



**US Army Corps
of Engineers**
Waterways Experiment
Station

Installation Restoration Research Program

Thermal Desorption VOC Sampler: Improvements and Field Trial Performance (Dover AFB)

*by Karen F. Myers, James M. Brannon, Richard A. Karn,
Cynthia B. Price, Dan Y. Eng, Ann B. Strong*



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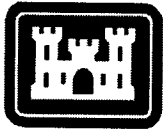
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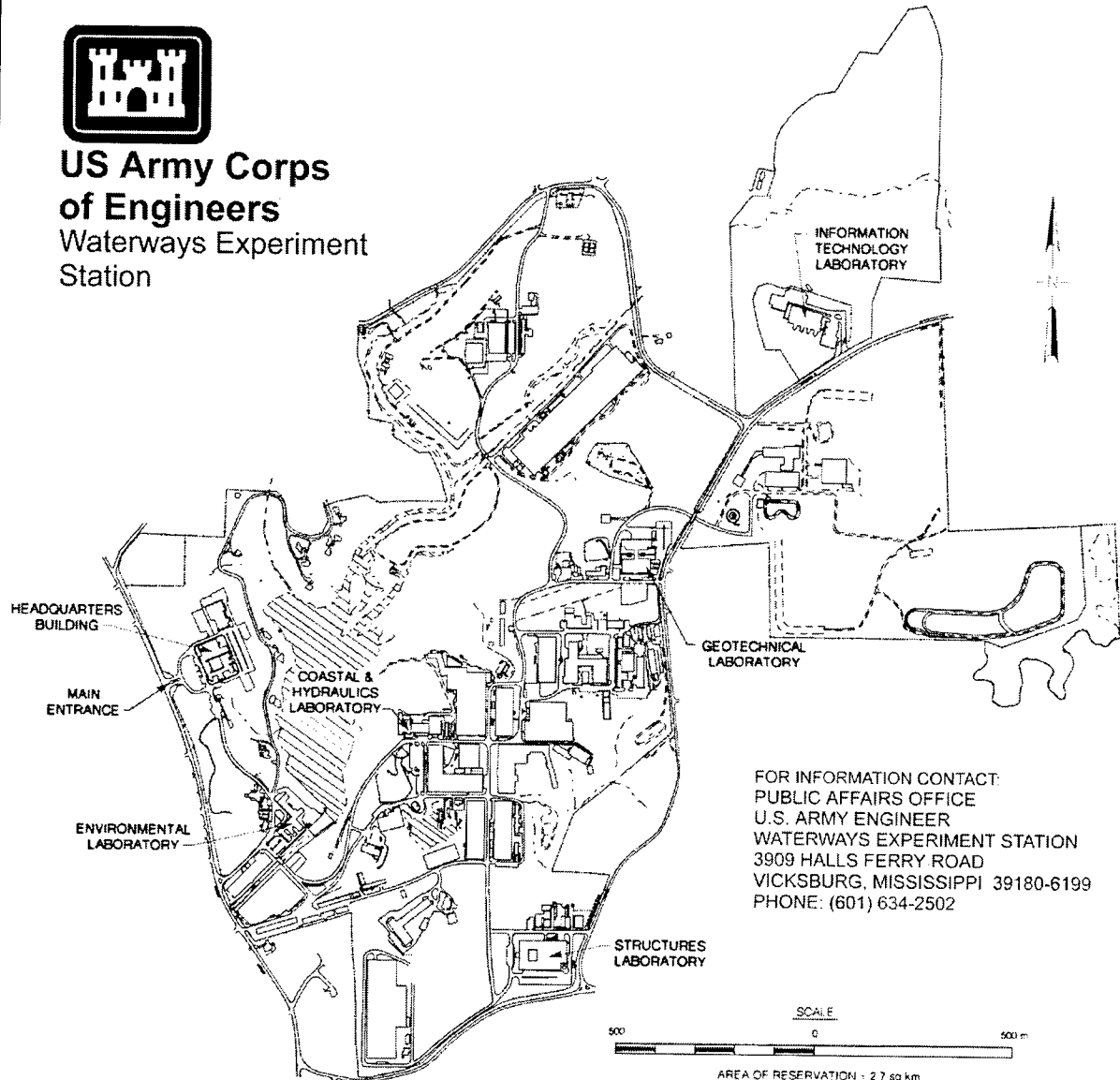
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Contents

