3.

In addition to indigenous soil organic carbon, anthropogenic sources of organic carbon (such as residual petroleum) act as a highly effective partition medium for organic contaminants. Boyd and Sun (1990) showed that residual petroleum was approximately 10 times more effective than soil organic matter as a partition medium for pentachlorophenol or toluene. Soil distribution coefficients were predicted as the sum of the partitioning into natural organic matter and partitioning into the residual oil or polychlorinated biphenyls (PCB) phase. Oil-water distribution coefficients were evaluated in a manner similar to that of octanol-water distribution coefficients. In soils that contained residual petroleum or PCBS, the magnitude of the oil-water coefficient greatly enhanced the NOC uptake and was believed to limit the effectiveness of some remediation efforts (Boyd and Sun, 1990). Bouchard et al. (1990) studied the same phenomena on soils that were treated with unleaded gasoline in the laboratory to form a residual hydrocarbon fraction. By comparing sorption of benzene and naphthalene on treated and control soils, they showed that the most profound effect occurred on those sorbents low in natural organic carbon.

Estimation of VOC sorption based on K_{oc} values is recommended only for soils that contain more than O.1% organic carbon (or more than O.2% organic matter). No procedure exists for the estimation of VOC sorption in soil that is very low in organic matter. Mineralogical effects related to the surface charge of individual mineral species will affect sorption when organic matter is low. In soils that contain mixed wastes, such as the soils in landfills, the nature of the organic matter will have the greatest effect where the organic input is extremely fresh (virtually undegraded) or where organic carbon is exceptionally aged (coal is an extreme example). The presence of anthropogenic, nonpolar organic liquid wastes will further increase sorption of NOCs.

Soil sorption of polar VOCs (e.g. ketones, aldehydes, nitriles) is generally nonlinear and varies with the type and quantity of clay minerals in the soil. Estimates of sorption for polar compounds may be based on empirical relationships generated by chemical class (Karickhoff, 1984).

NONEQUILIBRIUM SORPTION

True sorption equilibrium may require weeks to months to achieve (Karickhoff, 1984). A growing body of literature is addressing the impact of nonequilibrium or rate-limited sorption-desorption on estimates of organic chemical distribution coefficients and on solute transport modeling (Brusseau and Rao, 1989). Equilibrium sorption occurs rapidly (2 to 48 h), and little change is observed when the experimental time is doubled, as represented by sorption coefficients (K_d or K_{oc}) "Sorption nonequilibrium" denotes slow sorption-desorption processes and nonreversible sorption. The term "chemical nonequilibrium" refers to rate-limited interactions between the sorbate and sorbent (e.g. chemisorption). Conventional VOCs are largely devoid of functional groups that participate in chemisorption, thus irreversible sorption is unlikely. Intraaggregate or intraorganic matter diffusion in soil is believed to be the rate-limiting process for NOC sorption (Steinberg et al., 1987; Hamaker and Thompson, 1972; Pignatello, 1990b; Brusseau et al., 1991, Ball and Roberts, 1991b).

The term "nonequilibrium" refers more generally to the concept that numerous physical and chemical factors preclude equilibrium in field environments. The existence of secondary soil structures, including aggregates, fractures, and bedding, creates what are termed transport or physical nonequilibrium effects (Brusseau and Rao, 1989). Transport-related nonequilibrium, resulting from the existence of a heterogeneous flow domain, is discussed in the section on modeling in this review. Nonequilibrium sorption is a term that spans a scale ranging from microscopic effects on soil surfaces to macroscopic diffusion or "mass transfer" effects within pores of varying sizes.

Laboratory sorption data have been found to exhibit a two-stage approach to equilibrium: a short initial phase of fast uptake, followed by an extended period of much slower uptake (Brusseau and Rao, 1989; Harmon et al., 1989). Sorption is viewed as a rapid partitioning of NOCs into organic matter (within hours or days), followed by a much slower uptake phenomenon involving intraaggregate or intraorganic matter diffusion. Batch resorption studies similarly show a rapid release phase followed by an extended slow resorption phase (Pavlostathis and Mathavan, 1992). Brusseau and Rao (1989) estimated that, following the initial rapid phase of sorption, approximately 100% more sorption will occur by slow sorption processes. Measurement techniques do not distinguish the scale of the continued sorption, and therefore slow diffusion into microsites is incorporated into the term nonequilibrium sorption.

Evidence for nonequilibrium sorption in a field soil was first reported by Steinberg et al. (1987). The soil fumigant 1,2-dibromoethane (EDB) was being detected in ground water, but extensive searching had not identified the source. Hot methanol (75 °C for 24 h) was used to extract the overlying agricultural soils. Some of the soil had received no known applications of EDB for as long as 19 years before the hot solvent extraction. EDB residues in the lOO ng/g range were found in the soils. The residue was resistant to volatilization and microbial degradation, and the release into aqueous solution was extremely slow at 25 °C. Increasing the temperature to 75 °C released greater than 25% of the EDB from a fine sandy loam soil in less than 3 h. Release of residual EDB to aqueous extracts from pulverized soil increased with degree of pulverizing (time in ball mill), leading the authors to conclude that the EDB residues were occluded in soil micropores.

Pignatello (1990a) studied the potential of several halogenated hydrocarbons (all VOCs) to form slowly reversible or “residual” VOC fractions in soils. Nine halogenated aliphanes were added to soil. The residual fraction was defined as the proportion of VOCs that remained after repeated washing with water residual VOCs were subsequently extracted with hot acetone. Results demonstrated the trend toward formation of a residual sorbed fraction of VOCs that increases with equilibration time. The residual VOC concentrations varied among the compounds and by treatment. In general, the alkenes (TCE, tetrachloroethene, and 1,3-dichloropropene) produced greater residual concentrations than the alkanes (carbon tetrachloride, 1,1,1-trichloroethane, 1,2-dibromopropane, 1,2-dibromo-3chloropropane, and l,2-dibromoethane).

Further studies (Pignatello, 1990b) presented additional data, demonstrating the effects of (1) incubation time, (2) initial concentration, and (3) different soil pretreatments on the formation of soil residual VOC concentrations). Again, residual concentrations increased with incubation time, but TCE residual concentrations appeared to level off after 8 days at a high loading rate (TCE-spike addition of 10^4 mg/kg). Tetrachloroethene was extremely fast at forming a large residual concentration; an order-of-magnitude increase in residual concentration after 7 days incubation was observed for tetrachloroethene (0.41 mg/kg after 1 day and 5.6 mg/kg after 7 days). The residual concentrations increased with increasing concentrations of chemical present during the sorption period. The residual concentrations showed a log linear increase with the final solution concentration. The slope of the concentration dependence varied by compound for example, tetrachloroethene, with a slope of 0.90, had a nearly linear response, and tetrachloroethene had a slope of 0.73. Residual TCE concentrations were close to half-order in TCE concentrations in the medium (slope of 0.49), whether soil was treated with pure compound or aqueous solution.

Ball and Roberts (1991a, 1991b) investigated the long-term sorption equilibria of ^{14}C-labeled tetrachloroethene and l,2,4,5-tetrachlorobenzene with low-carbon aquifer material (organic carbon content of less than 0.021% in bulk sample, less than O.1% in any specific particle-size fraction). Samples were sterilized and sealed in glass ampules to avoid losses from biodegradation and volatilization. Sorption was calculated by difference from initial solution concentration after accounting for other losses (e.g., headspace). Compound recovery from blanks was greater than 90% during the 100-day study. Rate studies showed that tetrachloroethene sorption by the bulk material reached equilibrium in 30 days but that pulverized material reached sorption equilibrium within 1 day. The estimated rate constants for pulverized material were between 40 and 80 times higher than rate constants for unaltered solids (Ball and Roberts, 1991b). The sorption capacities were essentially the same for bulk and pulverized material, indicating that rapid sorption experiments could be accomplished using pulverized samples. Pulverized samples had the added advantage of lower relative errors in sorption estimates (27.6% relative error for bulk samples versus 8% relative error for pulverized samples; Ball and Roberts, 1991a). Results were interpreted by a physical diffusion model (Ball and Roberts, 1991b). The effective pore diffusion coefficients were estimated to be roughly 2 to 3 orders of magnitude lower than bulk aqueous diffusivities in the aquifer material studied. Diffusive length was dramatically reduced by pulverizing, consistent with the proposed mechanism of intragranular diffusion (Ball and Roberts, 1991b).

Sorption by specific particle-size fractions revealed that sorption was greatest by the largest size fractions (Ball and Roberts, 1991a). The larger size fractions had the greatest organic matter contents and the greatest surface areas on a weight basis. (The larger particle-size fractions evidently consisted of soil aggregates.) Sorption coefficients exceeded values predicted on the basis of organic partitioning by an order of magnitude or more. Average measured log K_{oc} values were 5.1 and 3.6, and average calculated log K_{oc} values from the literature were 4.0 for tetrachlorobenzene and 2.4 for tetrachloroethene. Ball and Roberts (1991a) suggested that either an exceptionally adsorptive organic phase existed in the aquifer material or that mineral matter was partly responsible for the observed sorption.

Pavlostathis and Mathavan (1992) studied (1) the resorption kinetics of five field-contaminated soils and (2) the effect of residence time (up to 15 months) on a laboratory-contaminated soil. Resorption of TCE, tetrachloroethylene, toluene, and xylene in soil-water mixtures was biphasic. A fast resorption phase was complete within 24 h, followed by a very slow resorption phase. Methanol extractions of the soil pellet following centrifugation of the soil-water samples (13 h at 20 °C, and 30% soil by weight) showed that a substantial portion of the sorbed contaminant mass (48 to 94%) resisted resorption in deionized water after 7 days. The rate and extent of resorption did not correlate with the soil properties surveyed (organic carbon content, cation exchange capacity, or specific surface area) or with the sorbate water solubility. In a separate study, soil spiked with TCE was treated with sodium azide to reduce biological activity and was stored in the dark at 4 °C. Samples were analyzed at 2.5, 5.5, and 15.5 months by six successive washings in deionized water followed by extraction of the soil pellet with methanol. The TCE that resisted resorption in water was 10% of the total amount that sorbed at 2.5 months but increased to 45% of the total amount that sorbed at 15.5 months. The partition coefficient, as observed by the successive washings, also increased with time; K_P was 0.4 mL/g at 2.5 months and 1.5 mL/g at 15.5 months. The amount of TCE that resisted resorption might be shown to be even greater if a hot methanol extraction were used (demonstrated by Sawhney et al. [1988] for EDB-contaminated soil).

VAPOR-SORBED DISTRIBUTION

Although sorption of chemicals on saturated soil has been studied extensively, reports on the sorption of VOCs on unsaturated or dry soils are relatively few. Of these studies, those that compare vapor uptake on dry versus wet soil show that dry soil vapor uptake is greater than that of wet soils, is nonlinear, and is suppressed by the presence of water in a nonlinear manner (Chiou and Shoup, 1985; Poe et al., 1988; Chiou, 1989; Ong and Lion, 1991a, 1991b; Rhue et al, 1988). Chiou and Shoup (1985) explain soil as a dual sorbent in which the mineral matter functions as a conventional adsorbent (physically covering soil surfaces) and organic matter functions as a partition medium. Polar water molecules are strongly adsorbed on mineral surfaces and effectively displace organic compounds as the soil water content or relative humidity increases. In the absence of water vapor, strong mineral adsorption of organic vapors exceeds the effect of partitioning with organic matter.

Chiou and Shoup (1985) studied the vapor sorption of water and five organics (benzene, chlorobenzene, p-dichlorobenzene, m-dichlorobenzene, and l,2,4-trichlorobenzene) on an oven-dried (140 °C) soil. Gravimetric determinationsof VOC sorption were performed using a dynamic, temperature-controlled, vapor-sorption apparatus. Results of soil uptake were plotted against relative vapor concentrations (equilibrium partial pressure divided by saturation vapor pressure of the compound) to normalize the activity of each compound with respect to its own pure state and to allow for the comparison of vapor uptake between different compounds and between vapor and normalized liquid uptake (equilibrium liquid concentration divided by the volubility of the compound) of the same compound. Sorption isotherms for all compounds on dry soil were distinctly nonlinear. The capacity of the soil for sorption was greatest for water and the presence of water vapor sharply reduced the soil sorption capacity for the organic compounds Water-saturated sorption was about 2 orders of magnitude less than dry-soil sorption of the VOCs Chiou and Shoup (1985) observed that at 90% relative humidity the vapor sorption isotherms for m-dichlorobenzene and 1,2,4-trichlorobenzene fall close to the corresponding isotherms for aqueous solution. For benzene, however, the 90% relative humidity isotherm deviated from the aqueous isotherm (positively) by more than a factor of 5. The authors suggested that error in the measurement of the relative humidity may have caused this deviation.

Poe et al. (1988) looked at vapor phase sorption of five VOCs (benzene, dichloropropane, methylcyclohexane, ethyl ether, and methanol) on four air-dry soils and found consistent adsorption capacities among them. The relative order of adsorption in the four soils remained the same regardless of the chemical compound. The soil that had the highest clay content and largest surface area adsorbed the greatest amount of each VOC. For the two soils that had similar clay content and surface area, however, the soil that sorbed the greatest amount of VOCs had a lower organic carbon content, suggesting that organic matter may block mineral surface sites. Both Poe et al. (1988) and Chiou and Shoup (1985) found that sorption increases as compound polarity increases.

Ong and Lion (1991a) used a headspace technique to study the sorption of TCE over a range of moisture contents by soil components, viz., alumina, hydrated ferric oxide, montmorillonite, kaolinite, and humic-coated alumina. They found that sorption by oven-dry solids was 2 to 4 orders of magnitude greater than sorption by wet solids. A description of vapor sorption as a function of moisture content was presented (Figure 2). When moisture contents ranged from oven-dry to water sufficient to provide monolayer coverage of solid surfaces, vapor sorption decreased linearly with moisture content. Water sufficient to form 1 to 5 monolayer on solid surfaces exhibited complex behavior, attributed to interactions between TCE vapor and surface-bound water. At approximately five monolayer of water a sorption minimum was observed, and above five monolayer sorption increased slightly with moisture content. Ong and Lion (1991a) showed that the gradual increase in sorption at moisture contents greater than five monolayer could be accounted for by vapor dissolution, as predicted by Henry's Law constant (see Vapor-Aqueous Distribution Section below). Five monolayer of water corresponds to 25% moisture by weight on the high-surface area alumina and to 2.9% moisture by weight on the low-surface area kaolinite in this study.

Gravimetric studies of TCE and water vapor sorption on soil minerals (montmorillonite, kaolinite, iron oxide, silica, and alumina) and on humic-coated alumina and humic acid showed that surface area serves as a good measure of the adsorptive capacity of dry solids (Ong and Lion, 1991b). However, variability in relative sorption isotherms among the sorbents (calculated as the ratio of the sorbed quantity to the monolayer capacity) demonstrated that other factors are also involved. Specific sorbate-sorbent interactions and vapor condensation in micropores are cited to explain the variability among sorbents. Sorption of TCE onto the mineral solids in the presence of water at several levels of relative humidity (RH) showed that the polar water molecules are sorbed preferentially over the nonpolar VOCs Addition of water to humic acid resulted in a large increase in the amount of TCE sorbed; TCE sorption by humic acid at 80% RH was much greater than at O% RH and much greater than saturated aqueous sorption. Expansion of the oven-dry humic acid due to hydration and exposure of internal surfaces for sorption/condensation as the RH increases was proposed. Although montmorillonite also expands with the addition of water, its sorption capacity for TCE decreased, indicating that the interlamellar pores were not readily available for the uptake of TCE.

Equilibrium vapor-phase adsorption of VOCs is described by the classical Brunauer-Emmett-Teller (BET) isotherm (Jurinak and Volman, 1957; Chiou and Shoup, 1985 Poe et al., 1988; Rhue et al., 1988), indicating that multimolecular layer adsorption occurs. At very high vapor pressures, increased uptake of VOCs through vapor condensation is regulated by available pore space (Ong and Lion, 1991b). This effect is most likely to occur close to field sources of contamination, such as nonaqueous-phase organic liquids.

Vapor sorption of VOCs has not been shown in the field, but Ong and Lion (1991a) suggest that field conditions dry enough to permit vapor sorption exist.

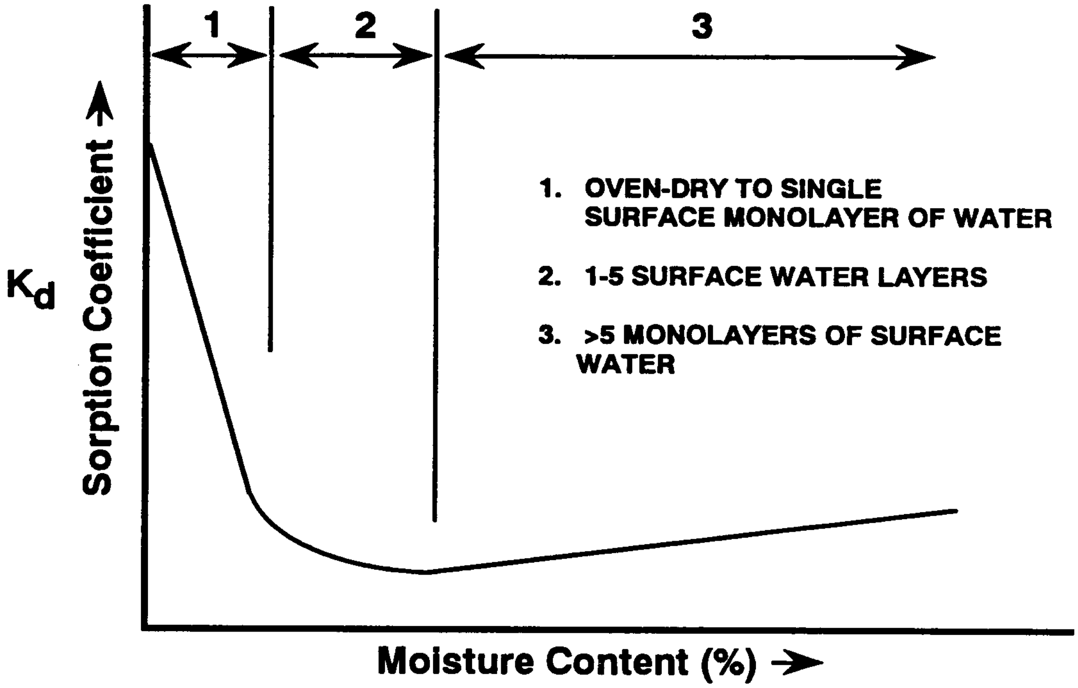

Figure 2. Vapor phase sorption as a function of moisture content (after Ong and Lion, 1991a.)

Vapor extraction systems generally require moist air to improve the efficiency of vapor removal (V. Fong, personal communication). Smith et al. (1990) found that vapor sorption would not be important at the Picatinny Arsenal in New Jersey. In the laboratory, they measured the vapor-phase sorption of TCE and water using the experimental apparatus of Chiou and Shoup (1985). As an example, a surface soil sample of 4% organic carbon and 13.5% clay reached water vapor saturation at 6% moisture on a weight basis. The vapor saturation soil-moisture content is defined as the mass of water sorbed by the soil in equilibrium with water vapor at its saturation vapor pressure. The field soil moisture concentrations were all much greater than the vapor saturation moisture contents (on the day these were sampled) and thus they concluded that vapor-phase sorption was unimportant at this site.

VAPOR-AQUEOUS DISTRIBUTION

Vapor-aqueous equilibrium distributions for dilute solutions at or below one atmosphere pressure are directly proportional. Henry's Law states that the equilibrium distribution of a compound, i, between gas and liquid phases is linearly related

$$P_i = H_i X_i$$

where P_i is the partial pressure of compound i, H_i is Henry's Law constant for compound i at a given temperature, and Xi is the mole fraction of compound i. The distribution can be expressed in terms of the concentration of a compound in a liquid, yielding a proportionality constant, or Henry's constant, that has units of kPa $m^3 mol^{-1}$ (or atm $m^3 mol^{-1}$). Also, a dimensionless form of Henry's constant (gas phase molarity/liquid phase molarity) is common; this form is related to the other two constants by expressing the gaseous partial pressure in terms of moles through the ideal gas law.

Although strictly applicable only for dilute solutions, Henry's Law has been found to persist to the point of saturation for many chemicals (Spencer and Cliath, 1970). Hence, the dimensionless Henry's Law constant, K_H, may be calculated as the ratio of saturated vapor density, C_G* (g/m^3), to water solubility, C_L*(g/m^3)

$$K_H = C_G^*/C_L^*.$$

Further evaluation of the use of vapor pressure and volubility data to estimate Henry's constants was reported by Munz and Roberts (1987) who found good agreement between experimental and predicted values for seven halocarbons (bromoform, hexachloroethane, chloroform, TCE, 1,1,1-trichloroethane, carbon tetrachloride, and dichlorodifluoromethane) and poor agreement for one compound (tetrachloroethene). They suggested that errors in the estimation of Henry's Law constant occur due to the wide range of volubility values reported in the literature for many compounds. No effect of solute concentration on the Henry's Law constant for the solute was observed for solute-liquid mole fractions as large as 10^{-3} (Munz and Roberts, 1987).

For soil that is saturated or unsaturated, but not dry, Henry's Law constants can be used to estimate the distribution of a VOC between the liquid and gaseous phases The effect of temperature on Henry's Law constant must be considered Henry's Law constant increases by a factor of approximately 1.6 for every 10 °C rise in temperature (Munz and Roberts, 1987). Data to demonstrate the effect of temperature (10 °C and 30 °C) on the Henry's Law constant of five VOCs can be found in Munz and Roberts (1987).

NAPL-AQUEOUS/VAPOR DISTRIBUTIONS

Soil contamination by a NAPL (e.g., gasoline, chlorinated solvents) produces a residual soil-NAPL fraction. Pools or “gaglia” of pure phase liquid are retained in pore spaces by capillary forces. The residual NAPL saturation, or amount of NAPL that will be held against gravity, depends on the soil pore structure but is estimated to range from 5 to 40% of the pore space of most soils. With time, the residual fraction dissipates by volatilization and solubilization. Complex NAPL mixtures, such as petroleum derived fuels and lubricants, change in composition as the volatile and soluble components weather in chemical sequence from the residual fraction (Bouchard et al., 1990).

The release of a VOC from residual NAPL will be governed by (1) the VOC volubility in combination with the rate of water flowing through the soil and (2) the VOC volatility in combination with the vapor concentration gradients and pressure gradients acting on the vapor phase. The aqueous volubility of some chlorinated solvents alone and in binary mixtures was reported by Broholm et al. (1992). Solubilities at 23 °C to 24 °C ranged from 242 mg/L for tetrachloroethene to 8,668 mg/L for chloroform. The chlorinated solvents exhibit ideal behavior in mixtures. That is, the aqueous concentration of a compound can be predicted by the mole fraction of the compound in the organic phase.

SUMMARY OF INTERPHASE TRANSFERS

Rapid sorption of VOCs by wet or moist soils is generally predicted from the organic-carbon partitioning coefficient (K_{oc}) for the compound and from the soil organic carbon content. The K_{oc} is estimated through empirical log-log correlations with the octanol-water partitioning coefficient (K_{ow}) or water volubility of the compound. An order-of-magnitude error is associated with the 95% confidence limits of these correlations (Hassett and Banwart, 1989). Deviations from predicted values by a factor of 3 may be attributed to qualitative differences in soil organic matter (Rutherford et al., 1992). Sorption is controlled by mechanisms other than organic partitioning and K_{oc} predictions are indefensible if (1) the soil contains less than 0.1% organic carbon (or 0.2% organic matter) or (2) the compounds contain polar functional groups (e.g, ketones or nitriles).

Slow sorption processes, termed “nonequilibrium sorption” are believed to be controlled by diffusion within soil organic matter (intraorganic diffusion) or by diffusion into soil micropores. Following the initial rapid “equilibrium” sorption phase, an estimated 100% greater sorption may occur given sufficient time (Brusseau and Rao, 1989). With time, the soluble, volatile, and easily desorbed phases dissipate, and the nonequilibrium fraction becomes the dominant form of soil contamination (Steinberg et al., 1987). The significance of the nonequilibrium fraction will be defined by the prevalence of this phenomenon and the resulting rates of resorption. No data are available for identifying rates and conditions under which nonequilibrium VOCs are released.

Dry soil sorbs 2 to 4 orders of magnitude more volatile compounds than the same soil sorbs when wet. Vapor sorption proceeds by physical adsorption, rather than by organic partitioning. Polar water molecules rapidly and effectively displace surface-adsorbed VOCs The significance of vapor sorption under field conditions has not been documented, but cannot be dismissed without investigation.

Vapor-aqueous distributions of VOCs are predicted using Henry’s Law constants. The values are often estimated by the ratio of the saturated vapor density to the water volubility of a compound. Henry’s Law constants increase by a factor of approximately 1.6 for every 10 °C rise in temperature (Munz and Roberts, 1987).

Residual NAPL saturation in soil is a function of soil porosity and is not predicted by K_{oc} sorption. Contamination by NAPLs results in a NAPL residual saturation fraction held by capillary forces (against gravity) in soil pores (Bouchard et al., 1990).

SECTION 3

DEGRADATION

VOCs may be lost from the soil or a soil sample by either microbiological or abiotic degradation. A comparison of sterilized and viable samples is generally used to distinguish between the degradation mechanisms. Field studies, and occasionally laboratory studies, commonly report dissipation rates because additional pathways of chemical losses (volatilization, sorption, or movement with soil water) are not measured during the study. This section discusses reports on microbiological and abiotic degradation, and on the factors affecting degradation rates.

MICROBIOLOGICAL DEGRADATION

Although microorganisms are sharply reduced in number and kind with soil depth, significant microbial degradation occurs for some chemicals throughout the vadose zone and into saturated substrata (e.g. Wilson et al., 1983; Barker et al., 1987; Sulfita, 1989). Data on the biodegradation of many organic compounds in soil is summarized by Dragun (1988). It is evident that the experimental conditions influence results, and that published values used to estimate biodegradation rates must be carefully evaluated before equating results to field or sample storage conditions.

Soil microbiological transformation of low-molecular-weight aliphatic and aromatic hydrocarbons figures prominently in the environmental fate of these compounds. Generally, the shorter the hydrocarbon chain, the more rapid the oxidative biodegradation (Alexander, 1977). For example, bacteria able to oxidize volatile hydrocarbons proliferate in the vicinity of natural gas leaks, consuming available 0_2 and creating locally O_2-deficit regions (Alexander, 1977). Benzene, toluene, xylene, ethylbenzene, and naphthalene exist in a dynamic state in soils, and they are both synthesized by and destroyed by microorganisms (Alexander, 1977; Dragun, 1988). The total biological oxygen demand for degrading these aromatics is very large (values such as 9 moles of 0_2 per mole of toluene), which implies that the subsurface degradation will be limited frequently by 0_2 diffusion.

Barker et al. (1987) studied the biodegradation of benzene, toluene, and m-, p-, o-xylene injected into the water table in a shallow sand aquifer in Borden, Ontario. Essentially complete removal of a field-injected pulse was reported within about 1.2

years; benzene was the most persistently retained compound in the system. Horizontal layers of near-zero dissolved oxygen in the saturated strata corresponded to contaminant persistence 32 days after injection. This finding confirmed that diffusion of oxygen was controlling the field biodegradation rates. Laboratory experiments with anaerobic microcosms and sealed vials demonstrated that the losses could be attributed to biodegradation under aerobic conditions. Phenolic and acidic breakdown products were detected in anaerobic microcosms. Results in septum-sealed vials showed zero-order kinetics and lack of anaerobic transformation products, indicating that oxygen leaked into the vials. Laboratory zero-order rate constants were compared with field ground-water degradation rate constants, and the laboratory rate was about 1.5 times the field rate for benzene and toluene. Field rates were higher than laboratory rates for m- and p-xylene.

Halogenated aromatics degrade only under aerobic conditions (Kobayashi and Rittman, 1982). Wilson et al. (1983) found chlorobenzene to biodegrade at a rate of approximately 5% per week under aerobic conditions, although there was no significant degradation under anaerobic conditions. Vadose material collected from depths of 1.2 and 3.0 m showed degradation of chlorobenzene, but no degradation was observed in aquifer materials (5-m depth) or in autoclaved (sterilized) samples (Wilson et al., 1983). Wilson and McNabb (1983) found 1,2-dichlorobenzene and 1,4-dichlorobenzene much more likely to degrade than l,3-dichlorobenzene in aquifer material.

In contrast to the compounds discussed above, microbial degradation of volatile aliphatic chlorinated hydrocarbons occurs primarily by reductive dehalogenation, that is, the replacement of chlorine by hydrogen under anaerobic conditions (Smith and Dragun, 1984). Reductive dehalogenation of tetrachloroethene, l,1,1-trichloroethane, TCE, and tetrachloromethane has been demonstrated at Eh values below 300 mV and pH 6.8 to 7.0, although carbon-halogen bonds do not rupture in microcosms devoid of viable microorganisms (Parsons et al., 1985). Such highly reducing conditions do not commonly occur in most soils but could occur in water-logged soils, under landfills, or in highly contaminated soils exposed to fluctuating water tables.

Cline and Viste (1985) have shown that anaerobic degradation of chlorinated solvents occurs under landfills and under solvent recovery plants. Three landfills used for disposal of municipal and industrial wastes received the parent compounds (solvents) 1,1,1-trichloroethane, TCE, and tetrachloroethene. Breakdown products included dichloroethanes, chloroethane, dichloroethenes (cis- and trans-), and vinyl chloride. The breakdown products dominated in ground water downgradient from the waste disposal boundaries. Data from solvent recovery sites and an industrial site showed that locations receiving both chlorinated and nonchlorinated solvents had much higher percentages of breakdown products downgradient than sites receiving only chlorinated solvents. The authors concluded that the nonchlorinated carbon source promotes rapid co-metabolism of the chlorinated solvents by microorganisms.

The reaction of vinyl chloride is a notable exception to anaerobic degradation among the halogenated aliphanes. It is often a breakdown product of other, more highly chlorinated compounds and is highly persistent under anaerobic conditions. In contrast, vinyl chloride degrades rapidly under aerobic conditions (Sims, 1990; Hartmans and de Bent, 1992). Dragun (1988) reports chloroethane as a degradation product, and Hartmans and de Bent (1992) observed an intermediate epoxide chlorooxirane degradation product (a reactive species), but subsequent degradation products were not identified.

No detectable degradation of l,2-dichloroethane, 1,1,2--trichloroethane, TCE, or tetrachloroethene was found in soil and sediment samples collected near Lula, Oklahoma, from vadose depths of 1.2 and 3 m and from below the water table at 5 m (Wilson et al., 1983). These compounds were highly refractory in a related laboratory study that found no degradation when samples were incubated for 16 weeks in a N_2 atmosphere. The same study found that bromodichloromethane was degraded in sediment from the saturated zone, chlorobenzene was degraded in vadose soil, and toluene was rapidly degraded by microorganisms in soil collected at all depths. There was no detectable degradation of any of the chemicals tested after the soils were autoclave.

Under certain circumstances, such as in the presence of natural gas, oxidation and dechlorination of halogenated aliphanes may occur. A study by Wilson and Wilson (1985) showed that TCE was rapidly and effectively removed from a soil column exposed to a stream of natural gas (0.6%). Soil columns poisoned with sodium azide, or in the absence of natural gas, allowed significantly more TCE to pass through. Enzymes produced by methanotrophs were credited with the degradation of TCE in the soil exposed to natural gas. The authors concluded that other chlorinated aliphanes will also undergo oxidation and dechlorination in the presence of natural gas.

ABIOTIC DEGRADATION

Mineral surfaces often serve as catalysts for abiotic organic reactions such as hydrolysis, elimination, substitution, redox, and polymerization (e.g. a review by Voudrias and Reinhard, 1986) Transition metal cations on or in clays can act as Lewis acids by accepting electrons from organic compounds. The dissociation of water coordinated to exchangeable cations of clays results in Brønsted acidity. At low water content, the Brønsted sites may produce extreme acidities at the clay surface. Dragun (1988) lists benzene, ethylbenzene, naphthalene, and toluene as chemicals that may undergo free-radical oxidation in soil. Reactivity on clay surfaces is highly specific and is most commonly observed with compounds that have polar functional groups. For example, acetonitrile undergoes hydrolysis to form acetamide in the presence of a Wyoming bentonite, but not in the presence of a Montana vermiculite (Dragun, 1988). Although abiotic degradation of some compounds on some soils may occur, the extent of such reactions cannot be estimated from available data.

Chemicals that may rapidly polymerize in the presence of water include at least three VOCs: acrolein, acrylonitrile, and vinyl acetate (Dragun, 1988). Vinyl acetate has been removed from the Revised Priority List of Hazardous Substances (56 FR 52169,17 October 1991), and information on the environmental significance of the polymerization reaction for the other two compounds was not found.

Abiotic reactions of chlorinated aliphatic VOCs in water have been documented. Hydrolysis and oxidation, the principal chemical reactions, yield products that tend to be water-soluble intermediates which are often difficult to detect at trace levels. Evidence for these reactions is, therefore, the disappearance of the chemical under sterile conditions at carefully controlled temperatures. Tetrachloroethene and TCE have been reported to degrade in water, with half-lives of about 0.75 and 0.9 years, respectively, at room temperature (Dilling et al., 1975). The hydrolysis of 1,1,1-trichloroethane has been reported with a half-life of 0.5 to 0.8 years at 25 °C (Dilling et al., 1975).

Hydrolysis rates reported for a given chemical can vary over a few orders of magnitude depending on initial concentration or on procedural differences. The hydrolysis half-life of trichloromethane has been reported as 1.25 years Dilling et al., 1975) and 3,500 years (Mabey and Mill, 1978). Similarly, the hydrolysis half-life for dichloromethane is reported as 1.5 years Dilling et al., 1975) and 700 years (Mabey and Mill, 1978). Smith and Dragun (1984) suggested that if the longer half-lives (calculated from kinetic studies carried out at elevated temperatures) are reliable, the shorter experimental values must result from processes other than hydrolysis. However, variable hydrolysis half-lives reported for tetrachloromethane, i.e., 7 years at 1,000 mg/L and 7,000 years at 1 mg/L, have been attributed to a hydrolysis reaction that is second order in tetrachloromethane (Mabey and Mill, 1978).

Recognizing variation in the data, these values all suggest that hydrolysis should not interfere with typical laboratory procedures to measure halogenated alkanes in water over holding times of a few days. Hydrolysis rates in the presence of soil may be slower or faster than those reported in water, depending on the soil and compound-specific effects of pH, Eh, sorption, or surface-catalyzed reactions_ Abiotic soil degradation studies are inherently less conclusive than studies in water as exemplified in the study of Anderson et al. (1991) reviewed below.

FACTORS AFFECTING DEGRADATION RATES

When biotransformation does occur, it will usually be more rapid than abiotic transformation (Vogel et al., 1981 Dragun, 1988). Environmental half-lives from abiotic processes for halogenated aliphatic compounds are generally on the order of years to hundreds of years (Vogel et al., 1987), although the same compounds exhibit half-lives of days to weeks in the presence of microbially active soil or static-flask culture conditions (Dragun, 1988). Unfortunately, however, soil biodegradation rates elude quantitative description. Dragun (1988) discusses some of the reasons that estimation techniques have not been devised, including the many soil and environmental factors that influence biodegradation rates and the widely varying protocols and lack of studies to relate protocols used in biodegradation studies. Some general guidelines are given, such as: (1) increasing the number of chlorine atoms within the molecule decreases the biodegradation rate; (2) water soluble chemicals are usually degraded faster than less water soluble chemicals; (3) unsaturated aliphatic organics have faster biodegradation rates than corresponding saturated aliphatic organics; and (4) n-alkanes, n-alkylaromatics, and aromatic hydrocarbons in the C_5 to C_9 range are biodegradable, but in most environments volatilization competes very effectively with biodegradation as a fate process.

Smith and Dragun (1984) suggested that laboratory-derived half-lives should be taken as lower limits (the most rapid that could be expected), and not necessarily the half-lives expected to be found under field conditions. In contrast, Barker et al. (1987) demonstrated that laboratory-derived rates were slower than field- measured degradation rates for m- and p-xylene (in water-saturated strata). The initial concentration of a substrate can change the kinetics of degradation, as shown by

Boethling and Alexander (1979) and by Mabey and Mill (1978). Trace levels of organic compounds will degrade at much slower rates than at higher concentrations. Also, it is likely that many laboratory studies involving VOCs have unaccounted volatile losses or sorption "losses" that increase the apparent degradation half-life (e.g. Anderson et al., 1991; discussed below).

Pavlostathis and Jaglal (1991) have argued that organic pollutants buried within micropores of soil aggregates are, for the most part, inaccessible to microorganisms. Many soil bacteria range in size from 0.5 to 0.8 µm, and more than half the pore volume in a silt loam soil may be represented by pores of radii less than 1 µm. Therefore, the contaminant in solution generally constitutes the readily bioavailable fraction, and resorption rates will greatly influence the biodegradation rate of sorbed compounds. Evidence for the bioavailability of chemicals in solution has been demonstrated by Steinberg et al. (1987). They found that EDB residues in old tobacco field soil had resisted degradation even though fresh ^{14}C EDB additions degraded relatively rapidly.

One recent study attempted a mass balance of VOCs incubated in soil in the laboratory (Anderson et al., 1991). The study followed the disappearance rate of 15 volatile and semivolatile organic compounds in two soils using experimental procedures to distinguish between biodegradation and abiotic losses (including volatilization). Chemicals included in the study and reported half-lives are shown in Table 2. All samples were incubated in the dark at 20 °C. Losses were attributed to "abiotic processes" because differences in disappearance of organic compounds between sterile (autoclave 1 h on 3 consecutive days) and nonsterile samples were not significant. Sterilization was checked by measuring CO_2 efflux for the experimental period of 7 days and by incubation of soil extracts on nutrient agar plates.

In this study, dissipation of ^{14}C toluene was traced in one of the soils (Anderson et al., 1991). After 7 days, 20% of the recoverable radioactivity was in the charcoal traps (volatile losses), 4% was recovered in soil methanol extracts (cold), and 65% was associated with the soil organic matter (extracted twice with NaOH), leaving at least 10% unaccounted for. The authors stated that short-term spike and recovery analyses of individual compounds yielded consistent recoveries, which were used as correction factors. Mass balances in sterile soils were not obtained. The authors suggested that problems with storage and holding times or possibly nonreversible sorption contributed to losses. Spike levels were a nominal 100 mg for each chemical/kg soil dry weight. To minimize volatilization, however, chemicals were not mixed when added to the soil. This procedure may have caused

TABLE 2 LABORATORY DISSIPATION HALF-LIVES OF SOME ORGANIC COMPOUNDS*

Compound	Half-life (days)
benzene	<2.0
ethylene dibromide	<2.0
toluene	<2.0
cis-1,4-dichloro-2-butene	2.0
chlorobenzene	2.1
pxylene	2.2
1,2,3-trichloropropane	2.7
1,2-dichlorobenzene	4.0
chloroform	4.1
methyl ethyl ketone	4.9
carbon tetrachloride	5.0
tetrahydrofuran	5.7
nitrobenzene	9.1
2-chloronaphthalene	11.3
hexachlorobenzene	11.3

* Data from Anderson et al., 1991

locally toxic levels of some compounds in the soils and may have limited the opportunity for the compounds to contact soil microbes. Organic partitioning appeared to be the major sink for toluene (soil had 1.5% organic carbon), and this toluene was not recovered by soil extraction with cold methanol.

SUMMARY OF DEGRADATION

Degradation of naturally occurring aromatics (e.g., BTEX compounds) is likely to be caused by microorganisms in aerobic soils, but abiotic degradation is also plausible (Dragun, 1988). The biodegradation rate of such compounds has been shown to be limited by oxygen diffusion (Barker et al., 1987). Degradation of halogenated aromatics is similar to that of the unhalogenated aromatics in that it is predominantly aerobic biodegradation. The degradation rate of halogenated aromatics, however, is generally slower than that of the unhalogenated species (Dragun, 1988).

Halogenated aliphatic compounds (e.g., chloroform, TCE) degrade by reductive dehalogenation, that is, the replacement of the halogen by hydrogen under anaerobic conditions. Biomediated dehalogenation occurs as a consequence of microbial degradation of other organic carbon sources, or co-metabolism (Cline and Viste, 1985; Wilson and Wilson, 1985). Abiotic dehalogenation has also been reported, but estimates of abiotic half-lives in water vary widely (e.g$_a$ less than 2 years Dilling et al., 1975] and more than 700 years [Mabey and Mill, 1978] for dichloromethane).

The kinetics of degradation are affected by many factors, including the substrate concentration (Boethling and Alexander, 1979; Mabey and Mill, 1978). Laboratory estimates of degradation rates cannot be applied directly to field situations, and comparisons among laboratory studies are subject to artifacts of differences among procedures. Sterile control conditions are difficult to verify and volatile losses during experimental procedures are difficult to avoid (Anderson et al., 1991).

SECTION 4

MOVEMENT OF VOCS IN THE VADOSE ZONE

VOCs may move through soil by diffusion of the vapor or aqueous phases, or by advection or convection[1] of the vapor, aqueous, or NAPL phases. This section first provides general discussions of studies on vapor diffusion, vapor advection, aqueous convection, and volatilization. Field studies are then reviewed separated into (1) studies that had *a priori* data concerning the time and amount of soil contamination and (2) studies where the objective of the field investigation was to describe the concentration or extent of soil contamination.

VAPOR DIFFUSION

In general, vapor diffusion will dominate the soil movement of compounds with high vapor pressures (Taylor and Ashcroft, 1972; Kreamer et al., 1988). The rates of vapor diffusion in soil are obviously slower than in free air. "Effective" soil diffusion coefficients are influenced by the tortuosity of the channels, which is estimated by such parameters as overall porosity and the volumetric air and water saturation levels. The Millington-Quirk tortuosity formula (Millington and Quirk, 1961)[2] is frequently used to estimate soil vapor diffusion coefficients (e.g., Jury et al., 1983 Sleep and Sykes, 1989). A summary of formulas for estimating soil diffusion coefficients and values calculated for many VOCs using the Millington-Quirk equation is given by Roy and Griffin (1990). In general, effective diffusion coefficients for VOCs are estimated at 0.1 to 0.4 m^2/day, depending on porosity variables, temperature, and compound.

---

[1] The terms "advection" and "convection" refer to movement due to bulk flow of a phase. Here, the term "advection" is used for bulk flow of the gas and NAPL phases and "convection" for bulk flow of the aqueous phase.

[2] Millington and Quirk (1961) reported the empirically derived formula for effective gas diffusion coefficients, D_{ge}, in unsaturated soil as:

$$D_{ge} = (a^{10/3}\phi^{-2})D_g^*$$

where a is the gas-filled porosity, ϕ is the total soil porosity, and D_g^* is the diffusion coefficient in air. The factors that compose the coefficient modifying D_g^* are often termed the "tortuosity" of the medium. It should be noted that the tortuosity varies with soil moisture content.

Use of the term “diffusion coefficient” varies among groups of researchers. Studies may define a lumped effective diffusion coefficient or unapparent diffusion coefficient to refer to the observation of a combined diffusion/retardation coefficient.

VAPOR ADVECTION

At the soil surface, gaseous advection due to changes in barometric pressure, temperature gradients, rainfall or irrigation, or wind are generally said to penetrates to depths of many centimeters. For example, a 2-mbar change in barometric pressure is estimated to cause air replacement to a depth of 8 cm in 12 h (Taylor and Ashcroft, 1972, p. 367). At the soil surface, temperature gradients will generally move vapors downward during the day and upward during the night, moving from warm to cold areas (Hillel, 1971, pg. 118).

The effect of barometric fluctuations below 1 m is generally small (Kreamer et al., 1988). Massmann and Farrier (1992), however examined situations in which the barometric fluctuations might be significant. They argued that some storm systems can produce barometric pressure changes of 20 to 30 mbar during a 24-h period and that these storm circumstances can occur several times a year or more, depending on the geographical location. Model calculations showed that “fresh air may migrate several meters into a highly permeable subsurface during such large barometric pressure cycles and the depth of penetration increases as the thickness and permeability of the vadose zone increase. Massmann and Farrier (1992) thus suggested that the concentration of gaseous VOCs may be lower when barometric pressures are high and that soil gas measurements will show the largest fluctuations during times of rapidly rising or falling barometric pressures. Their analysis, however, omitted the effects of soil water on gas permeability and on diffusion coefficients.

Falta et al. (1989) have suggested that gas phase advection may dominate the transport of VOCs that originate from a NAPL in soils of high permeability. As organic liquids that have high vapor pressures and low molecular weights evaporate, the density of the gas in contact with the liquid changes with respect to the ambient soil gas. This density contrast results in an advective gas flow. Organic hydrocarbons and solvents have vapor densities that are greater than air, so the resulting density-driven flows will be downward. Falta et al. (1989) cited the contamination of ground water beneath waste management facilities at Idaho National Engineering Laboratory (INEL) as a likely example of this phenomenon. At INEL, the water table is 177 m deep and yet carbon tetrachloride, present in the waste, has been found in the ground water. The magnitude of density-driven flows is a function of the saturated vapor pressure of the organic liquid, the gas-phase permeability, and the gas-phase retardation coefficient. Contaminants that are likely to be affected by density-driven flow include TCE, chloroform, l,1,1-trichloroethane, methylene chloride, 1,2-dichloroethene, l,2-dichloroethane, l,1-dichloroethane, carbon tetrachloride, Freon 113, and possibly benzene. Contaminants that are not likely to be affected by density-driven flow include toluene, ethylbenzene, xylene, chlorobenzene, naphthalene, and phenols (Falta et al., 1989).

AQUEOUS CONVECTION

Aqueous convection of VOCs refers to the movement of the VOCs dissolved in soil solution. Gravity flow predominates, but evapotranspiration moves water and dissolved species upward in the soil surface. Lappala and Thompson (1983) suggested that ground-water convection can also affect VOC movement. They postulated that the frequency and magnitude of ground-water level fluctuations may provide the driving force for moving ground-water contaminants into the vapor phase. If the capillary fringe is lowered into contaminated ground water, the previously clean capillary water becomes increasingly mixed with contaminated water during recurring fluctuations. VOCs can then volatilize into air-filled pores, thus establishing a vertical concentration gradient in the soil gas phase.

VOLATILIZATION-GASEOUS DIFFUSION AND AQUEOUS CONVECTION COMBINED

Volatilization refers to the gaseous loss of chemicals to the atmosphere from the soil surface. The potential volatility of a chemical is related to its inherent vapor pressure. Actual volatilization from soil depends on interphase transfers, movement to the soil surface, and vaporization into the atmosphere.

The rate at which a chemical moves away from the surface is controlled primarily by diffusion. There is relatively little air movement close to the soil surface consequently, a vaporized substance is transported from the soil surface through this stagnant air boundary layer only by molecular diffusion. The rate of movement away from the surface will be proportional to the diffusion coefficient and the vapor density of the chemical at the evaporating surface. Factors such as wind velocity and surface cover (plants) alter volatilization through their effect on the thickness of the stagnant air layer.

Jury et al. (1990) simulated volatilization of chemicals that resided in subsurface soils. They amended the input data for some of the chemicals with results reported in Jury et al. (1992). They calculated relative volatile losses for 35 organic chemicals placed in a 30-cm-thick layer 100 cm below a soil surface. Two uniform soil conditions were simulated in soils of sandy or clayey texture and (1) with no water evaporation or (2) at a low, steady 0.1 cm/day water evaporation rate. Results showed that when no water evaporation occurred, four compounds would lose more than 50% of the initial concentration by surface volatilization in the sandy soil over the first year. These four compounds were dichlorodifluoromethane, chloromethane, 1,1,1-trichloroethane, and bromoethane. Only dichlorodifluoromethane lost more than 50% by volatilization under analogous conditions in the clay soil. When water evaporation was simulated, seven chemicals underwent cumulative volatilization losses of 50% or more in 1 year in the sandy soil (including the four compounds listed above that exhibited >50% volatilization without water evaporation and TCE, ethylene dibromide, and dichloromethane). Again, only dichlorodifluoromethane volatilized 50% or more in the clay soil. Although there were no field data to validate these model results, the data imply that appreciable quantities of the most volatile compounds will escape readily from buried sources. Volatilization from the soil surface can be an important mechanism for the removal of the above-mentioned VOCs from the vadose zone.

FIELD STUDIES OF VOC FATE AND MOVEMENT

Field studies attempt to define rates of dissipation and movement of VOCs in soil. These studies generally measure the distribution pattern of VOCs and relate the results to prominent factors postulated to affect the dissipation and movement of soil VOCs The studies reviewed here have been termed either “field experiments” in which the researchers were able to control or had some *a priori* knowledge of the contamination event, or “field investigations” in which case the researchers were studying contamination without *a priori* knowledge of the characteristics of the contamination event. In general, the studies have assumed that VOCs move by vapor diffusion, tempered by the ability of the soil to transmit gas.

Field Experiments

Weeks et al. (1982) measured gaseous concentrations of two fluorocarbons (released to the atmosphere during the 40 years prior to this study) as deep as 44 m in unconsolidated sedimentary deposits in the Southern High Plains of Texas. They estimated lumped gaseous-diffusion coefficients for the combined effects of tortuosity, sorption, and solubility. Assuming that gaseous diffusion was the primary mechanism for transport of these highly refractory compounds, the lumped effective diffusion coefficients of 0.04 m^2/day and 0.09 m^2/day for fluorocarbons F-11 and F-12, respectively, occurred in the sediments as opposed to theoretical values of 0.78 m^2/day and 0.86 m^2/day in free air. Convective transport resulting from movement of air to fill the voids caused by a declining water table (estimated to have declined at 0.3 to 0.6 m/year since the early 1950s) was considered, but the contribution of convective transport was deemed small enough to be ignored.

In a similar study, Kreamer et al. (1988) used a fluorocarbon tracer, bromochlorodifluoromethane, to observe gaseous diffusion in a shallow (35 m) deposit of aeolian sand near Barnwell, South Carolina. The objective was to quantify the *in situ* gaseous tortuosity at the existing moisture content (a lumped gaseous-diffusion coefficient as in Weeks et al., 1982). Kreamer et al. (1988) performed independent measurements of the free-air diffusion coefficient of the tracer, air-water, and soil-water tracer distribution coefficients and of the soil porosity and moisture content in appropriate subsamples. A network of piezometers distributed radially and vertically from the buried tracer source was sampled and analyzed continuously for 3 days before the fluorocarbon source was introduced and for 7 days following the placement of the source. Kreamer et al. (1988) computed a “sorption-affected” porosity value with which to compare the field data because the field-measured concentrations are modified by soil-water and air-water partitioning. Variability in the data (attributed to analytical error) and uncertainties in the porosity and volumetric moisture content of the sand (only one undisturbed core was obtained) greatly weakened the study. The tortuosity of the geologic unit was determined to be about 0.4 (dimensionless) and the sorption-affected porosity was reported to be 0.22 (also dimensionless).

A study by Poulsen and Kueper (1992) iooked at the advective movement of a NAPL. The authors released tetrachloroethene to cleared areas 5 cm below the soil surface. A nonvolatile hydrophobic dye was mixed with the tetrachloroethene. Two 6-L releases were followed, one consisting of a slow drip (100 rein) over approximately l-cm^2 surface area, the other consisting of a rapid (90 s) ponded episode over approximately 1,000-cm^2 surface area. Excavation of each area began a day after the release. The distribution pattern of the dye was observed and a 2-mL piston subsampler was used to collect soil for tetrachloroethene analysis. The movement observed in the stratified sandy subsurface indicated that capillary forces dominated. Tetrachloroethene was distributed in distinct stringers occupying sand laminations separated by a few to several centimeters and characterized by subtle variations in texture, color, and grain size. The bedding in the upper 1.86 m dipped to the northeast and the slow-drip release closely followed the bedding. The ponded release produced a greater concentration of tetrachloroethene in the upper portion overriding the bedding in the upper 0.5m. The depths of migration were approximately 3.2 m for the slow release and 2.0 m for the rapid release. Average residual concentrations were 0.49% and 1.26% for the slow and rapid releases, respectively.

Field Investigations

The diffusion of TCE from contaminated ground water at a depth of approximately 42 m was measured by analysis of data on shallow (<2 m deep) soil gas (Marrin and Thompson, 1987). At a nearby unspecified distance, unlined solvent evaporation ponds had been used to dispose of halocarbon solvents from 1951 to 1977. In 1984, the gaseous TCE plume spanned 3 orders of magnitude (<0.001 to 2 µg/L) on a 0.5-km^2 area of adjacent property. Soil gas TCE values within a 10-m radius of each of five ground-water monitoring wells were shown to correlate with ground-water TCE concentrations. A limited number of vertical soil gas profiles showed that TCE concentrations generally increased with depth. Caliche zones did not affect TCE gas concentration gradients, but a sharp decrease in the concentration gradient occurred across clay lenses. Nearly saturated strata showed anomalously low TCE concentrations. Overall, the TCE diffused approximately 40 m in this arid environment in much less than 30 years, assuming that transport to ground water from the pond and subsequent lateral transport by ground-water flow would have required more time than the vertical gaseous diffusion.

Kuhlmeier and Sunderland (1985) reported on the distribution of petroleum hydrocarbons from leaking buried storage tanks at a site near Livermore, California. The leaks occurred over a period of 6 months and permeated approximately 24.4 m of unsaturated lacustrine and fluvial sediments before reaching ground water. Soil borings were sampled from a split-spoon sampler at 1.5-m intervals; stainless steel liners were covered with aluminum foil, sealed with duct tape, and placed on dry ice after sampling and during transport to a laboratory for subsequent analysis by SW-846 Method 8020 (volatile aromatics). Model predictions of the movement of benzene, toluene, and xylene (BTX) were compared with the laboratory data. Field data showed a marked increase of BTX in clay zones as compared to sandy units (e.g., 3,000 to 4,800 mg/kg BTX were found in a clay layer, overlying l,138 mg/kg in the sandy unit). This attenuation by clay indicates an increased adsorption coefficient in the finer textured deposits. It was also reported that organic carbon had no effect on sorption (total organic carbon varied between 0 [sic.] and 3%). Unexpectedly, little or no lateral dispersion of BTX was observed. This is particularly surprising in light of theory and numerous observations that horizontal flow occurs along the interface between coarse and fine lenses. Kuhlmeier and Sunderland (1985) suggested that the volume of gasoline released was large enough to create advective NAPL flow gradients.

Johnson and Perrott (1991) studied the vapor transport of gasoline in a soil that had a high water content. Soil vapor concentrations of butane, pentane, hexane, benzene, toluene, oxygen, methane, and carbon dioxide were measured periodically for a year at fixed sampling ports near some underground storage tanks in Portland, Oregon. Data indicated relatively constant gasoline-component concentrations at sampling points near the center of the vapor plume. Lower gasoline concentrations that increased during the year were detected a few meters away. The different components of gasoline vary in their physiochemical properties such that calculated retardation coefficients vary widely however, isoconcentration contours showed that the pattern and extent of contamination were very similar for all components. Environmental factors of barometric-pressure fluctuations and water-level fluctuations did not show significant effects on vapor concentrations. Vapor concentrations did appear to be directly affected by soil temperature. The soil temperature dropped approximately 10 °C during the winter and plots of winter vapor concentrations with time showed a decrease; the curve shape was similar to that of the temperature curve. In contrast to vapor movement around tanks that are placed in engineered backfills (e.g., pea gravel), vapor movement in high-water content soils is very slow. Model predictions estimated that less than 1% of the source concentration of a nonsorbing compound (unit retardation factor) would travel 7 m after 8 years. Methane, resulting from anaerobic degradation, was a good indicator of the contaminated zone. However, the slow diffusion in this soil and general persistence of gasoline components led the authors to conclude that once the vapors entered the soil, future leak detection using vapor sampling may not be possible.

Smith et al. (1990) presented data on soil gas TCE concentrations, TCE-water vapor sorption isotherms, and concentrations of TCE sorbed by soil at a site above a contaminated aquifer at Picatinny Arsenal in New Jersey. TCE-containing wastewater had been discharged into lagoons and into a nearby unlined, overflow dry well from 1960 to 1981. Soil gas data closely paralleled changes in the concentration of TCE in the shallow ground water. Temporal effects in vertical gas concentration profiles were influenced by the ground-water temperature.

Increased ground-water temperatures in July and October (as opposed to the temperatures in December and February) generally resulted in increased concentrations of TCE in the soil gas.

SUMMARY OF VOC MOVEMENT

Movement of VOCs in soil results from diffusion and advection. Diffusion is driven by concentration gradients. Advection can be driven by pressure, density, gravity, or thermal gradients. Gaseous molecular diffusion coefficients exceed those of liquid coefficients by 4 to 5 orders of magnitude and therefore, gaseous diffusion will dominate over liquid diffusion (Sleep and Sykes, 1989). Density-driven NAPL advection is estimated to dominate VOC movement in highly permeable soils when the NAPL source is present in excess of the soil residual saturation level and the NAPL relative vapor density is greater than that of air (Falta et al., 1989). When present, large-scale heterogeneities-such as bedding, textural discontinuities, structural changes, anthropogenic materials and other debris, channels, cracks, and fissures-can create distinct flow paths for liquid and gaseous movement (Falta et al, 1989; Kreamer et al., 1988; Poulsen and Kueper, 1992).

Gaseous diffusion measured *in situ* was assumed to have prompted the movement of two fluorocarbons in deep deposits in Texas (Weeks et al., 1982). The fluorocarbons were found to have moved 44 m in approximately 40 years. Movement of TCE upward through a deep deposit in Arizona, presumed to be diffusing from contaminated ground water at approximately 42 m, was observed at a depth of 2 m (Marrin and Thompson, 1987). The diffusion time was shorter than that in Texas, less than 30 years, in response to a greater concentration gradient. In Oregon, which has a more humid environment, and in a soil said to be of high moisture content, gaseous diffusion of gasoline components was estimated at approximately 7 m lateral in 8 years (Johnson and Perrott, 1991). The appearance of carbon tetrachloride in ground water at 177 m suggests a mechanism other than diffusion moving the VOC at a site in Idaho (Falta et al., 1989).

Calculations based on physiochemical properties of soils and NAPLs and on environmental parameters have demonstrated the possible importance of gas advection in VOC movement. First, large barometric pressure fluctuations can cause air to migrate several meters in a highly permeable soil. This movement may be reflected in soil gas measurements read before and after large storms pass (Massmann and Farrier, 1992). Second, gas advection can be driven by density gradients By examining the saturated vapor pressure and sorption coefficients (K_{oc}) of many VOCs as well as their soil permeability characteristics, Falta et al.

(1989) showed that density-driven gaseous advection could dominate flow of many organic solvents, including TCE, chloroform, 1,1,1-trichloroethane, methylene chloride, l,2-dichloroethene, 1,2-dichloroethane, 1,1-dichloroethane, carbon tetrachloride, Freon 113, and possibly benzene. Contaminants that are not likely to be affected by density-driven flow include toluene, ethylbenzene, xylene, chlorobenzene, naphthalene, and phenols (Falta et al., 1989).

Field studies have shown that NAPL advection is sensitive to small variations in soil permeability and capillary characteristics (Poulsen and Kueper, 1992). The migration pattern of tetrachloroethene followed subtle changes in bedding of a stratified sand deposit. Characteristics of source release also affected the NAPL migration. Tetrachloroethene was observed to migrate deeper and retain a smaller residual fraction when applied slowly over a small soil area as opposed to a rapid application over a large soil area. Kuhlmeier and Sunderland (1985) observed deep vertical movement (24.4 m) of BTX with almost no lateral spread, even though textural discontinuities were present in the lacustrine and fluvial deposits. They postulated that rapid leaks of underground storage tanks caused the strongly vertical movement by NAPL advection.

SECTION 5

MODELING THE MOVEMENT OF SOIL VOCS

Modeling VOC vapor transport in unsaturated soil is a recent phenomenon for environmental scientists (primarily put forth by civil engineers, soil physicists, and hydrologists). Early research on soil gases, such as radon, oxygen, carbon dioxide, and pesticides, although basic to the recent surge of interest, did not involve extensive modeling and did not address factors peculiar to VOCs such as the nonaqueous-phase liquids characteristic of petroleum spills or vapor-density gradients arising from dense organic solvents. Multiphase, multicomponent flow models exist in petroleum engineering, however, and this knowledge has been recognized and used to formulate environmental applications (Pinder and Abriola, 1986). Much of the current environmental interest follows the advent of “soil venting” or “vapor extraction” as a means of remediating vadose zone contamination.

Table 3 compares some characteristics of 14 models that are entirely or partly designed to simulate VOC movement in soil or porous media. The models selected are representative of the major features and processes that researchers incorporate in soil-VOC models. The list includes some relatively simple screening/ management models (Jury et al., 1983; Silka, 1988; Falta, et al., l989; Shoemaker et al., 1990), laboratory soil-column descriptions of vapor movement (Gierke et al., 1990; Gierke et al., 1992; Brusseau, 1991), one field-scale description accompanied by field data (Metcalfe and Farquhar, 1987), and many field-scale models that define theory and evaluate model approaches to VOC movement in porous media (Abriola and Pinder, 1985; Corapcioglu and Baehr, 1987; Sleep and Sykes, 1989; Mendoza and McAlary, 1990; Katyal et al., 1991; Massmann and Farrier, 1992). All of the models embrace vapor diffusion and most of the models incorporate aqueous-vapor partitioning.

The purpose of this discussion is to draw attention to the intent and extent of these models, to indicate directions under development, and to outline some of the knowledge gained from this form of analysis. The models are discussed in three subsections screening/management models, laboratory soil column simulations, and field-scale simulations.

TABLE 3. COMPARATIVE FEATURES OF SOME VAPOR-TRANSPORT MODELS

Model Features	Jury et al., 1983	Abriola & Pinder, 1985	Corapcioglu & Baehr, 1987	Metcalfe & Farquhar, 1987	Silka, 1988	Falta et al., 1989	Sleep & Skyes, 1989
Dimensions	1	1	1	2	2	2	2
Aqueous-vapor distribution	x	x	x		x	x	x
Solid-aqueous distribution	x		x		x	x	
Vapor-solid distribution							
Degradation	x		x				
Vapor diffusion	x		x	x		x	x
Vapor advection (P=pressure, D=density)				P		D	P,D
Water flow (S=steady state, T=transient)	S	T	S				T
Immiscible phase (S=sink/source term, F=flow)		S,F	S,F			S	S
Sorption nonequilibrium							
Physical nonequilibrium							x
Multicomponent equation set							
Application (S=screening/management, L=laboratory soil column, F=field reseach)	S	F	F	F	S	S	F

(continued)

TABLE 3. (continued)

Model Features	Gierke et al., 1990	Mendoza & McAlary, 1990	Shoemaker et al., 1990	Brusseau, 1991	Katyal et al., 1991	Gierke et al., 1992	Massmann & Farrier, 1992
Dimensions	1	2	1,2	1	2	1	12
Aqueous-vapor distribution	x	x	x	x	x	x	
Solid-aqueous distribution	x	x	x	x	x	x	
Vapor-solid distribution			x			X	
Degradation			x		x		
Vapor diffusion	x	x	x	x	x	x	x
Vapor advection (P=pressure, D=density)	P	D		P	P,D	P	P
Water flow (S=steady state, T=transient)	S		S		T		
Immiscible phase (S=sink/source term, F=flow)					S,F		
Sorption nonequilibrium				x			
Physical nonequilibrium	x			x	x	x	
Multicomponent equation set					x		x
Application (S=screening/management, L=laboratory soil column, F=field research)	L	F	S	L	F	L	F

* Model can accomodate vapor sorption if certain parameters are redefined.

SCREENING/MANAGEMENT MODELS

Jury et al. (1983) described a model designed for comparing the soil behavior of new and existing organic chemicals. Although the model was presented almost 10 years ago, the simplified approach with direct analytical solutions to equations has bestowed the status of a “back-of-the-notebook” calculation for some of the equations. The model assumes linear equilibrium distributions between vapor, liquid, and adsorbed chemical, net first-order degradation rates, steady-state upward or downward water flow, volatilization from the soil surface through a stagnant air boundary layer, and homogeneous soil properties, all defined by user input variables. Experimental evidence demonstrated that the model correctly predicted the relative volatilization loss of five pesticides that were exposed to identical conditions in the laboratory (Jury et al., 1984). The simulation of surface volatilization of buried sources of VOCs was reported by Jury et al. (1990) and discussed earlier in this report.

Silka (1988) developed a simple, two-dimensional vapor transport model as a tool for interpreting soil-gas surveys. The model extends the total concentration equations of Jury et al. (1983) to two dimensions, but omits the equations for water movement and neglects biodegradation. As with many models, field experimentation lags behind model development and no test of this model was presented. Model runs demonstrated the importance of soil water to the design and results of soil-gas surveys.

Falta et al. (1989) explored the simulated effect of gas-density gradients in unsaturated porous media. Using thermodynamic properties of the compounds and estimates of retardation by sorption, they screened 14 common ground-water contaminants for the relative impact of density-driven flow as a function of media permeability. Results showed the contaminants that were most likely to be influenced by density-driven flow (reviewed previously in this report) and that density-driven flow will be significant only if the permeability of the medium is at least 10^{-11} m^2.

Shoemaker et al. (1990) presented a screening model that encompasses vapor sorption whenever soil moisture is dry enough for this process to occur. They developed one- and two-dimensional solutions to the analytical model of Jury et al. (1983). An “effective” or “two-phase” sorption coefficient is defined as the sum of the solid-aqueous sorption coefficient and the vapor-solid coefficient. The vapor-solid sorption is dependent on the soil water content, but the data currently are limited to a few laboratory studies for a few soils and soil-like materials. The authors concluded that effects of vapor-phase sorption are greatest in soils of high surface area that has an accompanying low water content. For soils that have high water contents or low specific surface area, liquid-phase sorption models would be adequate (quantification of these concepts was not provided). Shoemaker et al. (1990) suggest that sorption be measured under field conditions to determine the influence of vapor-phase sorption *in situ.*

LABORATORY SOIL COLUMN SIMULATIONS

In the screening models, all interphase transfer processes are facilitated by assuming equilibrium with respect to interphase partitioning. Although these assumptions simplify the transport analysis, they are rarely valid, and the consequences of these assumptions are likely to be magnified in descriptions of long-term or large-scale (field) transport phenomena. Asymmetrical breakthrough curves representing laboratory soil column results provide evidence that the supposition of equilibrium sorption is not generally valid (Brusseau and Rao, 1989). Any of the interphase transfers that VOCs undergo (e.g., air-water, NAPL-water, water-solid) may be rate-limited or exist out of equilibrium in soil. Laboratory soil columns can be employed to estimate the effectiveness of techniques for describing transport of VOCs in porous media.

Harmon et al. (1989) reviewed the modeling approaches for dealing with nonequilibrium transport phenomena. They provided a concise summary of chemical and physical nonequilibrium model approaches. Chemical nonequilibrium models are generally two-site models. Sorption is described as rapidly reversible for some fraction of sorption sites (the local equilibrium assumption) and characterized by slow resorption kinetics for the remaining fraction of sorption sites. The fraction of sites in each category and kinetic rate constants for forward and reverse sorption are required input parameters. Physical nonequilibrium models are generally based on a two-zone description of soil water (mobile/immobile) with a mass transfer coefficient between the two zones. Diffusion-based physical models assume that rapid chemical sorption occurs in the mobile water and that kinetically limited sorption occurs in immobile regions. The transfer of water or contaminant between these regions is modeled either by Fick's second law of diffusion (a second-order differential equation taking the geometry of the immobile region into account) or, more simply, by assuming a first-order rate transfer equation.

Gierke et al. (1990) developed a model to study the relative contributions of gas and water advection, gas and water dispersion, mass transfer resistance, diffusion in immobile water, sorption, and volatilization on the spreading and retardation of VOC breakthrough in soil columns. They found the rates of mass transfer across the air-water and the mobile-immobile water interfaces to be fast (mass transfer rates across the air-water interface and mobile-immobile interface were 4.8 and 660 times the transport rate by advection in mobile water, respectively) Both liquid dispersion and diffusion in immobile water were important for describing TCE transport. Vapor dispersion was lower than predicted by a factor of 10, and vapor diffusion was not an important transport mechanism for TCE when the average pore water velocities were greater than about 0.07 cm s^{-1} in sand, or greater than about 0.02 cm s^{-1} in aggregated porous "soil material" (a fired clay used as an industrial insulator). Henry's Law constant for TCE was almost twice as large as values in the literature and the authors surmise that sorption onto packing and column materials produced this artifact.

Gierke et al. (1992) redesigned their experimental conditions to distinguish between the impacts of different physical nonequilibrium mechanisms on organic vapor transport. Gas flow rates were varied to simulate soil venting, and both granular and aggregated soils were fabricated (as in previous work) under moist and dry conditions with toluene as the test compound. The authors reevaluated some of their conclusions from Gierke et al. (1990) and concluded that fingered or preferential flow could explain the large liquid dispersion coefficients observed in that study. Under dry conditions, toluene vapor transport in the granular and aggregated "soil material" was affected only by gas advection, gas diffusion in the mobile gas region, and vapor sorption. Gas-water mass-transfer was never important. Nonequilibrium effects were observed in columns that consisted of moist, uniformly sized fired-clay aggregate the effects were attributed to intraaggregate diffusion in immobile water. The toluene breakthrough for moist aggregated material took eight times longer than for moist sand, an effect explained by the higher moisture content of the aggregated material and the impact of intraaggregate diffusion.

Brusseau (1991) developed a model that accounts for both physical and chemical nonequilibrium processes under forced gas advection and an immobile liquid phase. The model used mass transfer coefficients for water-solid, air-water, and mobile-immobile water. Brusseau tested the model using data from the literature, including the data of Gierke et al. (1992). Values for all parameters, independent of curve fitting, were obtained by a variety of estimation techniques. Model predictions for each data set were shown to fit soil column breakthrough curves better than when the local equilibrium concept was employed.

FIELD-SCALE SIMULATIONS

The models discussed so far have simplified water flow, which, if incorporated, is modeled as steady-state flow. In moist or fine-textured media, VOC dissolution and transport in water are probably significant and must be included if the model is intended to estimate actual field concentrations. Simplified representations, such as those discussed above, have limited, specific conditions of application and thus reduce the model complexity. Field-scale research models may also possess limited application, e.g., Metcalfe and Farquhar (1987) and Massmann and Farrier (1992) both depict vapor transport over short periods of time. The more comprehensive field models that attempt to portray long-term transport in a heterogeneous porous medium have exceeded our ability to obtain experimental data. Both input and output data are extensive in these models. The complex models are not designed to be used as general field tools, but to further our understanding of processes and computing capabilities. Such models are often verified numerically that is, the validity of the numeric computer code solution is tested against a simplified version of the model that can be solved analytically. Lack of data, however, precludes determining the validity of the model as a tool for describing VOC transport in soil.

Abriola and Pinder (1985) began developing a model to depict the multiphase (solute, gas, and NAPL) migration of a petroleum spill in porous media. They presented equations governed by mass conservation principles and volume averaging theory to describe a contaminant composed of two distinct components, one of which may be volatile and slightly water soluble and the other which is both nonvolatile and insoluble in water. Pinder and Abriola (1986) suggested that three assumptions incorporated into their model are undergoing scrutiny (1) the use of Darcy’s Law to represent the convective flux of a fluid phase (neglects hysteresis effects and the observation of preferential migration pathways), (2) the supposition of immobile air (no vapor advection), and (3) the use of equilibrium partitioning.

Corapcioglu and Baehr (1987) devised a model for describing surface petroleum spills that could be extended to include any number of reactive constituents (such as BTX). The model utilizes mass conservation of oxygen as the limiting factor (upper boundary) in the microbial degradation of petroleum hydrocarbons. The general model can be divided into two subproblems to describe an oil spill: (1) oil plume establishment in the unsaturated zone, and (2) solute and vapor transport subsequent to immiscible plume establishment.

To describe the pressure variation created during gas venting by a vacuum withdrawal system, gaseous advection must be modeled in addition to gaseous diffusion. Metcalfe and Farquhar (1987) use the equations for hydrodynamic dispersion in porous media, as outlined in Bear (1979), to depict gaseous advection/dispersion. Metcalfe and Farquhar (1987), rather than use mass conservation equations, based their equations on molar quantities as a way to handle the obvious density differences between air and VOCs (in this instance, methane). They produced a conservative, two-dimensional model for vapor movement in the unsaturated zone. The model was tested by simulating methane migration from a landfill in Ontario over summer and winter boundary conditions (assuming impermeable frozen soil during the winter). Using measured gas concentrations as initial conditions, subsequent data (generally 1 month later) were simulated by the model. The actual field data were spatially far more variable than the model predictions, but model results were generally within 50% of observed values.

Sleep and Sykes (1989) borrowed the concept of mass transfer approximation from chemical engineering to represent nonequilibrium interphase transfers in a field-scale model. Empirically determined mass-transfer coefficients are employed to express the driving force between equilibrium and actual concentrations. Mass transfer coefficients for air-water, NAPL-air, and NAPL-water are incorporated in their model, although sorption is neglected. Model results simulating the movement of a buried TCE source provided qualitative evidence for the importance of the mass transfer coefficients. The model could not be verified because comparable field data do not exist.

Mendoza and McAlary (1990) and Mendoza and Frind (1990) employed a radial coordinate system, density-driven flow, and equilibrium sorption estimates in a model designed to simulate VOC gas transport over a few weeks. They investigated the effect of surface boundary conditions and found that an impermeable cover over the ground surface will increase the lateral migration of the vapor plume. A permeable ground surface that allows natural venting of gases will reduce the lateral extent of the vapor plume. Diffusion is the dominant vapor transport mechanism for TCE in a deposit with a permeability of medium sand. Density-driven vapor advection becomes important in coarse sands or gravels for compounds with high vapor pressures and high molecular weights.

An EPA-sponsored model to simulate the two-dimensional flow and transport of three fluid phases (water, NAPL, and gas) has been generated by Katyal et al. (1991). The model allows the user to analyze flow only or coupled flow and contaminant transport. It can be used to analyze the two-phase flow of water and NAPL, or three-phase flow of water, NAPL, and gas at variable pressure. Transport of as many as five components can be described, assuming either local equilibrium mass transfer or first-order, kinetically controlled mass transfer. Required inputs are extensive, encompassing the air-water capillary retention function, NAPL surface tension and interracial tension with water, NAPL viscosity, maximum residual NAPL saturation, soil hydraulic conductivity, component densities, mass transfer coefficients, and boundary condition data. Methods for estimation of certain parameters are included. Resulting outputs are equally extensive, including saturations, velocities, and concentrations for each phase at every node at specified intervals. The computing is rendered more efficient by incorporating time-lagged interphase mass-transfer rates and phase densities.

Massmann and Farrier (1992) have argued (as have others, including Brusseau [1991] and Thorstenson and Pollock [1989]) that the validity of the classical single-component advection-diffusion equation to describe vapor transport should be bracketed by the material permeability and the total pressure gradient. They evaluated the limits of the single-component advection-diffusion equation through a set of fully coupled multicomponent equations. They concluded that the advection-diffusion equation is adequate if media permeabilities are greater than about 10^{-10} cm^2. The equation significantly overestimates gas fluxes for low-permeability materials, becoming egregious for permeabilities of 10^{-12} to 10^{-13} cm^2. Large atmospheric barometric pressure fluctuations can occur that create significant subsurface gas pressure gradients and thus affect vapor movement. These conditions may cause horizontal pressure gradients in heterogeneous soil, depending on site geometry, material properties and the amplitude and period of the barometric fluctuations. Massmann and Farrier (1992) did not address the effects of gas density and soil water in their analysis.

SUMMARY OF MODELS

Mathematical modeling of soil-VOC movement has many objectives and various strategies for meeting those objectives. Models have been developed to screen for differences among compounds or to serve as management tools, such as to guide the interpretation of soil gas surveys. Research on heterogeneous flow domains, or transport-related nonequilibrium, is partly pursued by use of laboratory soil columns and models to describe observations. Field-scale simulations to describe flow and transport of contaminants created by spills of immiscible solvents or petroleum, can expand our understanding of theory and our computing skills. Research models are incorporating much more than the traditional homogeneous soil, equilibrium sorption, single contaminant, and isobaric conditions that characterized earlier model efforts. Modeling research, however, runs far ahead of the field data needed to calibrate and validate existing models. Accurate quantitation of soil VOCs is crucial to model validation.

SECTION 6

OBTAINING AND MAINTAINING VOC SAMPLES

Quantification and control of potential errors arising during sample collection, handling, preparation, storage, and analysis are recognized as critical for meeting data quality objectives of environmental samples (van Ee et al., 1990). Specified procedures for obtaining soil VOC for analysis by SW-846 Methods 8240/8260 are minimal. For soil VOCs the need to standardize sampling procedures has been recognized, but the methods for studying soil volatiles under controlled conditions to verify sampling improvements have been troublesome. Issues of bulk sample acquisition including recommendations for soil sampling devices and subsampling techniques have been raised and reviewed by Lewis et al. (1991) Volatile losses have been seen to contribute negative bias throughout each period that the soil is exposed to air. Sampling and subsampling methods are driven by the need to minimize exposed soil surface area, time of exposure, and soil disaggregation to reduce negative sample bias (Lewis et al., 1991). Although the natural or man-made variability that typify soils affects soil sampling for other analytes as well, homogenization and observation techniques to manage variability (e.g., mixing, compositing, and visual inspection of soil samples) are drastically reduced in VOC sampling. Abbreviated sampling procedures exacerbate the problem of securing representative samples for VOC analysis and certainly contribute to the large variability reported for field soil-VOC concentrations (Hewitt et al., 1992, Mitchell, et al., 1993).

This section first describes the general procedures used for VOC sampling. Studies related to sampling methods are then discussed, separated into laboratory and field investigations. Studies emphasizing the storage and preservation of soil-VOC samples are presented in a separate subsection. Finally, a summary of sampling and preservation results is provided.

CURRENT SAMPLING METHODS

Soil samples for VOC analysis are obtained by coring, augering, or scooping devices. Coring is generally preferred because it disturbs the sample least. Lewis et al. (1991) provide a detailed discussion of sampling devices for obtaining soils for analysis of VOCs.

The suggested container for the initial soil sample is a 125-mL wide-mouth jar (SW-846 Method 8240), but the choice of sample containers is often determined by site characteristics and the intended purpose of the sampling effort (Lewis et al., 1991). Either 40-mL volatile organics analysis (VOA) vials are used, or wide-mouth bottles (125-, 250-, or 500-mL) with Teflon-lined, foam-backed lids are used. Soil typically fills the container, leaving as little headspace as practicable. Another option is to collect 1- to 5-g soil samples in the field and place these into 40-mL VOA vials. These can be capped in the field with a lid that can be connected directly to a purge-and-trap sparger (Lewis et al., 1991). Alternatively, brass core liners are capped and sealed in the field.

When transferring soil from a coring device to a wide-mouth bottle or vial, the sampler's objectives are minimum disturbance to the sample and shortest possible transfer time. Depending on the diameter of the soil core and the diameter of the jar, soil can be extruded directly into the jar if the sample is fairly cohesive, or subsampled with a subcorer. Plunger/barrel-style subcoring devices (10-mL plastic syringes with the needle end cut off) are suggested for collecting and extruding approximately 5 g of soil into a 40-mL VOA vial (Lewis et al., 1991) Procedures that include soil compositing and mixing, either in the field or with cold (4 °C) procedures in the laboratory, have not been specifically excluded, although mixing procedures are known to create large losses of analyte.

The final subsampling and transfer steps are performed by personnel at an analytical laboratory (excluding the 1- to 5-g samples placed in VOA vials in the field). The standard procedure is to empty samples into an aluminum pan, briefly "homogenize," and remove an aliquot into a sparging vessel for PT analysis. SW-846 Method 8240 requires a l-g (wet weight) aliquot for analyte concentrations expected in the 0.1 to 1.0 mg/kg range and a 5-g (wet weight) aliquot if concentrations less than 0.1 mg/kg are expected. Recognizing the losses associated with the subsampling step, SW-846 Method 5035 ("Determination of Volatile Organic Compounds in Soils Using Equilibrium Headspace Analysis and Capillary Column Gas Chromatography/Mass Spectrometry;" to be included in the Third Update to SW-846) dictates the use of a soil sampler which delivers 5 g of soil to a 40-mL VOA vial. The balance between sample representativeness (which would prescribe ample homogenization) and preservation of volatile analytes is increasingly disposed to sample preservation.

Described above are EPA procedures. The American Society for Testing and Materials (ASTM) has independently voted acceptance of procedures for sampling solid wastes; D 4547-91, "Standard Practice for Sampling Waste and Soils for Volatile Organics" (ASTM, 1991). The ASTM D 4547-91 procedures encompass two methods of sampling loose granular materials and three methods to handle the sample once it is collected. These procedures include (1) collecting a sample in a metal ring and shipping the entire soil/ring sample to a laboratory, (2) subsampling with a metal coring cylinder and placing the subsample in methanol, and (3) subsampling as in (2) but placing the sample into a VOA vial that is capped with a lid modified for direct connection to a PT sparger.

LABORATORY SAMPLING STUDIES

Opening of a vial or jar to take a subsample has been shown by many researchers to cause large losses of VOCs. Amin and Narang (1985) showed that chilled [sic.] clay that was spiked and mixed for 15 to 30 s on an ice-cold surface had losses ranging from 7% for carbon tetrachloride to 36% for 1,1,2,2-tetrachloroethane. Unchilled soil that was transferred from one sample tube to another showed losses ranging from 14% to 53% (Amin and Narang, 1985). Maskarinec et al. (1988) estimated an average 60% volatilization loss of VOCs during sample transfer steps; this estimate was determined by comparing a pour, mix, and subsample procedure with sample placed directly into vials that have lids which can be attached to a PT sparger. Zarrabi et al. (1991) showed analyte losses of 20% to 80% from the subsampling step, again using the modified-lid vials.

Siegrist and Jenssen (1990) have evaluated the effects of sample disturbance, container headspace, and sample transfer steps on VOC measurements. Six VOCs in aqueous solution were added to soil by saturated upward flow (15 pore volumes) through a column of soil. The column was "desaturated under suction for less than an hour. Subsequently, the column was sealed and stored overnight at 10 °C prior to sampling. The sampling procedure consisted of concurrently inserting 10 stainless-steel sampling tubes, each 10 cm long with an aluminum-foil-covered top, into the soil column through a sampling template. These tubes were removed sequentially and placed into five container treatments. The procedure was repeated, thus providing duplicates of the five container treatments. Undisturbed samples were extruded directly into containers and disturbed samples were generated by removing soil from the cores in 7 to 10 aliquots during the transfer step. Disturbed samples were placed in jars or freezer bags that had little headspace, but these treatments gave poor recoveries of VOCs Undisturbed samples that had little container headspace gave better recoveries than those that had large container headspace.

Core extrusion into methanol yielded the highest VOC concentrations (Siegrist and Jenssen, 1990). Improvement in VOC recovery that was attributed to methanol preservation was 81% for TCE and approximately 10% for chlorobenzene. VOC recoveries in the methanol treatment were 28 to 83% less than the predicted concentrations based on calculated soil sorption estimates. The highly volatile methylene chloride showed extremely high replicate variability and no significant effect due to any treatment. The study did not use a PT preparation step in the analysis it employed solvent extraction that was modified for the methanol treatment.

Use of methanol as a vapor trap and as an extractant for alkylbenzenes (ethylbenzene, toluene, and p-xylene) from oven-dry soil is described by Rhue et al. (1988). This study compared the efficiency of methanol for trapping ethylbenzene vapors with that of activated charcoal. Agreement between the two methods at relative vapor pressures of 0.09 to 0.31 was quite good (methanol trapped 97% of the amount trapped by activated charcoal). Rhue et al. (1988) then compared the measurement of vapor-adsorbed alkylbenzenes by soils and clays using a gravimetric method and methanol extracts. Gravimetric measurement has been used by many researchers (e.g., Chiou and Shoup, 1985; Ong and Lion, 1991a), but Rhue et al. (1988) preferred measuring vapor adsorption by methanol extraction of the solids (allowing them to analyze either vapor or sorbed concentrations by UV-Vis spectrophotometer or high pressure liquid chromatography). Methanol extraction and gravimetric measurements of alkylbenzene vapor adsorption were in good agreement (differences averaged less than 10%) for bentonite, kaolin, and a sandy aquifer sample.

A vapor fortification method to spike dry soil with VOCs has been described by Jenkins and Schumacher (1987) and has been further developed by Hewitt et al. (1992) and Hewitt (1993). Reproducible soil-VOC contamination is achieved in dry soil subsamples (1 to 2 g subsamples) by exposing soil to a vapor mixture of VOCs in a closed desiccator. Relative standard deviations (RSD) of less than 9% were observed for TCE, benzene, and toluene, and the RSD for trans-1,2-dichloroethene was 14 to 23% (Hewitt et al., 1992). Maximum concentrations of soil VOCs are achieved after 4 to 5 days of exposure (Hewitt, 1993). Dry spiked soil can then be sealed in glass ampules (Hewitt, 1993) or capped in 40-mL vials with a modified lid that is attached directly to the PT sparger (Hewitt et al., 1992). Soil concentrations of the spiked, dry soil remain constant for at least 14 days. The ampulated soil samples are suggested as blind performance evaluation materials and are also useful in studies of sampling and analytical methods.

FIELD SAMPLING STUDIES

Urban et al. (1989) recognized the potential for VOC losses during transportation and storage from jars that may not seal well and the potential for VOC losses during laboratory sample preparation. They compared data from samples that were immersed in methanol in the field and analyzed by the medium-level method (for samples containing contaminants at greater than 1 µg/g) with data from samples that were analyzed by the standard, low-level soil method specific in the EPA Contract Laboratory Program (CLP) Statement of Work (SOW, 7/87). Samples known to be contaminated with seven chlorinated solvents were obtained with a split-spoon sampler. Material was added to fill either an empty 40-mL vial or a preweighed 500-mL wide-mouth jar that contained 250 mL of methanol and a mixture of three surrogate compounds. Results showed excellent recoveries of surrogate compounds in the methanol-preserved samples. The samples preserved in methanol always had greater concentrations of each VOC than the corresponding 40-mL vial samples. For example, the results showed 2 to 50 times more TCE and 15 to 100 times more l,l,-dichloroethene in the methanol-immersed samples than in the corresponding 40-mL vial samples. A systematic bias was introduced by the protocol of collecting the methanol sample before the conventional sample in this study. The results, however, have been confirmed in other field investigations (Hewitt, 1992; J. Smith, personal communication).

Conventional sample collection and analysis were compared with limited disruption sampling and a field headspace method in a study by Hewitt (1992). For the conventional sample, a 40-mL VOA vial was filled with soil, shipped and stored at 4 °C, subsampled in the laboratory, and analyzed by PT/GC/MS within 14 days of collection. The limited disruptive method consisted of taking a subsample with a subcoring device in the field, placing it in either an empty vial that had a lid modified for direct attachment to a sparger or a vial containing methanol, and analyzing the sample by PT/GC/MS within 14 days of collection. (A hand-held VOC Photo Vac probe was used to determine whether the sample concentration was “low” or “high” and thus to be analyzed by the low-level or the high-level procedure.) The field method involved placing a subsample in a vial containing 30 mL of water the air above the soil/water was analyzed by direct injection in a GC within 2 days of collection. Results are shown in Figure 3. Log-log plots of collocated samples showed 1 to 2 orders of magnitude more TCE measured by the limited disruptive method as compared with conventional sample collection and analysis (Figure 3a). The headspace analysis and limited disruptive method gave very similar results (Figure 3b). Collocated headspace measurements were 1 to 3 orders of magnitude greater than measurements by the conventional procedures

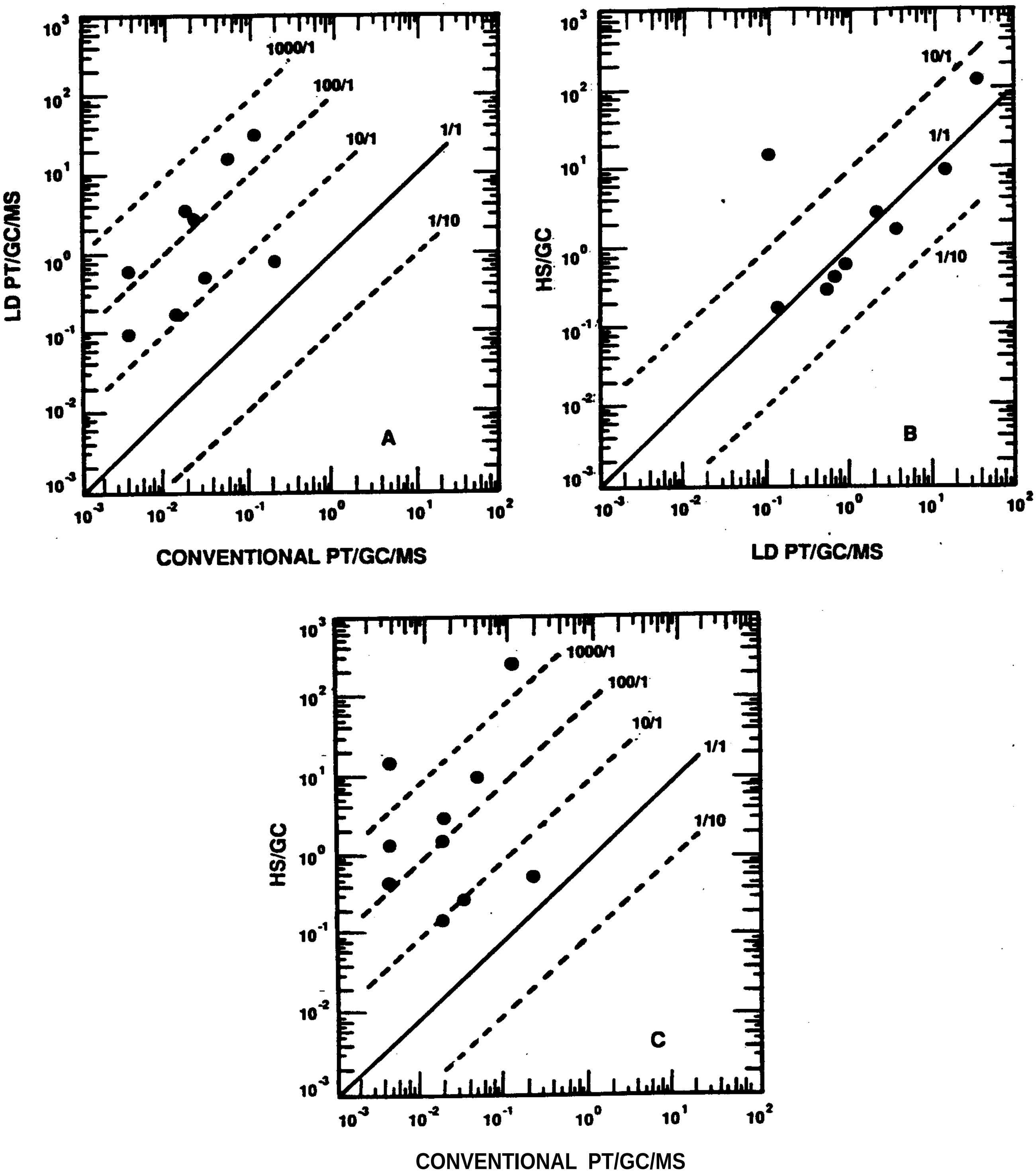

Figure 3. Collocated soil samples analyzed by conventional PT/GC/MS, limited disruption (LD) PT/GC/MS, and headspace (HS) GC. Soil concentrations in mg TCE/Kg soil (after Hewitt, 1992).

(Figure 3c). To determine whether degradation of TCE could be responsible for the discrepancies, seven headspace samples were set aside, stored inverted (soil on Teflon-lined septa) at room temperature, and monitored by repeated readings for 21 to 25 days. Little or no decrease in the TCE concentrations was observed. Loss of analyte during the sample transfer step (shown by Jenkins and Schumacher, 1987; Maskarinec et al., 1988; Siegrist and Jenssen, 1990) and throughout the storage time in the vial prior to conventional analysis are implicated in this study.

Three sampling procedures for TCE-contaminated soil were investigated by Slater et al. (1983). (1) Two subsamples (approximately 5 g each) were taken from the ends of freshly collected soil cores and placed in three successive plastic freezer bags. After cold storage, the soil was transferred to 5 mL of methanol. An aliquot of the methanol was subsequently analyzed by PT/GC with a Hall detector. (2) Brass !iners, with four sampling ports drilled into the sides and covered with Teflon tape, were capped with rubber, placed in freezer bags, and stored cold until analysis. Four subsamples were removed in the laboratory, placed in methanol, and analyzed as in Treatment 1. (3) Entire 15 x 2.5 cm soil cores were slid into glass jars, sealed, placed in three successive plastic freezer bags, and stored cold until analysis. The analysis consisted of a 20-h heated nitrogen purge of the entire jar and a charcoal trap collection of VOCs, followed by carbon disulfide extraction of the charcoal, then by gas chromatographic analysis of the extract. Treatments 1 and 2 were not adequately sealed, and TCE was detected in the plastic bags prior to soil analyses. Treatment 3 also had samples that were not properly sealed, although the concentrations in the plastic bags were less than occurred for treatments 1 and 2 Treatment 3 showed TCE levels 1 to 2 orders of magnitude greater than neighboring samples in the other two treatments (statistically significant at the 5% level). Coefficients of variation ranging from 0 to 190% were found on replicate subsamples by the first two treatments. (No coefficient of variation could be reported where the entire 800-g sample was analyzed in Treatment 3.) Slater et al. (1983) concluded that the differences in TCE concentrations resulted from natural soil heterogeneity. Variability in the 5-g samples resulted in a statistical analysis which concluded that eleven 5-g samples would have to be analyzed from a single 15 x 2.5-cm core section to be 60% confident that the estimated value for TCE was within 100 mg/kg of the true value.

The effect of sample size on soil-VOC concentrations, noted by Slater et al. (1983) above has been mentioned by other researchers as well. Bone (1988) suggested that sample size influenced results of VOC sediment samples that were sent to two different laboratories as a blind split. Acid and base-neutral extracts obtained by using standard priority pollutant protocols were in good agreement, but the

Eynon and Rushneck (1988) examined a curious phenomenon arising from the comparison of compounds detected by the Toxicity Characteristic Leaching Procedure (TCLP) and corresponding concentrations found by direct analyses. Many compounds were detected by the TCLP test without being detected by direct analysis, even though leaching procedures were not as analytically rigorous as direct analysis procedures. In this comparison of 112 samples, volatile compounds at or above the detection limit obtained by the TCLP test but below detection limits by direct analysis (Method 1624, USEPA, 1982) in three or more samples included methylene chloride (probably laboratory contamination), 2-propanone, toluene, 1,2-dichloroethane, ethylbenzene, 2-butanone, 1,1,1-trichloroethane, and chloroform. It was suggested that the relative sample size for the TCLP procedure is larger than that for direct analysis and that the larger sample size could explain the greater sensitivity of the TCLP.

Poulsen and Kueper (1992) contributed further to the determination of appropriate sample size. They demonstrated the effects of mesostructure (stratified sands) on the advection of a pure phase NAPL (tetrachlorethene). Within a few days after release of tetrachloroethene onto a field soil, the compound was distributed in distinct stringers occupying sand laminations that were separated by a few to several centimeters. Estimates of the appropriate sample size to recover pure stringers were on the order of cubic millimeters. Samples much larger than a few milliliters in volume would be necessary to obtain an estimate of the mean concentration in this soil. The authors used 50 g (or approximately 36 mL) samples to estimate bulk properties.

Spatial Variability

An arbitrary increase in the VOC sample size beyond the current 1- to 5-g size is likely insufficient to resolve VOC sampling problems. Sampling design must address the long- and short-range spatial variability of VOCs in the field. Mitchell et al. (1993) measured soil VOCs at a land treatment unit used for disposal of waste oils and solvents. Samples (176) were collected from 21 borings over approximately 650 m^2 (0.7 acre). Borings were collected to a depth of 6.4 m using a hydraulic probe and samples were obtained at approximately l-m intervals. A field GC and heated headspace technique (see “Field Methods for Determining Soil Gas and Soil VOCs) was used to analyze 10- to 20-g subsamples for seven chlorinated aliphatic compounds. Data obtained clearly demonstrated the extreme spatial heterogeneity of soil VOCs at the site. The total soil-VOC concentrations varied from 6 µg/kg to 154,000 µg/kg, and 90% of the sample VOC concentrations were between 94 µg/kg and 20,100 µg/kg. The authors suggest that very high sample densities are needed to estimate the total mass of VOC within contaminated soil or to visualize a three-dimensional soil-VOC distribution.

SAMPLE STORAGE AND PRESERVATION

Constraints on the Container Material

The ideal material for sample storage will maintain the sample integrity without degradation of container material. Sample integrity can be compromised by either sorption or leaching of organic contaminants of interest. Leaching may be resorption of sorbed compounds or a release of “free” plasticizers present in the bulk polymer.

Ten materials, including three metals, six synthetic polymers, and borosilicate glass, were evaluated for halocarbon loss in laboratory experiments (Reynolds et al., 1990). Borosilicate glass was the only material that did not diminish the halocarbon concentrations. Loss rates for stainless steel were negligible for all compounds tested except bromoform and hexachloroethane, which had losses amounting to 70% after 5 weeks. The more halogenated compounds were generally removed before the less halogenated compounds in solutions exposed to metals. Of the polymers, the rigid polymers polytetrafluoroethylene (PTFE, Teflon®; E.I. Du Pont De Nemours, Inc., Wilmington, DE) and rigid polyvinylchloride (PVC), were the best. At low concentrations of halocarbons in water, these polymers showed little adsorption during the 5-week experiment. At high concentrations, however, the hydrocarbon solvents cause compound-specific swelling of polymers. Sorption rates at high activities are dependent on concentration and this makes them difficult to estimate. Therefore, if methanol or other solvent preservatives are used, borosilicate glass is the best choice for storing samples. Also, after a polymer container is used, the containers can become an important source of contamination and should not be reused.

Use of stainless steel and polymer materials for suitability as well casing materials was reviewed by Parker (1992). Stainless steel is susceptible to corrosion in some soils (low pH, presence of H_2S, and high salt content). Sample integrity of metals is affected by stainless steel, but organics will not be affected by stainless steel as long as the soil is not corrosive and adequate decontamination procedures are followed. PTFE is highly resistant to chemical attack. However, the rate and extent of sorption of chlorinated alkenes and chlorinated aromatics from aqueous solution is greater for PTFE than for rigid PVC. For example, Parker et al. (1990) found that loss of TCE was 10% after 8 h for PTFE, but losses for rigid PVC were only 6% after 1 week. Rigid PVC is resistant to chemical attack unless exposed to a nearly saturated solution of a PVC solvent. PTFE leaches very little contamination, but rigid PVC was a very close second. Parker (1992) concluded that rigid PVC and stainless steel were the best choices for sampling organics, but that PVC should be used if sampling for both organics and metals. Only threaded PVC, PTFE, and stainless steel should be used because solvent bonding introduces additional contaminants.

Studies of VOC-Spiked Storage Times

Zarrabi et al. (1991) reported on a batch approach to achieve "homogeneous" VOC-spiked soils for use in studies of sampling methodology and potentially for use as performance evaluation samples. Methanol solutions of VOCs were added to moist soil in glass jars and mixed by tumbling for 120 seconds. Same-day results showed benzene recoveries of approximately 40% for one soil and less than 10% for another soil; chlorobenzene recoveries were 70% to 85% and 29% to 59%, respectively, for the same two soils. Coefficients of variation for benzene and chlorobenzene determinations ranged from 3% to 30%. Statistically significant VOC losses occurred within 3 days of spiking, and recoveries and variability in the data were "completely unacceptable" after 8 days.

Studies on storage of VOCs in water have shown that no leakage through septum seals will occur if vials (40-mL VOA) are properly filled and sealed (Maskarinec et al., 1990). The highly volatile chloromethane showed no loss over 56 days when stored in glass vials with Teflon-lined caps. In water, loss of l,1,2,2-tetrachloroethane with a concomitant increase in TCE occurred after 28 days at 4 °C. Trichloroethane appeared to degrade to dichloroethene; changes were noted only after 56 days at 4 °C. Degradation of aromatic volatiles, especially styrene and ethylbenzene, became apparent after storage for 28 days at 4 °C, but it could be stopped by adding any of three acid preservatives tested (hydrochloric acid, sodium bisulfate, and ascorbic acid). Degradation rates were faster at 25 °C. Within 28 days at 25 °C the disappearance of tetrachloroethane was accompanied by a concomitant rise in the concentration of TCE, and decreasing levels of trichloroethane were accompanied by increased concentrations of dichloroethene.

Storage of soil VOC-spiked standards, obtained by using the same water-spike mixture and the same compounds as above (stock solution was mixed and stored in a Tedlar bag; Maskarinec et al., 1990), has been less successful than the storage of VOC-spiked water samples. Maskarinec et al. (1988) followed the concentrations of a mixture of 15 volatile compounds in three soils for 56 days. The authors concluded at that time that 14 days should be the maximum holding time prior to soil-VOC analysis, although there is no rigorous data analysis to support the statement. In the same study, Maskarinec et al. (1989) showed very good initial recoveries of the highly volatile compounds bromomethane (66% mean recovery) and chloroethane (86% mean recovery) in three soils. The readily degradable compound, styrene, had very low recoveries in two of the soils, producing a mean recovery of 25%. Day-zero recoveries of 17 VOCs from three soils varied from 14 to l18% (mean recovery of 67% for all compounds) with standard deviations less than 25%.

Data on soil-VOC concentrations after storage of these samples were presented by Jenkins et al. (1993). Data were expressed as the maximum holding times (MHT) for the three soils, stored at 4, -20, or -70 °C. The sandy loam soil lost VOCs rapidly under all storage conditions; MHT values were 0 to 3 days for most of the compounds tested. The silt loam soil had MHTs of 0 to 14 days after storage at 4 °C (mostly less than 3 days). At -70 °C the MHTs for the silt loam were also low (mostly 0 to 1 days). At -20 °C, the silt loam MHTs were fairly high MHT values were 18 days or more for all compounds (but bromomethane) as calculated by the American Society of Testing and Materials (ASTM) method and MHT values of 3 to 56 as calculated by the alternate method. The third soil, an undescribed U.S. Army Toxic and Hazardous Materials Agency reference soil was presterilized by an unspecified method. This soil exhibited MHTs of more than 100 days (calculated by either method) for 10 of the compounds when stored at -20 °C. Tetrachloroethane was the only compound that had an MHT of less than 14 days at -20 °C.

Achieving a good sample seal after soil has touched the sealing surfaces of a vial is very difficult. This assertion was demonstrated by observing the loss of methanol from vials that had been smeared with soil and then wiped with a gloved hand before capping (Hewitt, 1992). Seven of ten soiled VOA vials showed continuous weight loss, but no weight loss was observed in stored VOA vials that had not been smeared with soil. The use of a syringe body with the nose removed to subcore soil in the split-spoon sampler is recommended because the syringe can be wiped free of soil particles, avoiding the problem of particles contacting the vial sealing surfaces.

Addition of polymer absorbents (molecular sieve 5A and florisil) to reduce sample volatilization losses during sample transfer steps increased spiked recoveries (significant at $p=O.05$) for 42 of 60 soil/compound combinations tested (Zarrabi et al., 1991). Still, recoveries in the presence of the solid absorbents were less than 50% for two of the three soils. In a 95% sand sample, the addition of the polymer absorbents and traditional sample transfer steps showed increased VOC recoveries over the modified sample lid/sparging procedure.

Amin and Narang (1985) reported that spiked frozen (-5 °C) sediment samples can be stored as long as 7 days without significant loss of volatiles. Sediment samples were sealed in vials, then spiked with a combination of 16 VOCs, immediately frozen, stored, and connected to a purging system without opening the vials. Losses were negligible on days 2, 3, 4, and 7, but losses of as much as 50% occurred between 14 and 60 days of storage. Addition of a small amount of methanol (1 mL methanol and 1.5 mL water per 5-g soil sample) preserved the volatiles exceptionally well; negligible losses occurred over a period of 90 days. Recoveries for 11 VOCs in samples preserved with methanol ranged from 57 to 99% on day 1 and from 28 to 95% on day 90. Information on how the GC data were quantified and when the internal standard (fluorobenzene) was added were not given.

A study of five preservation methods for gasoline-contaminated soil evaluated the following storage treatments (1) rubber-capped brass tubes, room temperature, (2) rubber-capped brass tubes, 4 °C, (3) rubber-capped brass tubes on dry ice, (4) 40-mL VOA vial with 5 mL methanol at room temperature, and (5)40-mL VOA vial with 5 mL methanol at 4 °C (King, 1993). Separate batches of laboratory-contaminated soil (at approximately 100 to 200 mg/kg as total petroleum hydrocarbons, TPHs) were used for each treatment. Six samples from each batch were analyzed for TPH concentration at 0, 3, 6, 10, and 14 days after sample mixing. Treatment 1 (tubes that had not been refrigerated) showed a mean concentration of 91 mg/kg on day O decreasing to less than 20 mg/kg by day 6. Treatment 2 (tubes with refrigeration) showed an initial concentration of 120 mg/kg decreasing to 34 mg/kg by day 6. Treatments 3, 4, and 5 did not show any deterioration exceeding the “precision of the analytical methods” (statistics not provided) during the 14-day holding time.

SUMMARY OF SAMPLING AND PRESERVATION METHODS

Lewis et al. (1991) reviewed sample design, selection of sampling devices, sample collection procedures, and shipping considerations for soil VOCs The topics covered by this review include sample preparation procedures and storage and preservation techniques.

Laboratory subsampling prior to analysis has been shown to create large losses of VOCs (Amin and Narang, 1985; Maskarinec et al., 1988; Siegrist and Jenssen, 1990; Zarrabi et al., 1991; Hewitt, 1992). For example, losses during subsampling and weighing were reported at 20% to 80% (Zarrabi et al., 1991) and averaging 60% (Maskarinec et al., 1988). Losses from chilled soil ranged from 7% to 36% as compared to losses ranging from 14% to 53% for nonchilled soil (Amin and Narang, 1985). Homogenizing the soil prior to weighing a sample creates higher losses than samples transferred without homogenization (Siegrist and Jenssen, 1990). Samples stored in containers with a large headspace lose more VOCs upon transfer than samples stored in containers with little headspace (Siegrist and Jenssen, 1990). The general trends outlined above mask the large variability of losses among compounds on the same soil and the reported variability in losses of a single compound among soil types.

Storage of soil samples for VOC analyses presents more challenges than storage of water samples because prevention of volatile and degradative losses is more complicated to accomplish and to verify. Soil samples are much more difficult to seal than water samples due to the difficulty of removing all particles that stick on the top rim of the jar. Slater et al. (1983) found that 31 of 54 jars of soil leaked VOCs during 3 to 5 weeks of storage, shown by the presence of VOCs in bags used to enclose the samples. Hewitt (1993) reported 7 of 10 vials leaked when sealed after carefully removing soil from the rims of the vials. The addition of polymer absorbents to prevent volatile losses may be helpful, especially in sandy soils, but a separate step to extract VOCs from the absorbents may be required (Zarrabi et al., 1991; Pignatello, 1990a). Soil placed in jars or vials via a subcorer should largely eliminate the leaky seal problem (Hewitt, 1993).

Contract Laboratory Program (CLP) storage procedures currently allow soil samples to be refrigerated (4 °C) for as long as 10 days after receipt at the laboratory (USEPA 1991). Studies generally show, however, large losses of analyte within 3 days when contaminated soils are stored at 4 °C (Maskarinec et al., 1989, Zarrabi et al., 1991; King, 1993).

Degradation in refrigerated water samples was successfully halted by the addition of acids, including sodium bisulfate (Maskarinec et al., 1990). In contrast, soils are much harder to acidify. If soils are acidified, artifacts arising from changes in the conformation of organic matter and changes in clay surface charges may affect soil VOCs. Biocides such as sodium azide (Pignatello, 1990a) or mercuric chloride (Zarrabi et al., 1991) can be used as preservatives, but these biocides are not easy to use and dispose of. The preservation of gasoline-contaminated, fine-grained sand by keeping samples on dry ice was demonstrated by King (1993); however, the results were reported as total petroleum hydrocarbons, so no compound-specific preservation can be distinguished. Jenkins et al. (1993) found that -20 °C was superior to -70 °C for preserving two soils, a silt loam and a presterilized soil (method unspecified). However, in a third soil, a sandy loam, significant losses of VOCs occurred at each temperature, -70 °C, -20 °C, and 4 °C (Jenkins et al., 1993).

The preservation of soil VOCs by adding the soil sample to a preweighed jar of methanol in the field has been recommended by many researchers (Jenkins and Schumacher, 1987; Bone 1988; Urban et al., 1989; Siegrist and Jenssen, 1990; Lewis et al., 1991; Hewitt et al., 1992; King, 1993) and accepted as a standard procedure by the ASTM (D 4547-91, “Standard Practice for .Sampling Waste and Soils for Volatile Organic”). Methanol acts as a biocide and prevents loss by volatilization. The amount of methanol necessary to prevent biodegradation and volatilization has not been determined however, Amin and Narang (1985) found that 1 mL added to 5 g of soil prevents loss of VOCs in frozen soil. Methanol provided a vapor trap that was as effective as activated carbon for retaining ethylbenzene in a closed system (Rhue et al., 1988). The analytical complications in a methanol-preserved sample are addressed in the next section.

SECTION 7

ANALYTICAL METHODOLOGY

This section describes (1) the SW-846 analytical methods (PT/GC/MS) used to measure soil VOCs when extremely accurate and sensitive data are essential and (2) studies of modifications that might improve the PT/GC/MS procedures. Methanol has been shown to be a useful preservative, and therefore, studies of the analytical sensitivity and precision that can be achieved with methanol extracts are also discussed. Finally, studies that describe analytical procedures for measuring the nonequilibrium or entrapped fraction of VOCs are presented.

SW-846 METHOD 8240 AND RELATED METHODS

SW-846 Method 8240 (USEPA, 1986, 1990) outlines the analysis of volatiles from solid waste matrices by PT extraction and packed column gas GC/MS detection. Proposed SW-846 Method 8260 (USEPA, 1990) is analogous to SW-846 Method 8240, except that a capillary gas chromatography column is used in place of the packed column and the method is accompanied by an expanded list of analytes. Related SW-846 methods (USEPA, 1990) include extractions, preparations, and screening methods Method 5030, purge and trap; Method 3580, waste dilution (methanol); Method 3810 (formerly Method 5020), screening by headspace analysis and Method 3820, screening by hexadecane extraction. Analysis of specific groups of analytes may be performed by other GC methods as follows: Method 8010, Halogenated Volatile Organics, by halogen specific detector; Method 8011, 1,2-Dibromoethane and 1,2-Dibromo-3-chloropropane; Method 8015, Nonhalogenated Volatile Organics, by flame ionization detector; Method 8020, Aromatic Volatile Organics, by photometric ionization detector (ketones and ethyl ether); Method 8021, Halogenated and Aromatic Volatiles, by electrolytic and conductivity detectors in series, capillary column; and Method 8030, Acrolein, Acrylonitrile, and Acetonitrile, by flame ionization detector.

SW-846 Method 8240 suggests screening samples by hexadecane extraction or by headspace analysis prior to GC/MS analysis to allow for the estimation of appropriate sample size (1 g, 5 g, or methanol extraction) Samples that are likely to contain greater than 1 mg/kg of an analyte are highly contaminated and must be first extracted into methanol (1 or 4 g wet soil in 10 mL methanol). An aliquot of the methanol is placed in water before purging to avoid overloading the gas chromatagraph/mass spectrometer.

Methods for the analysis of soil VOCs used in the Superfund Contract Laboratory Program (CLP) are essentially SW-846 8240 and 8260 (USEPA, 1990) with additional QA/QC data requirements. Both packed and capillary column methods are included as described in the Statement of Work for Organics Analysis, Exhibit D, Sections I through IV (USEPA, 1991). Optional sample screening by hexadecane extraction is described and a medium-level soil method by methanol extraction, analogous to the RCRA high-level soil method, is given in the CLP Statement of Work (USEPA, 1991). Similarly, methods for the analysis of VOCs in water and wastewater, "Purgeables"' Method 624 (EPA Environmental Monitoring Systems Laboratory-Cincinnati) and "... isotope dilution GC/MS Method 1624 (EPA Office of Water Regulations and Standards, Industrial Technology Division), also use PT devices with GC/MS detection.

MODIFICATIONS OFFERED TO IMPROVE SOIL PURGE-AND-TRAP ANALYSIS

PT analysis, as originally developed for the EPA, involved a 5-mL water sample, an 11-min purge with an inert gas at 40 °C to a Tenax-GC trap, and a 4-min resorption to a packed GC column (USEPA, 1982). Solid-sample matrices are run in like manner by adding 5 mL of water to approximately 5 g of solids, often producing a foam, which makes stripping difficult, clogs the equipment, and requires cleaning between samples (Amin and Narang, 1985). Historically, soils and other solid samples analyzed with the PT extraction have low recoveries and erratic precision (Lesnik, 1993).

Modifications to the PT technique that are designed to improve recovery of VOCs from water are briefly mentioned. Whole column cryotrapping was suggested by Pankow and Rosen (1988) as an alternative to the Tenax-GC traps. Cryotraps placed after the Tenax trap are another option; many laboratories add it to remove water before introducing the sample into the GC (Westendorf, 1992) Increasing the purge temperature has also been suggested to improve purge efficiency, and recent work suggests an alternative to replace oil or water baths with mantle-style heaters (Jiang and Westendorf, 1992).

As compared with water samples, soil and sediments show poor spike recoveries and high detection limits (Hiatt, 1981; Charles and Simmons, 1987). The spike recoveries that are reported in accordance with SW-846 Method 8240/8260 procedures are in fact relative recoveries that do not reflect the absolute recoveries or "efficiencies" of compound recovery. Recoveries are calculated by the relative response factor of surrogate compounds, that is the peak area ratio of a surrogate to an internal standard compound. Both internal standards and surrogate additions are added just before the sample is sparged. The internal standards and surrogates are subject to the same matrix effect, and the response ratio does not quantify that matrix effect.

Ward (1991) has suggested that the internal standard be introduced in a microvolume sample loop placed between the sample vial and the GC inlet. A valve would allow the internal standard to be swept out by the carrier gas during the purge step. In this configuration, the internal standard would be used to monitor the GC/MS system, and the surrogates would portray the matrix effects.

Techniques to improve extraction efficiencies from soils and solid matrices over that achieved during the conventional purge (designed to extract VOCs from water) have been developed. Cryogenic vacuum extraction was developed by Hiatt (1981) for extraction of VOCs from sediment and fish tissues. Method 5032, to be included in the Third Update to SW-846, is a vacuum distillation/cryogenic trap procedure followed by GC/MS, applicable for extraction of a wide array of organics from a variety of solid matrices (Lesnik, 1993).

Closed-loop stripping into a cryotrap with steam distillation of the volatiles onto a Porapak N column was described by Amin and Narang (1985). VOCs were then extracted from the absorbent column with methanol and the eluate was analyzed by GC. Recovery of VOCs from spiked, frozen soil samples ranged from 60 to 100%.

Although altering the conductivity of the solution has been reported to increase recovery of VOCs from water samples (attributed to salting out), recoveries from soil samples generally do not increase with the conductivity of the solution. Charles and Simmons (1987) investigated the effect of sediment type and conductivity of the desorbing solution (0.01 M and 0.1 M KH_2PO_4) on the recovery of PT analyses. The salt content of the desorbing solution did not affect VOC recoveries from any of the three soils. Zarrabi et al. (1991) tested saturated NaCl solution as a purging solution and found improved recovery of ketones but slightly lower recoveries for the majority of VOCs.

The largest single improvement to soil-VOCs analysis by PT is arguably the modified lids for 40-mL VOA vials that can be attached directly to a sparging apparatus to avoid the laboratory subsampling step (Maskarinec et al., 1989; Zarrabi et al., 1991; Hewitt et al., 1992). Teflon couplings (valves and fittings) are added in place of the standard Teflon-faced septum and screw cap that also allow the addition of water and internal spiking solution to the sample before sparging. This modified lid configuration has been discussed in the section “Obtaining and Maintaining VOC Samples.”

ANALYTICAL SENSITIVITY OF SOLVENT EXTRACTS

Analytically, soil methanol extracts are constrained to have lower sensitivity than the conventional water PT extraction. The soil is effectively diluted when it is placed in methanol in any proportion except equal parts of soil and methanol. Furthermore, the addition of methanol to water in the sparger decreases the recovery of at least some compounds by decreasing the aqueous-vapor distribution coefficient. Kiang and Grob (1986) showed that headspace concentrations of eight VOCs decreased as methanol in water increased from 1 to 20%. The effect was most pronounced for the dichlorobenzenes. Control values with no methanol addition were not presented because the VOC spike solution was in methanol.

Zarrabi et al. (1991) reported that the addition of methanol to soil in the sparger at 1 and 10%o just before purging gave mixed results depending on the soil. Differences were not significant at the 5% level as compared with the control (no methanol). Trends in the data showed that 1% methanol had no effect or improved the VOC recovery for a soil consisting of 95% sand and 0.14% organic carbon, but 10% methanol tended to decrease the VOC recovery in the same soil.

The CLP SOW methods (USEPA, 1991) and SW-846 Methods 8240, 8260,and 3580 (USEPA, 1990) use methanol to dilute samples that are too high in one or more analyte. Methanol is added to soil (1:10 soil:methanol) and the methanol extract is diluted into water (1:5 methanol:water, but this may vary) to quantify soil VOCs at levels of 500 to 1,000 µg/kg. Using the high-level methanol extraction method (SW-846 Method 8240), Hewitt et al. (1992) reported a detection limit on the order of 1000 µg/kg. The relative standard deviation of laboratory vapor-fortified soil by PT of the methanol extract ranged from 0.5 to 38%, with a mean value of 12% at high-level fortification and 16% at low-level fortification (Hewitt et al., 1992). Urban et al. (1989) reported a detection limit of about 250 µg/kg for five VOCs (100 to 200 g wet soil in 250 mL methanol) using the medium-level methodology in the CLP SOW for Organics Analysis (7/87). Slater et al. (1983) used approximately equal parts of wet soil and methanol and reported a quantification limit of 1,000 µg/kg for TCE using a GC with a Hall detector.

Urban et al. (1989) showed that methanol-preserved samples contained as much as an order of magnitude more VOCs than samples collected and analyzed by low-level methods. Duplicate analyses of methanol-preserved samples were examined as well as duplicates generated by spiked soil/methanol samples left overnight to equilibrate. Analyses of TCE, present in high concentrations in the samples (at 1,000 to 11,000 µg/kg), gave relative percent differences of 0 to 6% in duplicates. Spiked duplicate studies using five compounds (1,1-dichloroethene, TCE, benzene, toluene, and chlorobenzene) showed recoveries well within the CLP acceptance criteria (which vary by compound, but generally fall between 60 and 140%) and relative percent recoveries less than 9% (CLP acceptance values of 21 to 24%) for all compounds, except 1,1-dichloroethene. Recovery of 1,1-dichloroethene was inconsistent; two of the four samples showed 86 to 96% duplicate recoveries of 1,1-dichloroethene with 0.3 to 1.0 relative percent differences; two other samples showed 50 to 80% recoveries and 28 to 36 relative percent differences for this compound.

A comparison of methanol and tetraethylene glycol dimethyl ether (tetraglyme) for extraction of soil VOCs was reported by Jenkins and Schumacher (1987). They found that methanol was better than tetraglyme at recovering four volatiles from soil. Three vapor-contaminated soils were studied. Methanol was found to extract 28.4% higher amounts of chloroform from a soil high in organic matter (6.7% organic matter). Methanol was also easier to handle than tetraglyme because it is less viscous and does not foam during the PT analysis. Tetraglyme, like other ethers, is susceptible to the formation of peroxides, which can be dangerous.

EXHAUSTIVE EXTRACTIONS TO RECOVER SORBED VOCs

Sawhney et al. (1988) investigated methodologies for recovering 1,2-dibromoethane (EDB) from field-contaminated soil samples. They noted that most methods for analyzing organics in soil are predicated on short-term spike-recovery results (usually less than 24 h equilibration time). Soil samples that had years to equilibrate with EDB in the field were tested for residual levels by PT, thermal desorption, and solvent extraction techniques. Results for EDB recovered in their Cheshire fine sandy loam soil by PT and by using various solvent extractions are compared in Table 4. Hot methanol (75 °C for two 24-h periods) was used by the authors as a base to compare extraction efficiencies. Purging as recommended by SW-846 Method 8240 (11 min at 40 °C) resulted in 1.3% of the total recovered by using hot methanol (90 µg EDB/kg soil). A series of repeated purges for longer time periods, including two purges at 80 °C, amassed 26.1% of the EDB recovered by hot methanol. Acetonitrile and acetone, heated to 75 °C, led to slightly higher EDB recoveries than by hot methanol. Room temperature (20 °C) extractions using methanol, acetone, and acetonitrile for 24 h resulted in 60, 65, and 78% recoveries of the hot methanol extraction, respectively. Using a ratio of 5 g soil to 25 mL methanol, and a GC with an electron capture detector, their detection limit was 1.8 µg/kg. The concentration found in soils by hot solvent extraction ranged from 30 to 200 µg/kg; PT recovered 1-2 µg/kg.

Sawhney et al. (1988) also tried thermal resorption on the EDB-contaminated soil. Temperatures of 100 °C to 200 °C were investigated. They recovered essentially no EDB from field-contaminated soil, but subsequent extraction with a solvent showed that the EDB concentration remaining in the soil declined from 79% to 3.6% as the temperature increased, leading to the assumption that EDB was destroyed by the high temperature necessary for thermal desorption. In contrast to the field-contaminated soil, freshly spiked soil was completely and efficiently thermally desorbed at 120 °C and at 200 °C if desorbed immediately yet freshly spiked soil, allowed to sit for 18 h prior to thermal desorption, yielded only 49% in thermal desorption. Apparently, surface exposed EDB is desorbed rapidly, but entrapped EDB (which must diffuse from distant microsites) degrades before desorbing.

Pavlostathis and Jaglal (1991) investigated the water-induced resorption of TCE from a soil (silty clay texture, 0.13% organic carbon) that had been contaminated for at least 18 years. Their objective was to produce a laboratory-scale model of possible remediation techniques The effect of pH on TCE resorption was negligible. The ionic strength of the aqueous desorbing solution had no effect until the ionic strength exceeded 0.1 M, which produced a slightly decreased desorption. The authors characterized the “total” TCE in the field-contaminated soil as that obtained from a 13-h methanol extraction at 20 °C. Continuous leaching in a soil column (approximately 24,000 pore volumes) extracted 72% of the methanol-derived “total” soil TCE. Total soil TCE found by extraction with cold methanol was estimated at approximately 2000 µg/kg.

Steinberg (1992) investigated the residual vapor-phase sorption of 1,1,1-trichloroethrme, TCE, benzene, toluene, and ethylbenzene at spike concentrations of several parts-per-thousand. An oven-dried calcareous soil (9.8%) carbonate as CO_2, 0.16% organic carbon) was incubated for 2 to 87 h at temperatures of 5 °C, 25 °C, and 45 °C. The labile fraction was then allowed to evaporate at 32 °C for 24 h. The residual fraction was analyzed by (1) hot solvent extract, methanol slurry at 65 °C for 24 h; (2) PT as described in SW-846 Method 8010 (1,1,1-trichloroethane only); and (3) a “field extraction procedure” of hexane:water, 25 (volume basis). Sparging (Method 8010) recovered approximately 10% of the 1,1,1-trichloroethane, and the

TABLE 4. COMPARISON OF PURGE-AND-TRAP VERSUS SOLVENT EXTRACTION FOR ANALYSIS OF AGED, EDb-CONTAMINATED SOILS*

Extraction Method	Successive Purge[+]	Solvent	Time (hr)	Temperature (°C)	Relative Recovery Per Purge (%)	Total Relative Revocery (%)**
Purge and trap	1	NIA	0.18	40	1.3	
	2	N/A	0.18	40	1.0	
	3	N/A	0.5	40	3.6	
	4	N/A	0.5	80	9.6	
	5	N/A	0.5	80	10.9	
						26.1
Solvent	N/A	methanol	24 (2X)	75	N/A	100
	N/A	methanol	24	75	N/A	94
	N/A	methanol	16	75	N/A	93
	N/A	methanol	4	75	N/A	69
	N/A	methanol	48	20	N/A	68
	N/A	methanol	4	20	N/A	28
	N/A	acetonitrile	24	75	N/A	114
	N/A	acetonitrile	24	20	N/A	78
	N/A	acetone	24	75	N/A	113

Abbreviation : EDB = l,2-dibromoethane; N/A = not applicable

* Data compiled from Sawhney et al., 1988.

[+] Consectutive runs/purges on the same sample

** Based on recovery of two 24-hour extraction quick hexane extraction recovered approximately 40% of the residual concentration found by the hot solvent extraction. The increase in the residual fraction with incubation time was shown to be a pseudo first-order process. The effect of temperature showed a substantial activation energy for entrance of VOCs into the residual fraction.

Supercritical fluid extraction (SFE) is an innovative extraction technology that is most appropriate for semivolatiles research but may prove useful for volatiles. SFE may provide a rapid technology for extraction of semivolatiles. One of the unsolved problems for extraction of volatiles is the appropriate extractant. Solvents often produce large peaks that mask the VOC peaks of interest. Hawthorne et al. (1992) reported on SFE of semivolatiles and some relatively volatile organics, including n-octane. They noted that native analytes generally extract more slowly than spiked analytes from the same matrix and that recoveries are highly matrix dependent. An exhaustive SFE, if found, could greatly decrease the extraction time for slowly desorbing VOCs.

SUMMARY OF ANALYTICAL METHODOLOGY

PT methods that were developed for extracting VOCs from water have poor recovery and low precision when applied to soils. Surrogate recoveries (reported as the peak area ratio of surrogate/internal standard) do not reflect the extraction efficiency or actual recovery from a soil matrix because surrogate compounds and internal standards are introduced to the sample essentially simultaneously and therefore, are subject to the same matrix effects. The addition of a microvolume sample loop to add internal standards directly into the GC, bypassing contact with the soil, has been suggested to alleviate this problem (Ward, 1991).

The addition of salts to the sparging solution to produce a “salting out” of organics has not been effective in tests with soil (Charles and Simmons, 1987; Zarrabi et al., 1991). Vacuum extraction with a cryogenic trap recovers VOCs and other organics (including nonconventional VOCs) more efficiently than PT and will be offered as Method 5032 in the Third Update to SW-846 (Hiatt, 1981; Lesnik, 1993).

The use of methanol to immerse field samples as a preservative technique produces an analytical sensitivity of approximately 250 to 1,000 µg/kg when analyzed by PT/GC/MS (Slater et al., 1983 Urban et al., 1989; Hewitt et al., 1992). This loss of sensitivity results from the dilution of the soil in the methanol and the decreased vapor pressure of VOCs in methanol. As the amount of methanol in the sparger increases, the purging efficiency decreases. Using direct injection but more specific detectors than MS, detection limits can be decreased (e.g., 1.8 µg EDB/kg soil with an electrolytic conductivity detector, Sawhney et al. 1988). Methanol is generally superior to tetraglyme as a VOC extractant because recovery of VOCs from tetraglyme was poor from a soil high in organic matter (Jenkins and Schumacher, 1987).

More rigorous extraction techniques such as hot methanol or pulverization of the soil (discussed under “Nonequilibrium Sorption” in section “Interphase Transfers”) have shown that some fraction of the soil VOCs are entrapped in microsites in the soil or diffuse from them too slowly to be solubilized during the PT extraction. Levels of EDB in ground water exceeding health standards were traced to a slow diffusion of EDB from soils that had concentrations of 30 to 200 µg EDB/kg soil when extracted by hot methanol and 1 to 2 gg EDB/kg soil when extracted by PT (Sawhney et al. 1988). Thermal resorption was observed to destroy the entrapped EDB, but quantitatively recover fresh (less than 18 hr) additions of EDB (Sawhney et al., 1988).

Cold methanol was used to extract a soil that was contaminated with TCE 18 years prior to analysis (Pavlostathis and Jaglal, 1991). Continuous leaching (24,000 pore volumes) with water extracted 76% of the 2000 µg/kg found by extraction with cold methanol. A soil that was contaminated in the laboratory by exposure to a mixture of VOC vapors was extracted by hot methanol, hexane/water, and PT (Steinberg, 1992). PT and hexane extracted approximately 10% and 40%, respectively, of that which was extracted by hot methanol.

SECTION 8

FIELD METHODS FOR DETERMINING SOIL GAS AND SOIL VOCS

Field methods for assessing soil VOCs offer advantages under many circumstances. Literature that describes the uses of soil-VOC field methods is briefly reviewed below, followed by soil-gas studies, soil headspace methods, and finally, advanced field analysis techniques. Throughout this section, studies that compare field data with laboratory data were targeted.

JUSTIFICATION FOR FIELD METHODS

The EPA has encouraged development of field technologies for on-site analysis of samples at hazardous waste sites (Wesolowski and Alwan, 1991; Fribush and Fisk, 1992). This impetus has resulted in improved efficiency for many short-term environmental projects that are delayed by time-consuming, expensive, and cumbersome laboratory procedures (Spittler, 1992; Wesolowski and Alwan, 1991). Instrumentation that provides qualitative VOC screening includes total organic analyzers with photoionization (PID) or flame ionization (FID) detectors. These detectors have been available for approximately 20 years. Numerous brands and types of field-deployable GCS have been and continue to be developed which permit identification and quantification of volatiles with increasing precision and sensitivity. Field methods are no longer limited to screening methods. Mobile laboratory and field-deployable instrumentation is beginning to rival the identification and low detection limits of SW-846 Method 8240.

Field methods, calibrated by relating field data to laboratory results, can offer considerable reductions in cost and time (e.g., Cornell, 1992). Duplicates of a representative portion of the field samples (10% of the field samples is suggested) may be sent to the laboratory for analysis. Calibration curves of field versus laboratory data can then be generated. The greatest uncertainty in data derives from nonanalytical factors: site heterogeneity, sample-matrix variability, sample collection procedures, and sample handling, transport, storage, and preparation procedures. Cornell (1992) concludes that the analysis method will not seriously compromise data integrity as long as proper calibration of laboratory and field methods is observed.

Field measurements are particularly attractive for analyses of soil volatiles because VOC losses during storage are eliminated with field analyses. On the other hand, the relatively simple headspace analyses by hand-held total organic carbon detectors gives highly variable data that are subject to many interferences. Correlations between headspace analysis with total organic carbon detectors and laboratory PT analysis is poor (Siegrist, 1992). Total organic carbon analyses are particularly inappropriate in soils of high, naturally occurring organic contents (Nadeau and Tomaszewicz, 1988).

Field analyses for soil VOCs has been specifically recommended by Mitchell et a1.,(1993) for yet another reason. They examined the spatial heterogeneity of soil VOCs at a small (650 m^2) waste solvent landfill. The variability of VOC concentrations measured in 176 samples demonstrated that an enormous number of samples are needed to visualize the three-dimensional distribution of soil VOCs or to estimate the total concentration of soil VOCs Mitchell et al. (1993) advised that sampling designs ought to incorporate increased numbers of spatially separate measurements, to be achieved by using less expensive, on-site analyses.

SOIL-GAS MEASUREMENTS

Soil-gas measurements have become an increasingly important analytical tool at hazardous waste sites. They are a relatively rapid and cost-effective means to (1) locate a contaminant source; (2) delineate a ground-water contaminant plume; (3) plan monitoring-well, soil-boring, or vapor-extraction locations; (4) assess leakage of underground tanks, lines, and subsequent vapor migration; (5) monitor migration of gases from landfills, impoundments, industrial facilities; and (6) monitor the progress of a cleanup (Devitt et al., 1987). The relative concentration of a contaminant is measured, the spatial distribution is mapped, and correlations with soil or water contaminant concentration(s) are developed site by site. Analytical determinations of soil gas range from generalized organic-vapor sensors to field-deployable or mobile laboratory GCS. Reviews of methods and available technology for soil-gas sampling include Balfour et al. (1987), Devitt et al. (1987), Jowise et al. (1987), and Marrin and Kerfoot (1988).

Properly executed, soil-gas analysis gives a subsurface reading of the vapor phase concentration, and provides data that cannot be reproduced with confidence once the soil is removed from its place in the field. The measurements are used as relative comparisons at a given location because of the many soil, compound, and environmental factors that influence the vapor phase concentration (Reisinger et al. 1987; Marrin and Kerfoot, 1988). General correlations of soil gas and soil VOCs are often poor (C. L Mayer and E. N. Amick, personal communications, 1992). Soil gas concentrations may be unreliable if measured during periods of large barometric pressure changes, during or immediately after a rain, or across a site with considerable variation in soil texture (either vertically or horizontally). Golding et al. (1991) however, reported fairly good correlations of TPH in soil gas versus soil headspace and between soil gas and soil TPH by an Iowa laboratory procedure (Iowa Department of Natural Resources Method OA-1; methanol extraction followed by PT modeled after SW-846 Method 8015). The data were generated from 12 sites in Iowa near underground gasoline storage tanks Soil samples were removed from the same drill hole as soil-gas samples (soil samples collected subsequent to and deeper than gas samples). The data spanned 3 orders of magnitude of laboratory soil TPH (5 x 10^3 to 5 x 10^6 µg/kg) and logarithmic transformations were analyzed. Correlation coefficients of 0.63 to 0.73 revealed substantial scatter in the data, but statistically significant results at the 99% confidence level.

Influence of temporal, environmental, and site factors on soil-gas concentrations are reported by soil-gas researchers. Johnson and Perrott (1991) and Smith et al. (1990) noted that soil-gas concentrations corresponded positively with seasonal temperature fluctuations (increased soil-gas concentrations coincide with increased temperatures). Yeates and Nielsen (1987) noted that differences between winter and summer concentrations occur when the frozen soil acts as a “lid,” creating higher soil gas concentrations during winter because release to the atmosphere is inhibited. Jowise et al. (1987) reported that daily average variability for soil gas samples taken from the same drill hole and depth were approximately 7% (they considered this analytical variability) and the relative standard deviation of data from the same gas probes over 4 weeks was 40% (estimated to be 7% analytical and 33% field variability). Many studies noted that the vapor concentrations were lower in dense or fine-grained material and increased in coarse-grained material (Kuhlmeier and Sunderland, 1983 Marrin and Thompson, 1987), Concomitant changes in soil moisture with soil texture may account for some of this effect.

An understanding of the site and the fate and transfer properties of VOCs is critical when interpreting soil-gas data (e.g., Yeates and Nielsen, 1987). The presence and relative concentration of a VOC in the soil gas at the time of sampling will depend on many factors, including the distance from the source of contamination; physiochemical properties, age, and distribution of contaminants soil properties including porosity, water content, permeability, texture, and composition, large-scale geologic or anthropogenic barriers or conduits for diffusion; and environmental factors including temperature, barometric pressure, relative humidity, and wind velocity at the soil surface (Mehran et al., 1983). Given that the vapor phase is subject to short-term variability as a result of changes in temperature and soil water content, soil gas data are best applied to rapid assessment of recent spills or leaky tanks and to trace ground-water contamination under relatively coarse materials (Mehran et al., 1983).

Marks et al. (1989) reported on the correlation between soil gas and ground-water concentrations of benzene and toluene for 48 sites contaminated with petroleum hydrocarbons. Observed soil-gas concentrations were poor predictors of absolute levels of benzene and toluene in ground water. Soil-gas contamination, however, was a relatively good predictor of presence or absence of ground-water contamination based on Chi-square tests that included site-specific and pair-specific factors. Sandy soils had the lowest incidence of false positives and false negatives, and clayey soils had the highest incidence of false results. Where the distance between soil-gas and ground-water samples was less than 1.5 m, the accuracy of predictions was 90% for benzene and 75% for toluene. In contrast, where distances were more than 3 m, the correlation between soil gas and ground water fell to 53% for benzene and 63% for toluene.

A study used to design and implement soil clean-up at the Phoenix-Goodyear Airport (Rosenbloom et al., in press) found long-term soil-gas monitoring provided better estimates of the total mass of TCE than soil-VOC analyses. Soil-gas estimates were 2 to 100 times greater than soil-VOC estimates of the total mass of TCE (which may still have been lower than the actual quantity present). Soil VOCs were measured after field immersion of samples in methanol and thus only the highly contaminated soil samples contributed to the soil-VOC estimates of TCE mass. Total mass estimates were based on an equilibrium, steady-state model, and K_{oc} was used to estimate the sorption coefficient.

Smith et al. (1990) found good correlations between soil gas and shallow ground-water concentrations of TCE at Picanniny Arsenal in New Jersey. However, the concentrations of TCE in soil [measured by the hot methanol extract method of Sawhney et al. (1988)] were 1 to 3 orders of magnitude greater than predicted by soil-gas concentrations and aqueous-phase organic carbon partitioning. The contribution of the aqueous phase (Henry's Law) was less than 3% of the total mass of TCE sorbed. They suggested that the increased concentrations of TCE in soil resulted from nonequilibrium, or slow resorption of TCE from soil organic matter relative to the dissipation by degradation and diffusion of soil gas.

Fiber-optic organic-vapor sensors are a potentially novel method of analyzing soil gas. Lieberman et al. (1991) and Apitz et al. (1992) are using a pulsed-laser fiber-optic fluorescence technique for evaluation of fuels in soil. The fluorescent response of fuels varies with soil surface area of dry soils. Fluorescent response was decreased by the addition of water to sand and increased by the addition of water to clay (Apitz, et al., 1992). Barnard and Walt (1991) report on a fluorphor-polymer combination that responds to the adsorption of organic vapors They chose a system that is sensitive to benzene, toluene, ethylbenzene, xylene, and unleaded gasoline. Calibration for field use was to be assessed in the next phase of their research.

SOIL HEADSPACE METHODS

Soil headspace methods estimate soil VOCs by measuring the concentration of VOCs in the vapor phase above a soil-water mixture. Soil samples are placed in a suitable jar, vial, or plastic bag to which water is added or has already been added, and the headspace concentration is measured generally within a few hours after the sample was collected. The volume of water added is adjusted to create a constant headspace volume for comparison of standards and samples. After being shaken for a short time, a sample of the gas above the soil-water mixture is drawn by syringe and analyzed using a portable or field-deployable GC. If the jar is heated before a sample is drawn, it is called a heated headspace method.

Headspace methods assume rapid equilibrium between soil and water and between water and air. However, soil resorption rates have been shown to depend on VOC residence times after an initial rapid resorption phase and therefore, headspace methods potentially underestimate contaminant concentrations and may result in false negatives (Pavlostathis and Mathavan, 1992). Hewitt et al. (1992) contend that lower values and false negatives are more likely with samples that must be shipped, stored, and subsampled in the laboratory than with headspace analysis that is performed within a day of sample collection. In either case, an exhaustive resorption is not possible using water over a few days time. One may deduce that dynamic (PT) headspace procedures using 40°C and 11 minutes will extract essentially the same fraction of soil VOCs as headspace techniques and this was demonstrated by the comparison of collocated limited disruption PT/GC/MS and HS/GC samples (Hewitt, 1992) in the section “Obtaining and Maintaining VOC Samples.”

Static headspace is generally limited by the sensitivity of the procedure. Increasing the temperature or equilibration time of headspace analysis would be expected to increase the concentration desorbed. Inescapably, the detection limits of headspace analysis are limited by the volume of vapor that can be accommodated by direct injection (as opposed to the PT preconcentration step.)

Crockett and DeHaan (1991) evaluated the effects of various headspace procedures on (unidentified) GC peak heights in eight field-contaminated soils. They showed that increasing the amount of soil in a vial, while holding the headspace essentially constant, increased the vapor concentration of the VOCs although the rate of increase in peak height was less than the rate of soil mass added. Use of a saturated NaCl solution extractant in place of water produced significantly larger peaks for one of the eight test soils, and gave no statistically significant differences in the other soils. Methanol extraction (5 g soil in 5 mL methanol) followed by headspace analysis of an aliquot of the methanol in water showed variable recoveries by compound. As compared to water, methanol appeared to be more efficient in extracting or partitioning the late eluting peaks, but tended to be less efficient in extracting or partitioning the early eluting peaks. The relative effects of methanol as an extractant and on the partitioning of the VOCs between solution and vapor phases cannot be determined from this study. Dry-soil heated headspace analysis was more effective at recovering VOCs than water, although the authors reported analytical problems related to condensed water in the GC as a drawback to heated headspace analysis.

Hewitt et al. (1992) compared PT analyses, using modified VOA vial lids for low-level samples and the methanol extraction for high-level samples (per SW-846 Method 8240), with headspace analyses of laboratory- and field-contaminated soils. Soil samples of 1 to 3 g were extracted in 5 mL water for the low-level PT method, in 20 mL of methanol for the high-level PT method, and in 30 mL of water for the headspace analysis. A field-portable Photo Vac GC with a packed column and a photoionization detector that provided baseline resolution for benzene, toluene, TCE, and trans-1,2-dichloroethene was used for headspace analysis. In laboratory-fortified samples, the correlation between PT analysis and headspace analysis was essentially unity with a slope of 0.948 for a soil that had 1.45% organic carbon. A second soil with 6.69% organic carbon, gave statistically significant (0.5% level) higher concentrations by PT analysis for 19 of 28 compound/spike combinations. A statistically higher value (0.5% level) was found by headspace analysis only once. The higher concentrations measured by PT analysis were reported using both the high-level (methanol) PT procedure and the low-level (with modified sparger lids) PT procedure. The differences were greatest for the two compounds with the highest octanol-water partition coefficients, TCE, and toluene. Benzene and trans-1,2-dichloroethene results showed little difference between headspace and PT analysis at a high spike level. The PT analysis produced statistically higher values of these compounds at low spike concentrations. Analytical precision was better overall with the headspace method.

Results from field-contaminated soil samples showed no significant differences between using PT and headspace analyses when samples were collected by subsampling 2 to 3 g of soil directly from the split-spoon sampler (Hewitt et al. 1992). Field spatial variability created large standard deviations in the data for both methods of analysis and no differences due to the analysis method were observed. A second field-contaminated soil was sampled from a well-mixed bulk sample. It had been contaminated with TCE for at least 18 years and had been shown to exhibit slow aqueous resorption of TCE (soil donated from study of Pavlostathis and Jaglal, 1991). Good sample precision and statistically different means (0.5% level) between the two analysis methods were found. Methanol PT analyses (high-level method) always extracted more TCE than the headspace analysis. The method differences were not attributed to organic carbon levels (only 0.13% organic carbon in this soil), but rather to the slow resorption kinetics. Supporting data demonstrated increased concentrations of TCE in headspace samples as the extraction time (shaking) was increased by successive 10 min intervals.

Zoeller et al. (1992) compared laboratory GC/MS by SW-846 Method 8240 with a field static headspace method that incorporated a portable PT concentrator to lower the detection limits. They reported that for soil contamination of less than 5 ppm, GC/MS results were generally more reproducible than field methods, whereas at higher contaminant levels, field VOC analyses were comparable to GC/MS analyses. The methanol extraction for highly contaminated soil by Method 8240 reduced the precision and raised the detection limits thus generating field and laboratory data of similar quality.

ADVANCED FIELD EXTRACTION AND ANALYSIS METHODS

The concept of on-site, real-time analysis for VOCs and other pollutants using field-deployable GCs is enormously attractive. As a consequence, field analytical capabilities are constantly improving. The positive identification of compounds at low parts per billion soil concentrations is obtained by PT GC/MS. Other GC detectors may meet or exceed the sensitivity of the mass spectrometer, but lack the positive compound identification of the mass spectrometer. Field-deployable mass spectrometers are being developed (e.g., Trainor and Laukien, 1988; Eckenrode and Drew, 1991; Leibman et al., 1991; Wise et al., 1991).

Wise et al. (1991) described investigations of two different types of direct sampling mass spectrometers for use as rapid screening tools for VOCs in soil, water, and air. For water and soil samples, volatiles are purged from the sample without a preconcentration trap. Quantification is accomplished by integrating the area of a reconstructed purge profile for the ions corresponding to the target analytes. Purge efficiencies of 20 to 90% for benzene, TCE, and tetrachloroethene in five different soil matrices were reported relative to a Ph 7 water purge. (These efficiencies were achieved after spiked soils were left undisturbed for at least 1 h prior to analysis and are typical of vacuum-stripping spike efficiencies from soil). Continued research on the development of methods for the identification and quantification of compounds in complex mixtures was suggested.

Two other field-hardy instruments include PT systems. Trainor and Laukien (1988) described a complete GC/MS system that can be operated from a four-wheel drive vehicle. It is based on a quadruple analyzer and an electron-impact ionization source that has both full scan and selected ion monitoring capabilities. A field-portable GC/MS that has three operating modes, including a purge and thermal resorption mode and cryofocusing for light volatiles, has been marketed and discussed at scientific conferences (Eckenrode and Drew, 1991). Both instruments have been described as facilitating screening operations.

Leibman et al. (1991) discussed a transportable GC/MS designed to meet the procedures and QC criteria outlined in SW-846 Method 8260. They reported that the qualitative and quantitative analysis of 68 target compounds and associated internal standards and surrogates can be accomplished in the field in an automated sequence executed every 25 minutes. If only screening is required, a steeper GC oven temperature ramp can reduce the time per sample.

SUMMARY OF FIELD METHODS

Field methods for soil VOCs have the specific advantage of avoiding analyte loss during sample transport and storage. As with other types of analytes, efficiency of time and cost are gained by field analyses. With soil VOCs however, the gains in time and efficiency may need to be converted to increased numbers of sample analyses to provide sufficiently accurate data over spatially variable sites (Mitchell et al., 1993).

Soil gas measurements have many functions, but the uses rely mainly on relative vapor concentrations and site-specific correlations. The vapor phase concentrations are influenced by site, soil, compound, and environmental factors.

Vapors of TCE and gasoline components increase with increasing soil temperature (Smith et al., 1990; Johnson and Perrott, 1991). Higher vapor concentrations of TCE and BTX have been reported to occur in coarse-grained material as opposed to fine-grained material (Kuhlmeier and Sunderland, 1985; Marrin and Thompson, 1987). In general, correlations of soil-gas and ground-water contamination are best in coarse-grained soils and when the soil gas measurement is taken within 15 m of ground water (Marks et al., 1989). Vapor-phase fiber optic sensors are being developed that are expected to facilitate rapid measurement of soil gas for many VOCs (Barnard and Walt, 1991; Lieberman et al, 1991; Apitz et al., 1992).

Soil (static) headspace measurements lack the concentrating step that lowers the detection limit of PT, but have been. widely used for soil-VOC field analyses. Correlations of static soil headspace with soil-VOC measurements have been shown for soils with parts-per-million level contamination (Hewitt et al., 1992; Zoeller et al., 1992), but the soil headspace data may be suppressed in soils high in organic carbon (Hewitt et al., 1992). Also, concentrations of VOCs in soils with slowly desorbing compounds may be underestimated by soil headspace techniques (Hewitt et al., 1992). Addition of NaCl or methanol to the water in a static headspace measurement created mixed results in the recoveries of various VOCs from eight different soils (Crockett and DeHaan, 1991). Dry-soil heated headspace was more effective at recovering VOCs than water, but analytical problems were encountered related to condensation of water in the GC (Crockett and DeHaan, 1991).

Field extraction and analysis techniques that are utilizing detectors of high specificity have been reported. Field-deployable direct sampling mass spectrometers (Wise et al., 1991) and field-deployable PT/GC/MS systems based on a quadruple MS (Trainor and Laukien, 1988; Eckenrode and Drew, 1991) or ion trap detector MS (Liebman et al., 1991) have been undergoing field testing and use. Field instrumentation that can achieve the sensitivity and specificity of SW-846 Method 8240/8260 is eminently expected within a few years.

SECTION 9

CONCLUSIONS

FATE AND TRANSPORT OF SOIL VOCS

A schematic of the generalized fate of soil VOCs is presented in Figure 4. The four phases of soil VOCs are shown in ovals. Processes that affect the total concentration of soil VOCs are in rectangular boxes. Ultimately, losses from the vadose zone occur through volatilization, degradation, or movement to ground water. Nonequilibrium sorption of VOCs, that is, slow sorption or diffusion into microsites, creates an “entrapped” fraction of VOCs ("entrapped" preferred term of Travis and MacInnis [1992]). The quantity of NAPL present in a soil is affected by the amount of NAPL released, the rate of the release, and the soil porosity.

Equilibrium among the phases in the field is not presumed. Measurement of one phase, such as the vapor phase, does not generally provide estimates of the total VOC concentration in the soil (Marrin and Thompson, 1987 Smith et al., 1990; Rosenbloom et al., in press). Both errors in measurement and erroneous assumptions of equilibria contribute to poor predictions.

Estimates of soil sorption of nonpolar VOCs are based on hydrophobic partitioning (K_{oc} values). Such estimates do not account for: (1) sorption by soils low in organic matter (<0.2% organic matter), or (2) long-term nonequilibrium sorption (Smith et al., 1990). Sorption tends to correlate with soil texture or permeability in soils low in organic matter; this was reported in deep deposits in California where high VOC concentrations associated with clay deposits, low VOC concentrations associated with sand deposits (Kuhlmeier and Sunderland, 1985). Residual NAPL saturation may augment the measured soil concentrations at some sites, resulting in an artificially inflated estimate of the sorbed concentration for use in models.

Adsorption of VOCs by dry soil minerals is 2 to 4 orders of magnitude greater than VOC sorption by wet soils (Chiou and Shoup, 1985; Ong and Lion, 1991a). Adsorbed nonpolar VOCs are readily displaced by water molecules, and therefore as the relative humidity approaches 100%, the physically adsorbed VOCs are dislodged (Chiou and Shoup, 1985; Ong and Lion, 1991b). Vapor sorption has not been found under natural field conditions, but the requirement for humid air in vapor extraction systems can be attributed to vapor sorption.

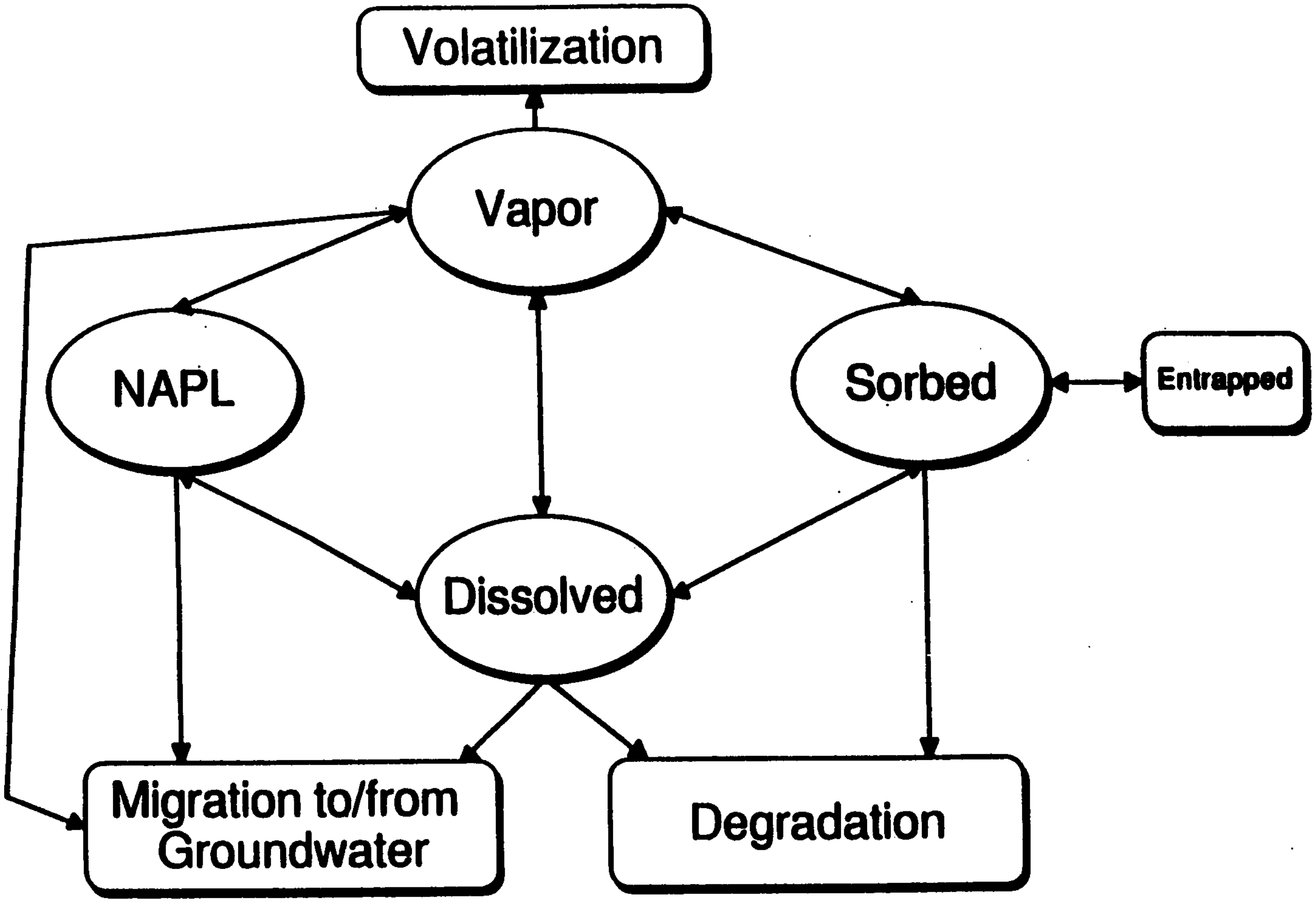

Figure 4. Fate of Soil VOCs

Degradation of naturally occurring VOCs is generally rapid in aerobic soils, mediated by soil microorganisms, and limited by the availability of oxygen (Alexander, 1977; Barker et al., 1987). Halogenated aromatics also biodegrade under aerobic conditions, although the rate is generally slower than that of the unhalogenated analogs (Kobayashi and Rittman, 1982; Wilson et al., 1983). Halogenated aliphatic compounds degrade anaerobically by biotic and abiotic processes, but at rates much slower than observed for the unhalogenated analogs (Smith and Dragun, 1984; Parsons et al., 1985). Evidence for anaerobic co-metabolism of chlorinated solvents, that is, anaerobic degradation of TCE, and similar chlorinated solvents in the ample presence of more easily degraded carbon compounds, has been shown (Cline and Viste, 1985; Wilson and Wilson, 1985).

Movement of VOCs in soil occurs by vapor diffusion, vapor advection, NAPL advection, aqueous diffusion, and aqueous convection. Vapor diffusion is more rapid than liquid diffusion. The rates of vapor diffusion in soil are influenced by chemical concentration gradients, soil permeability, moisture content, temperature, and physiochemical properties of the VOC. Rates of advection are influenced by soil permeability, moisture content, pressure gradients, thermal gradients, gravity, and physiochemical properties of the VOC or the VOC mixture.

Estimates of soil-VOC movement have traditionally been based on vapor diffusion and convection with soil solution. Presumably, vapor diffusion is responsible for the appearance of two fluorocarbons in deep Texas sediments 44 m deep, 40 years after manufacture of the compounds (Weeks et al., 1982). Another example was the appearance of TCE near the soil surface at a site in Arizona; here upward diffusion from contaminated ground water occurred over approximately 40 m in less than 30 years (Marrin and Thompson, 1987). Movement of NAPL spills and leaks in highly permeable soils, however, is probably dominated by NAPL advection. For example, carbon tetrachloride contaminating ground water 177 m deep (time of travel unknown) is believed to have moved by density-driven vapor advection (Falta et al., 1989). At a different site, benzene, toluene, and xylene (solvents less dense than water) were found to have traveled 24.4 m in less than 7 years, presumably moving by gravity-driven NAPL advection (Kuhlmeier and Sunderland, 1985).

Mathematical models of VOC movement are predominantly research tools. Few field data exist with which to calibrate or validate field-scale models. Differences in soil-gas and soil-VOC data generally cannot be resolved by current models. Accurate measurements of soil-VOC concentrations are necessary to support site characterization, remediation design, and monitoring efforts.

SAMPLE SIZE

Soil sample collection for VOCs is confined by the need for minimal soil perturbation and complete avoidance of soil homogenization procedures in an effort to minimize loss of volatile analytes (Hewitt, 1992). Combine this with the constraint of only l to 5 g soil used for PT/GC/MS soil-VOC analysis (SW-846 Method 8240/8260, USEPA, 1986, 1990), and a severe sampling problem results. Approximately 3 mL of unhomogenized soil is collected to represent a core that might be 2.5 x 15 cm in size or almost 300 mL in volume. Many researchers have noted that the small sample size used in a PT/GC/MS analysis aggravates the basic objective of characterizing soil-VOC levels at a field scale (Slater et al., 1983; Bone, 1988; Eynon and Rushneck, 1989; Poulsen and Kueper, 1992; Hewitt et al., 1992). An analysis that utilizes much larger soil samples, or homogenization/subsampling procedures that maintain the VOCs, should receive a high priority in the selection of soil-VOC sampling and analysis methods.

SAMPLE PRESERVATION AND ANALYSIS

Sample preservation for VOCs is critical. There is ample evidence that 20% to 100% of some VOCs are lost from soil stored cold (4 °C) in sealed vials or jars (Maskarinec et al., 1988; Urban et al., 1989; Siegrist and Jenssen, 1990; Zarrabi et al., 1991; Hewitt, 1992; King, 1993). A large part of the losses have been attributed to the laboratory subsampling step (Maskarinec et al., 1988; Zarrabi et al., 1991). Part of the reported losses are likely to arise from volatilization during storage because of the difficulty in ensuring adequate seals of sample jars or vials. Use of a subcorer that has been wiped free of particles to place soil in jars or vials has been shown to overcome the problem of poor seals (Hewitt, 1993). Losses caused by biodegradation, most commonly biodegradation of petroleum compounds, certainly occur in some soils. Degradation can be inferred in samples when the loss of certain compounds are accompanied by a concomitant increase in daughter products during storage (Maskarinec et al., 1989; Jenkins et al., 1993). Halogenated aliphanes, although refractory in aerobic culture studies, may degrade in some seemingly aerobic soils by co-metabolism in the presence of a suitable carbon source (Cline and Viste, 1985). Preservation against degradation may not be necessary for all compounds or in all soils, but refrigeration at 4 °C is not sufficient to halt losses in samples prone to degradation.

The procedures that have been used to quantify soil-VOC losses furnish possible preservation methods: (1) sample collection and storage in vials with lids modified to attach directly to the PT spargeq; (2) use of the modified lids as in

option (1) with the addition of a biocide such as mercuric chloride; (3) sample storage on dry ice;
(4) addition of polymer adsorbent beads, such as Tenax, florisil, or molecular sieve 5A to the soil sample; and (5) placing the sample in methanol in the field.

Sample collection into VOA vials with modified lids, option (l), fails to deal with the sample size problem and may still incur biodegradation losses, especially in samples contaminated by petroleum products. The addition of a biocide, option (2), may reduce biodegradation, but no studies were found that could demonstrate the effectiveness of biocides, and the disposal of biocide-contaminated soil is not trivial.

The effectiveness of dry ice as a preservative, option (3), is described in only one study and data were for TPH, not specific compounds (King, 1993). More data are needed to develop and evaluate preservation by dry ice. Similarly, the use of polymer adsorbent beads, option (4), has been attempted in only one study (Zarrabi et al., 1991). The use of adsorbent beads such as Tenax in a removable trap has not been tried.

Of the preservation methods identified, the immersion of a sample in methanol (5), has the most data on which to base an evaluation. The use of methanol will increase the method detection limits over those attainable by low-level SW-846 Methods 8240/8260. Low-level PT/GC/MS (SW-846 Methods 8240/8260) can detect low µg/kg levels of most VOCs, but the losses that occur before analysis have been observed at 1 to 3 orders of magnitude (Urban et al., 1989; Hewitt, 1992). Therefore, when subsampling steps are included, low-level PT/GC/MS is no more sensitive than methanol immersion or field headspace techniques and losses of the most volatile compounds by conventional PT/GC/MS (e.g., vinyl chloride) are practically guaranteed. No studies have been found comparing low-level PT/GC/MS without subsampling and high-level PT/GC/MS procedures.

PT is not an efficient extraction for soil VOCs That is, spike recoveries are erratic, varying with soil type, compound, and the time of contact between the soil and VOC. The addition of salts or methanol to the purging solution has been investigated, but results are uneven and no overall improvement is noted. Vacuum extraction with a cryogenic trap may be more efficient than PT, but data directly comparing the two procedures are lacking. The addition of surrogates into soil samples and internal standards directly into the GC has been suggested (Ward, 1991). These procedures would expedite monitoring GC/MS performance with the internal standards and establish the use of surrogates to measure the matrix effect.

FIELD METHODS

Factors cited in support of field analyses include: (1) improved time and cost efficiency (Wesolowski and Alwan, 1991; Fribush and Fisk, l992; Cornell, 1992); (2) large analyte losses during sample transport and storage are avoided (Siegrist, 1992), and (3) the large number of samples necessary to accurately characterize a heterogeneous site are only feasible using on-site techniques (Mitchell et al., 1993). The decision to rely on field methods or to corroborate field methods with laboratory methods should be based on data quality objectives, the relative importance of site-specific nonanalytical factors (such as, extreme site or soil heterogeneity), and the stability of the VOCs of interest (e.g., highly volatile vinyl chloride, readily degradable aromatic compounds). The development of performance evaluation materials (PEMs) is critical to the QA/QC of field methods. No soil-VOC methods can be adequately evaluated without accurate reporting of the efficiency of soil spike recoveries and the use of soil PEMs.

Correlations between soil-gas and soil-VOC concentrations are site-specific and often weak. Attempts to predict soil gas from soil-VOC concentrations or soil VOC from soil gas concentrations differ by orders of magnitude (Smith et al., 1990; Rosenbloom et al., in press). These data indicate at least one of the following: (1) assumptions of equilibria among sorbed, vapor, and aqueous phases do not correspond to field conditions, or (2) measurements of either soil-gas or soil-VOC concentrations are inaccurate or not sufficiently representative of the area over which the estimate is applied.

Soil-gas measurements are useful for rapid assessment of localized “hot spots” of contamination or to determine the relative spatial distribution of contaminant concentrations at a site. Soil-gas concentrations have been seen to increase when soil temperatures increase (Smith et al., 1990; Johnson and Perrott, 1991) Erratic soil gas behavior is predicted to occur during periods of rapidly changing barometric pressure as would be associated with large thunderstorms (Massman and Farrier, 1992).

Soil static headspace techniques are essentially PT techniques minus the preconcentration step. Static headspace measurements can be readily performed in the field and the correlation with laboratory PT analyses can be good, if the laboratory subsampling step is avoided (Hewitt et al., 1992). Two examples of soils that had lower recoveries of TCE measured by an (unheated) headspace method than by SW-846 Method 8240 have been reported: (1) soil high in organic matter (6.7% organic carbon) and, (2) soil that exhibited slow resorption of TCE (Hewitt et al., 1992). Therefore, corroboration with laboratory procedures are still necessary. Dry-soil heated headspace has been shown to be a more rigorous extraction procedure than water-heated headspace, but analytical complications of water condensing in the GC were reported (Crockett and DeHaan, 1991).

REFERENCES

Abriola, L. M., and G.F. Pinder. 1985. A multiphase approach to the modeling of porous media contamination by organic compounds 1. Equation development. Water Resour. Res. 21:11-18.

Alexander, M. 1977. Introduction to Soil Microbiology. John Wiley & Sons, Inc., New York

Amin, T.A., and R.S. Narang. 1985. Determination of volatile organics in sediment at nanogram-per-gram concentrations by gas chromatography. Anal. Chem. 57:648-651.

Anderson, T.A, J.J. Beauchamp, and B.T. Walton. 1991. Fate of volatile and semivolatile organic chemicals in soils: Abiotic versus biotic losses. J. Environ. Qual. 20:420-424.

Apitz, S.E., G.A.. Theriault, and S.H. Lieberman. 1992. Optimization of the optical characteristics of a fiber-optic guided laser fluorescence technique for the in situ evaluation of fuels in soils. In, Proceedings of The International Society for Optical Engineering, Vol 1637. January 22, 1992, Los Angeles, CA.

ASTM, 1991. Standard Practice for Sampling Waste and Soils for Volatile Organics, in, 1992 Annual Book of ASTM Standards, Volume 11.04, p. 108-111.

Balfour, W.D., C.E. Schmidt, and B.M. Eklund. 1987. Sampling approaches for the measurement of volatile compounds at hazardous waste sites. J. Hazardous Mater. 14:135-148.

Ball, W.P., and P.V. Roberts. 1991a. Long-term sorption of halogenated organic chemicals by aquifer material. 1. Equilibrium. Environ. Sci. Technol. 25:1223-1236.

Ball, W.P., and P.V. Roberts. 1991b. Long-term sorption of halogenated organic chemicals by aquifer material. 2. Intraparticle diffusion. Environ. Sci. Technol. 25:1237-1249.

Barker, J.F., G.C. Patrick and D. Major. 1987. Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. Ground Water Monitor. Rev. 7(Winter):64-71.

Barnard, S. M., and D.R. Walt. 1991. Fiber-optic organic vapor sensor. Environ. Sci. Technol. 25:1301-1304.

Bear, J. 1979. Hydraulics of Groundwater. McGraw-Hill, New York.

Boethling R.S., and M. Alexander. 1979. Microbial degradation of organic compounds at trace levels. Environ. Sci. Technol. 13:989-991.

Bone, LI. 1988. Preservation techniques for samples of solids, sludges, and nonaqueous liquids. pp. 409-414. In, L.H. Keith, ed., Principles of Environmental Sampling. American Chemical Society, Salem MA.

Bouchard, D.C., S.C. Mravik, and G.B. Smith. 1990. Benzene and naphthalene sorption on soil contaminated with high molecular weight residual hydrocarbons from unleaded gasoline. Chemosphere 21:975-989.

Boyd, S.A., and S. Sun. 1990. Residual petroleum and polychlorobiphenyl oils as sorptive phases for organic contaminants in soils. Environ. Sci. Technol. 24:142-144.

Broholm, K, J.A. Cherry, and S. Feenstra. 1992. Dissolution of heterogeneously distributed solvents residuals. Subsurface Restoration Conference, Dallas, TX, June 21-24, 1992. Environmental Protection Agency, R.S. Kerr Environmental Research Laboratory, Ada, OK.

Brusseau, M.L 1991. Transport of organic chemicals by gas advection in structured or heterogeneous porous media Development of a model and application to column experiments. Water Resour. Res. 27:3189-3199.

Brusseau, M.L, R.E. Jessup, and P.S.C. Rao. 1991. Nonequilibriurn sorption of organic chemicals: Elucidation of rate-limiting processes. Environ. Sci. Technol. 25:134-142.

Brusseau, M.L., and P.S.C. Rao. 1989. Sorption nonideality during organic contaminant transport in porous media. CRC Crit. Rev. Environ. Control 19:33-99.

Charles, M.J., and M.S. Simmons. 1987. Recovery studies of volatile organics in sediments using purge/trap methods. Anal. Chem. 59:1217-1221.

Chiou, C.T. 1989. Theoretical considerations of the partition uptake of nonionic organic compounds by soil organic matter. pp. 1-29. In, Sawhney, B.L., and K Brown, eds., Reactions and Movement of Organic Chemicals in Soils. SSSA Special Publication Number 22. Soil Science Society of America, Inc. Madison, WI.

Chiou, C.T., L.J. Peters, and V.H. Freed. 1979. A physical concept of soil-water equilibria for nonionic organic compounds. Science 206:831-832.

Chiou, C.T., and T.D. Shoup. 1985. Soil sorption of organic vapors and effects of humidity on sorptive mechanism and capacity. Environ. Sci. Technol. 19:1196-1200.

Cline, P.V., and D.R. Viste. 1985. Migration and degradation patterns of volatile organic compounds. Waste Management Res. 3:351-360.

Corapcioglu, M.Y., and A.L. Baehr. 1987. A compositional multiphase model for groundwater contamination by petroleum products 1. Theoretical considerations. Water Resour. Res. 23:191-200.

Cornell, F.W. 1992. Site investigations: The role of field screening and analysis devices. In, Proceedings of R&D ’92, National Research & Development Conference on the Control of Hazardous Material, February 4-6, 1992, San Francisco, CA. Hazardous Material Control Research Institute, Greenbelt, MD.

Crockett, A.B., and M.S. DeHaan. 1991. Field screening procedures for determining the presence of volatile organic compounds in soil. In, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, February 12-14, 1991, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Devitt, D.A,, R.B. Evans, W.A. Jury, T.H. Starks, B. Eklund, and A. Gholson. 1987. Soil Gas Sensing for Detection and Mapping of Volatile Organics. National Well Water Association, Dublin OH. 270 pp.

Dilling, W.L., M.B. Tefertiller, and G.J. Kallos. 1975. Evaporation rates and reactivities of methylene chloride, chloroform, 1,1,l-trichloroethane, trichloroethylene, tetrachloroethylene, and other chlorinated compounds in dilute aqueous solutions. Environ. Sci. Technol. 9:833-838.

Dragun, J. 1988. The Soil Chemistry of Hazardous Materials. Hazardous Materials Control Research Institute, Silver Spring, MD. 458 pp.

Eckenrode, B.A, and R.C. Drew. 1991. An evaluation of field processing and detection limits for volatiles and semi-volatiles using a portable GC/MS system. Pittsburgh Conference, March 4, 1991, Chicago, IL.

Eynon, B.P., and D. Rushneck. 1988. Comparison of results of TCLP and direct analyses of environmental samples. pp. 406-419. In, Proceedings of Eleventh "Annual Analytical Symposium. May 11-12, 1988, Norfolk, VA.

Falta, R.W., I. Javandel, K Pruess, and P.A. Witherspoon. 1989. Density-driven flow of gas in the evaporation of volatile organic compounds. Water Resour. Res. 25:2159-2169.

Fribush, H. M., and J.F. Fisk. 1992. Field analytical methods for Superfund. Environmental Lab 4:36-41.

Garbarini, D.R., and L.W. Lion. 1986. Influence of the nature of soil organics on the sorption of toluene and trichloroethylene. Environ. Sci. Technol. 20:1263-1269.

Gierke, .J.S., N.J. Hutzler, and J.C. Crittenden. 1990. Modeling the movement of volatile organic chemicals in columns of unsaturated soil. Water Resour. Res. 26:1529-1547.

Gierke, J.S., N.J. Hutzler, and D.B. McKenzie. 1992. Vapor transport in unsaturated soil column: Implications for vapor extraction. Water Resour. Res. 28:323-335.

Golding, R.D., M. Favero, and G. Thompson. 1991. Comparison of field headspace versus field soil gas analysis versus standard method analysis of volatile petroleum hydrocarbons in water and soil. In, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, Second International Symposium, February 12-14, 1991, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Hamaker, J.W., and J.M. Thompson. 1972. Adsorption. pp. 49-143. In, Goring C.A.I. and J.W. Hamaker, eds., Organic Chemicals in the Soil Environment. Vol I. Marcel Dekker, New York.

Harmon, T.C., W.P. Ball, and P.V. Roberts. 1989. Nonequilibrium transport of organic contaminants in groundwater. pp. 405-437. In, Sawhney B.L. and K Brown, eds., Reactions and Movement of Organic Chemicals in Soils. SSSA Spec. Publ. 22. Soil Science Society of America, Inc. Madison, WI.

Hartmans, S., and J.A.M. de Bent. 1992. Aerobic vinyl chloride metabolism in Mycobacterium aurum L1. Applied Environ. Microb. 58:1220-1226.

Hassett, J.J. and W.L. Banwart. 1989. The sorption of nonpolar organics by soils and sediments. In, Sawhney, B.L., and K Brow eds., Reactions and Movement of Organic Chemicals in Soils. SSSA Special Publication Number 22. Soil Science Society of America, Inc. Madison, WI.

Hassett, J.J., W.L Banwart, and R.A. Griffin. 1983. Correlation of compound properties with sorption characteristics of nonpolar compounds by soils and sediments: Concepts and limitations. p. 161-178. In, C.W. Francis and S.I. Auerbach eds., Environment and Solid Wastes. Butterworths, Boston.

Hawthorne, S.B., D.J. MiIler, J.J. Langenfeld, and M.D. Burford. 1992. Physiochemical and instrumental factors that can control SFE recoveries of neutral and ionic pollutants from environmental samples. Abstract No 679. Pittsburgh Conference Book of Abstracts. PittCon’92. March 9-12, 1992. New Orleans, LA.

Hewitt, A.D. 1992. Review of current and potential future sampling practices for volatile organic compounds in soils. Proceedings from the 16th Annual Army Environmental R&D Symposium, 23-25 June 1992, Williamsburg, VA.

Hewitt, A.D. 1993. Vapor fortification A method to prepare quality assurance soil samples for the analysis of volatile organic compounds. Abstract from the National Symposium on Measuring and Interpreting VOCs in soils: State of the art and research needs. January 12-14, 1993, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Hewitt, AD., P. H. Miyares, D.C. Leggett, and T.F. Jenkins. 1992. Comparison of analytical methods for determination of volatile organic compounds in soils. Environ. Sci. Technol. 26:1932-1938.

Hiatt, M.H. 1981. Analysis of fish and sediment for volatile priority pollutants. Anal. Chem. 53:1541-1543.

Hillel, D. 1971. Soil and Water. Academic Press, Inc., New York. 288 pp.

Holtz, R.D. and W.D. Kovacs. 1981. An Introduction to Geotechnical Engineering. Prentice-Hall Inc. Englewood Cliffs, NJ.

Howard, P.H. 1990. Handbook of Environmental Fate and Exposure Data for Organic Chemicals. Vols I, II, and III. Lewis Publishers, Inc. Chelsea, MI. 574 pp. Vol I; 684 pp. Vol II; 546 pp. Vol III.

Jenkins, R.A., C.K Bayne, M.P. Maskarinec, L.H. Johnson, S.K Holladay, and B.A. Tomkins. 1993. Experimental determination of pre-analytical holding times for volatile organics in selected soils. Abstract from the National Symposium on Measuring and Interpreting VOCs in soils: State of the art and research needs. January 12-14, 1993, Las Vegas, NV. U.S. Envirorunental Protection Agency, Las Vegas, NV.

Jenkins, T.F. and P.W. Schumacher. 1987. Comparison of methanol and tetraglyme as extraction solvents for determination of volatile organics in soil. Special Report 87-22. US Army Corps of Engineers, Cold Regions Research & Engineering Laboratory. Hanover, NH.

Jiang, K, and R.G. Westendorf. 1992. A comparison of sample heating techniques used in purge and trap gas chromatography. Abstract no. 895. Pittsburgh Conference Book of Abstracts. PittCon'92. March 9-12, 1992, New Orleans, LA.

Johnson, R.L., and M. Perrott. 1991. Gasoline vapor transport through a high-water-content soil. J. Contaminant Hydol. 8:317-334.

Jowise, P.P., J.D. Villnow, LI. Gorelik, and J.M. Ryding. 1987. Comparative analysis of soil gas sampling techniques. In, Proceeding of the National Conference on Hazardous Wastes and Hazardous Materials. Washington DC, U.S. Environmental Protection Agency, Washington DC.

Jurinak, J.J., and D.H. Vohnan. 1957. Application of Brunauer, Emmett and Teller equation to ethylene dibromide adsorption by soils. Soil Sci. 83:487-496.

Jury, W.A., D. Russo, G. Streile, and H. El Abd. 1990. Evaluation of volatilization by organic chemicals residing below the soil surface. Water Resour. Res. 26:13-20.

Jury, W.A., D. Russo, G. Streile, and H. El Abd. 1992. Correction to "Evaluation of volatilization by organic chemicals residing below the soil surface." Water Resour. Res. 28:607-608.

Jury, WA., W.F. Spencer, and W.J. Farmer. 1983. Behavior assessment model for trace organics in soil: I. Model description. J. Environ. Qual. 12:558-564.

Jury, W.A., W.F. Spencer, and W.J. Farmer. 1984. Behavior assessment model for trace organics in soil: IV. Review of experimental evidence. J. Environ. Qual. 13:580-586.

Karickhoff, S.W. 1984. Organic pollutant sorption in aquatic systems. J. Hydraulic Eng. 110:707-735.

Karickhoff, S.W., D.S. Brow and T.A. Scott. 1979. Sorption of hydrophobic pollutants on natural sediments. Water Res. 13:241-248.

Katyal, A.K, J.J. Kaluarachchi, and J.C. Parker. 1991. MOFAT: A Two-Dimensional Finite Element Program for Multiphase Flow and Multicomponent Transport. Program Documentation and User's Guide. EPA/600/2-91/020. U.S. Environmental Protection Agency, Ada, OK

Kiang, P. H., and R.L. Grob. 1986. A headspace technique for the determination of volatile compounds in soil. J. Environ. Sci. Health A21:71-1OO.

King, P.H. 1993. Evaluation of sample holding times and preservation methods for gasoline in fine-grained sand. Abstract from the National Symposium on Measuring and Interpreting VOCs in soils: State of the art and research needs. January 12-14, 1993, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Kobayashi, H., and B.E. Rittmann. 1982. Microbial removal of hazardous organic compounds. Environ. Sci. Technol. 16: 170A-183A.

Kreamer, D.K, E.P. Weeks, and G.M. Thompson. 1988. A field technique to measure the tortuosity and sorption-affected porosity for gaseous diffusion of materials in the unsaturated zone with experimental results from near Barnwell, South Carolina. Water Resour. Res. 24:331-341.

Kuhlrneier, P.D., and G.L. Sunderland. 1985. Distribution of volatile aromatics in deep unsaturated sediments. In, Proceedings of the Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone, November 19-21, Stapleton Plaza Hotel, Denver, CO. National Water Well Association, Dublin, OH.

Lappala, E. G., and G.M. Thompson. 1983. Detection of groundwater contamination by shallow soil gas sampling in the vadose zone. In, Proceedings of the Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone. Dec. 8-10, 1983. Las Vegas, NV. National Well Water Association, Dublin, OH.

Leibman, C.P., D. Dogruel, and F.P. Vandemeer. 1991. Transportable GC/ion trap mass spectrometry for trace field analysis of organic compounds. Field Screening Methods for Hazardous Wastes and Toxic chemicals, February 12-14, 1991, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Lesage, S., and R.E. Jackson. 1992. Practical organic analytical chemistry for hazardous waste site investigations. In, S. Lesage and R.E. Jackson (eds.), Groundwater Contamination and Analysis at Hazardous Waste Sites. Marcel Dekker, Inc., New York NY.545 pp.

Lesnik, B. 1993. New SW-846 methods for the analysis of conventional and non-conventional volatile organics in solid matrices. Abstract from the National Symposium on Measuring and Interpreting VOCs in soils: State of the art and research needs. January 12-14, 1993, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Lewis, T.E., A.B. Crockett, R.L. Siegrist, and K Zarrabi. 1991. Soil sampling and analysis for volatile organic compounds. EPA/540/4-91/001. U.S. Environmental Protection Agency, Cincinnati, OH. 24 pp.

Lieberman, S.H., G.A. Theriault, S.S. Cooper, P.G. Malone, R.S. Olsen, and P.W. Lurk. 1991. Rapid, subsurface, in situ field screening of petroleum hydrocarbon contamination using laser induced fluorescence over optical fibers. In Proceeding of Field Screening Methods for Hazardous Wastes and Toxic Chemicals, February 12-14, 1991, Las Vegas, NV.

Lyman, W.J., W.F. Reehl, and D.H. Rosenblatt. 1990. Handbook of Chemical Property Estimation Methods. American Chemical Society. Washington DC.

Mabey, W., and T. Mill. 1978. Critical review of hydrolysis of organic compounds in water under environmental conditions. J. Phys. Chem Ref. Data 7:383-415.

Marks, B.J., D.A Selby, R.E. Hinchee, and G. Davitt. 1989. Soil gas and groundwater levels of benzene and toluene--Qualitative and quantitative relationships. In, Proceedings of the Conference on Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration. National Water Well Association, Nov 15-17, 1989, Houston TX.

Marrin, D.L., and H.B. Kerfoot. 1988. Soil-gas surveying techniques. Envirom Sci. Technol. 22:740-745.

Marrin, D.L., and G.M. Thompson. 1987. Gaseous behavior of TCE overlying a contaminated aquifer. Ground Water 25:21-27.

Maskarinec, M.P., LH. Johnson, and C.K Bayne. 1989. Preparation of reference water and soil samples for performance evaluation of volatile organic analysis. J. Assoc. Off. Anal. Chem. 72:823-827.

Maskarinec, M.P., L.H. Johnsou and S.K Holladay. 1988. Recommendations for holding times of environmental samples. In, Proceedings Waste Testing and Quality Assurance. Vol II. July 11-15, 1988. The Westin Hotel, Washington DC.

Maskarinec, M.P., LH. Johnson, S.K Holladay, R.L Moody, C.K Bayne, and RA Jenkins. 1990. Stability of volatile organic compounds in environmental water samples during transport and storage. Environ. Sci. Technol. 24:1665-1670.

Massmann, J., and D.F. Farrier. 1992. Effects of atmospheric pressures on gas transport in the vadose zone. Water Resour. Res. 28:777-791.

Mehran, M., MJ. Nimmons, and E.B. Sirota, 1983. Delineation of underground hydrocarbon leaks by organic vapor detection. In, Management of Uncontrolled Hazardous Waste Sites, October 31-November 2, 1983, Washington DC, Hazardous Materials Control Research Institute, Silver Spring, MD.

Mendoza, CA, and E.O. Frind. 1990. Advective-dispersive transport of dense vapors in the unsaturated zone 1. Model development. Water Resour. Res. 26:379-387.

Mendoza, CA, and T.A. McAlary. 1990. Modeling of ground-water contamination caused by organic solvent vapors. Ground Water 28:199-206.

Metcalfe, D. E., and G.J. Farquhar. 1987. Modeling gas migration through unsaturated soils from waste disposal sites. Water, Air, and Soil Pollution 32:247-259.

Millington, RJ., and J.P. Quirk. 1961. Permeability of porous solids. Trans. Faraday Soc. 57:1200-1207.

Mingelgrin, U., and Z. Gerstl. 1983. Reevaluation of partitioning as a mechanism of nonionic chemicals adsorption in soils. J. Environ. Qual. 12:1-11.

Munz, C., and P.V. Roberts. 1987. Air-water phase equilibria of volatile organic solutes. Journal Am. Water Works Assoc. 79:62-69.

Nadeau, R.J., and F. Tomaszewicz. 1988. Influence of naturally occurring volatile compounds on soil gas results. In, Proceedings of Field Screening Methods for Hazardous Waste Site Investigations, October 11-13, 1988. U.S. Environmental Protection Agency, Las Vegas, NV.

Ong, S.K, and L.W. Lion. 1991a. Mechanisms for trichloroethylene vapor sorption onto soil minerals. J. Environ. Qual. 20:180-188.

Ong, S.K, and LW. Lion. 1991b. Trichloroethylene vapor sorption onto soil minerals. Soil Sci. Soc. Am. J. 55:1559-1568.

Pankow, J.P., and M.E. Rosen. 1988. Determination of volatile compounds in water by purging directly to a capillary column with whole column cryotrapping. Environ. Sci. Technol. 22:398-405.

Parker, L.V., AD. Hewitt and T.E. Jenkins. 1990. Influence of casing materials on trace-level chemicals in well water. Ground Water Monitor. Rev. 10(Spring):146-156.

Parker, LV. 1992. Suggested guidelines for the use of PTFE, PVC, and stainless steel in samplers and well casings. In, Nielsen D.M. and M.N. Sara, eds., Current Practices in Ground Water and Vadose Zone Investigations. ASTM STP 1118. American Society for Testing and Materials, Philadelphia, PA. 431 pp.

Parsons, F., G.B. Lage, and R. Rice. 1985. Biotransformation of chlorinated organic solvents in static microcosms. Environ. Toxic. Chem. 4:739-742.

Pavlostathis, S.G., and K Jaglal. 1991. Desorptive behavior of trichloroethylene in contaminated soil. Environ. Sci. Technol. 25:274-279.

Pavlostathis, S.G., and G.N. Mathavan. 1992. Resorption kinetics of selected volatile organic compounds from field contaminated soils. Environ. Sci. Technol. 26:532-538.

Pignatello, J.J. 1990a. Slowly reversible sorption of aliphatic halocarbons in soils. I. Formation of residual fractions. Environ. Toxic. Chem. 9:1107-1115.

Pignatello, J.J. 1990b. Slowly reversible sorption of aliphatic halocarbons in soils. II. Mechanistic aspects. Envirom Toxic. Chem. 9:1117-1126.

Pinder, G.F., and LM. Abriola. 1986. On the simulation of nonaqueous phase organic compounds in the subsurface. Water Resour. Res. 22:109S-119S.

Piwoni. M.D., and P. Banerjee. 1989. Sorption of volatile organic solvents from aqueous solution onto subsurface solids. J. Contain. Hydrol. 4:162-179.

Plumb, R.H. 1991. The occurrence of Appendix IX organic constituents in disposal site ground water. Ground Water Monitoring Rev. ll(Spring):157-164.

Poe, S.H., KT. Valsaraj, L.J. Thibodeaux, and C. Springer. 1988. Equilibrium vapor phase adsorption of volatile organic chemicals on dry soils. J. Hazardous Mater. 19:17-32.

Poulsen, M.M., and B.H. Kueper. 1992. A field experiment to study the behavior of tetrachloroethylene in unsaturated porous media. Environ. Sci. Technol. 26:889-895.

Reisinger, H.J., D.R. Burris, LR. Cessar, and G.D. McCleary. 1987. Factors affecting the utility of soil vapor assessment data. In, Proceedings of the First National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods, May 18-21, 1987, Las Vegas, NV. National Water Well Association, Dublin, OH.

Reynolds, G.W., J.T. Hoff, and R.W. Gillham. 1990. Sampling bias caused by materials used to monitor halocarbons in groundwater. Environ. Sci. Technol. 24:135-142.

Rhue, R.D., P.S.C. Rao, and R.E. Smith. 1988. Vapor-phase adsorption of alkylbenzenes and water on soil and clays. Chemosphere 17:727-741.

Rosenbloom, J., P. Mock P. Lawson, J. Brown, and H.J. Turin. in press. Site-specific soil clean-up levels for volatile organic compounds. Groundwater.

Roy, W.A., and R.A Griffin. 1990. Vapor-phase interactions and diffusion of organic solvents in the unsaturated zone. Environ. Geol. Water Sci. 15:101-110.

Rutherford, D.W., C.T. Chiou, and D.E. Kile. 1992. Influence of soil organic matter composition on the partition of organic compounds. Environ. Sci. Technol. 26:336-340.

Sawhney, B.L., JJ. Pignatello, and S.M. Steinberg. 1988. Determination of 1,2-dibromoethane (EDB) in field soils: Implications for volatile organic compounds. J. Environ. Qual. 17:149-152.

Schwarzenbach, R.P., and J. Westall. 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. Environ. Sci. Technol. 15:1360-1367.

Shoemaker, C.A., T.B. Culver, L.W. Lion, and M.G. Peterson. 1990. Analytical models of impact of two-phase sorption on subsurface transport of volatile chemicals. Water Resour. Res. 26:745-758.

Siegrist, R.L 1993. VOC measurement in soils: The nature and validity of the process. Abstract from the National Symposium on Measuring and Interpreting VOCs in soils: State of the art and research needs. January 12-14, 1993, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Siegrist, R.L. 1992. Volatile organic compounds in contaminated soils: The nature and validity of the measurement process. J. Hazard. Mat. 29:3-15.

Siegrist, R.L., and P.D. Jenssen. 1990. Evaluation of sampling method effects on volatile organic compound measurements in contaminated soils. Environ. Sci. Technol. 24:1387-1392.

Silka, L.R. 1988. Simulation of vapor transport through the unsaturated zone–Interpretation of soil-gas surveys. Ground Water Monitor. Rev. 8 (Spring):l15-123.

Sims, R.C. 1990. Soil remediation techniques at uncontrolled hazardous waste sites. A critical review. J. Air Waste Manage. Assoc. 40:704-732.

Slater, J.P., F.R. McLaren, D. Christenson, and D. Dineen. 1983. Sampling and analysis of soil for volatile organic compounds: I. Methodology Development. In, Proceedings of the Conference on Characterization and Monitoring of the Vadose (Unsaturated) Zone. Dec. 8-10, 1983. Las Vegas, NV. National Well Water Association, Dublin, OH.

Sleep, B.E., and J.F. Sykes. 1989. Modeling the transport of volatile organics in variably saturated media. Water Resour. Res. 25:81-92.

Smith, J.A., C.T. Chiou, J.A. Kammer, and D.E. Kile. 1990. Effect of soil moisture on the sorption of trichloroethene vapor to vadose-zone soil at Picatinny Arsenal, New Jersey. Environ. Sci. Technol. 24:676-683.

Smith, L.R., and J. Dragun. 1984. Degradation of volatile chlorinated aliphatic priority pollutants in groundwater. Environ. Int. 10:291-298.

Spencer, W.F., and M.M. Cliath. 1970. Resorption of lindane from soil as related to vapor density. Soil Sci. Soc. Am. Proc. 34:574-578.

Spittler, T. 1992. Field analysis. An interview with Dr. Thomas Spittler. Analytical Consumer. March 1992, pp. 9-10.

Steinberg S.M. 1992. Persistence of several volatile aromatic and halogenated hydrocarbons in a low organic carbon calcareous soil. Chemosphere 24:1301-1315.

Steinberg S.M., J.J. Pignatello, and B.L Sawhney. 1987. Persistence of 1,2-dibromoethane in soils: Entrapment in intraparticle micropores. Environ. Sci. Technol. 21:1201-1208.

Sulfita, J.M. 1989. Microbial ecology and pollutant biodegradation in subsurface ecosystems. Chapter 7. In, Transport and fate of contaminants in the subsurface. Seminar Publication. EPA/625/4-89/O19. U.S. Environmental Protection Agency, Cincinnati, OH.

Swallow, KC. 1992. Nonpriority pollutant analysis and interpretation. In, S. Lesage and R.E. Jackson (eds.), Groundwater Contamination and Analysis at Hazardous Waste Sites. Marcel Dekker, Inc., New York, NY.545 pp.

Taylor, S.A., and G.L Ashcroft. 1972. Physical Edaphology. The physics of irrigated and nonirrigated soils. W.H. Freeman and Company, San Francisco, CA 533 pp.

Thorstenson, D.C., and D.W. Pollock. 1989. Gas transport in unsaturated zones: Multicomponent systems and the adequacy of Fick’s Laws. Water Resour. Res. 25:477-507.

Trainor, T.M., and F.H. Laukien. 1988. Design and performance of a mobile mass spectrometer developed for environmental field investigations. In, Field Screening Methods for Hazardous Waste Site Investigations, October 11-13, 1988, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Travis, C.C., and J.M. MacInnis. 1992. Vapor extraction of organics from subsurface soils, Is it effective? Environ. Sci. Technol. 26:1885-1887.

Urban, M.J., J.S. Smith, E.K Schultz, and R.K Dickinson. 1989. Volatile organic analysis for a soil, sediment or waste sample. In, Proceedings of the Fifth Annual Waste Testing and Quality Assurance Symposium, July 24-28, 1989, Washington DC. U.S. Environmental Protection Agency, Cincinnati, OH.

USEPA. 1982. Methods for Organic Chemical Analysis of Municipal and Industrial Wastes. Test Method 624, Purgeables. EPA-600/4-82-057. U.S. Environmental Protection Agency, Cincinnati, OH.

USEPA. 1986. Test Methods for Evaluating Solid Waste, SW-846. 3rd Edition. Office of Solid Waste and Emergency Response. U.S. Environmental Protection Agency, Washington DC.

USEPA. 1990. Update II to SW-846. Methods Section. Office of Solid Waste. U.S. Environmental Protection Agency, Washington DC.

USEPA. 1991. Statement of Work for Organics Analysis. USEPA Contract Laboratory Program. Document Number OLMO1.8, Revision 8, Augusg 1991. U.S. Environmental Protection Agency, Research Triangle Park NC.

van Ee, J.J., L.J. Blume, and T.H. Starks. 1990. A Rationale for the Assessment of Errors in the Sampling of Soils. EPA/600/4-90/013. Office of Research and Development, Environmental Monitoring Systems Laboratory, Las Vegas, NV.

Vogel, T.M., C.S. Criddle, and P.L. McCarty. 1987. Transformations of halogenated aliphatic compounds. Environ. Sci. Technol. 21:722-736.

Voudrias, E.A., and M. Reinhard. 1986. Abiotic organic reactions at mineral surfaces. In, Davis, J.A. and KF. Hayes, eds., Geochemical Processes at Mineral Surfaces. American Chemical Society, Washington, DC. pp. 462-486.

Ward, S.E. 1991. GC/MS VOC method improvements. Environmental Lab 3:42-45.

Weeks, E.P., D.E. Earp, and G.M. Thompson. 1982. Use of atmospheric fluorocarbons F-11 and F-12 to determine the diffusion parameters of the unsaturated zone in the southern high plains of Texas. Water Resour. Res. 18:1365-1378.

Wesolowski, D., and A. Alwan. 1991. Field measurement of organic compounds by gas chromatography. In, Simmons, M.S. ed., Hazardous Waste Measurements. Lewis Publishers, Chelsea, MI. 315 pp.

Westendorf, R.G. 1992. Theory and operation of water management methods in purge and trap gas chromatography. Abstract no. 893. Pittsburgh Conference Book of Abstracts. PittCon’92. March 9-12, 1992. New Orleans, LA.

Wilson, J.T., and J.F. McNabb. 1983. Biological transformation of organic pollutants in groundwater. EOS 64(33).

Wilson, J.T., J.F. McNabb, D.L. Balkwill, and W.C. Ghiorse. 1983. Enumeration and characterization of bacteria indigenous to a shallow water-table aquifer. Groundwater 21:134-142.

Wilson, J.T., and B.H. Wilson. 1985. Biotransformation of trichloroethylene in soil. Applied and Environ. Microb. 49:242-243.

Wise, M.B., G.B. Hunt C.V. Thompson, M.V. Buchanan, and M.R. Guerin. 1991. Screening volatile organics by direct sampling ion trap and glow discharge mass spectrometry. In, Field Screening Methods for Hazardous Wastes and Toxic Chemicals, February 12-14, 1991, Las Vegas, NV. U.S. Environmental Protection Agency, Las Vegas, NV.

Yeates, G.L., and D.M. Nielsen. 1987. Design and implementation of an effective soil gas monitoring program for four-dimensional monitoring of volatile organics in the subsurface. In Proceedings of the NWWA Focus Conference on Ground Water Issues, April 21-23, 1987, Indianapolis, IN.

Zarrabi, K, C.K Fitzsimmons, S. Ward, S. Butala, T.E. Lewis, J.R. Parolini, V.G. King, and T.W. Nail. 1991. Investigation of sample and sample handing techniques for the measurement of volatile organic compounds in soil. (In preparation for submission to journals)

Zoeller, A., X. Zhang, and E. Overton. 1992. VOC analyses of contaminated sediments using a field GC system and conventional GC/MS: How good are the results? Abstract No. 144P. In, Pittsburgh Conference Book of Abstracts, PittCon'92. March 9-12, 1992. New Orleans, LA.

☆U.S. GOVERNMENT PRINTING OFFICE: 1993 - 750-002/80278

United States
Environmental Protection Agency
Center for Environmental Research Information
Cincinnati, OH 45288

Please make all necessary changes on the below label, detach or copy, and return to the address in the upper left-hand corner.

If you do not wish to receive these reports CHECK HERE ☐; detach, or copy this cover, and return to the address in the upper left-hand corner.

BULK RATE
POSTAGE & FEES PAID
EPA
PERMIT No. G-35

Official Business
Penalty for Private Use
$300

EPA/600/R-93/l40