Preface	v
Conversion Factors, Non-SI to SI Units of Measurement	vii
1—Introduction	1
Background	1
Objectives	2
2—Experimental Section	3
Thermal Desorption VOC Sampler Description	3
Analytes	5
Methods	6
3—Results and Discussion	11
Laboratory Results	11
Field Results	13
4—Conclusions	24
SF 298	

List of Tables

Table 1. Samples Taken in Hole 17, Dover Air Force Base	8
Table 2. Samples Taken in Hole 18, Dover Air Force Base	8
Table 3. Samples Taken in Hole 19, Dover Air Force Base	9
Table 4. Percent Recoveries of Expanded Target Compound List From Soils at 10 and 20 Percent Moisture	12
Table 5. Percent Recoveries of Original Target Compound List From Soils at 10 and 20 Percent Moisture	12
Table 6. Percent Recoveries From 500-ng Spikes After 30 min of Sampling From the Tube Evaluation Test	13

Table 7.	Dover AFB VOC Sampler Field Soil Desorption Concentrations for Hole 19 Compared With Laboratory Soil Extractions by EPA Method 8260 and to Field Methanol Extractions Analyzed by EPA Method 8260 for Verification Hole 20	15
Table 8.	VOC Concentration Comparisons From Hole 19 and Hole 20	17
Table 9.	Concentrations of VOCs Desorbed From Soils From Hole 17 Using the VOC Sampler and Analyzed by GC/PID	19
Table 10.	Concentrations of VOCs Desorbed From Soils From Hole 18 Using the VOC Sampler and Analyzed by GC/PID	20
Table 11.	Comparison of VOC Sampler Soil Gas Concentrations From Hole 19 to Laboratory Soil Extractions by GC/MS and to Methanol Soil Field Extractions Analyzed by EPA Method 8260 From Hole 20	21
Table 12.	Vapor Samples From Holes 17 and 18 by Field GC/PID	22

Preface

The work reported herein was funded by the U.S. Army Environmental Quality Technology (EQT) Research Program, Work Unit AF25-CT-005, and by the Strategic Environmental Research and Development Program (SERDP). Mr. George Robitaille was the EQT Technical Monitor for the U.S. Army Environmental Center, and Dr. M. John Cullinane, U.S. Army Engineer Waterways Experiment Station (WES), was the Program Manager. Dr. John Harrison was the SERDP Program Manager.

Personnel who cooperated in the execution of the study and the preparation of this report included Ms. Karen F. Myers, Mr. Richard A. Karn, and Ms. Ann B. Strong, Environmental Chemistry Branch (ECB), Environmental Engineering Division (EED), Environmental Laboratory (EL), WES; Dr. James M. Brannon and Ms. Cynthia B. Price, Ecosystem Processes and Effects Branch (EPEB), Environmental Processes and Effects Division (EPED), EL; and Mr. Dan Y. Eng, Design and Development Branch (JD), Instrumentation Systems Development Division (ISDD), Information Technology Laboratory (ITL), WES. The authors also wish to acknowledge Messrs. Jeff F. Powell, Don Harris, and Karl F. Konecny for technical support and Dr. William M. Davis for ion trap MS analysis during the field study. The report was reviewed by Drs. Judith C. Pennington and William M. Davis, EPEB.

This report was prepared under the general supervision of Ms. Strong, Chief, ECB; Mr. Norman R. Francingues, Jr., Chief, EED; Dr. Richard E. Price, Chief, EPED; Dr. John Harrison, Director, EL; Mr. Bobby E. Reed, Chief, JD; Mr. George P. Bonner, Chief, ISDD; and Dr. N. Radhakrishnan, Director, ITL.

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(Dover AFB)," Technical Report IRRP-98-1, U.S. Army
Engineer Waterways Experiment Station, Vicksburg, MS.

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Conversion Factors, Non-SI to SI Units of Measurement

Non-SI units of measurement used in this report can be converted to SI units as follows:

Multiply	By	To Obtain
feet	0.3048	meters
inches	2.54	centimeters

1 Introduction

Background

The U.S. Department of Defense has become increasingly concerned with the environmental fate and remediation of the by-products of the day-to-day operation of military motor pools, machine shops, and cleaning facilities, operations that routinely use organic solvents and fuel. The first steps to remediation are identifying the type of contamination, defining its spatial distribution, and locating its point of origin. Conventional technology requires laboratory analysis of soil samples taken from multiple borings across the site, operations that are time-consuming and expensive.

Researchers at the U.S. Army Engineer Waterways Experiment Station (WES) have developed a volatile organic compound analysis system (VOC sampler) for the site characterization and analysis penetrometer system (SCAPS) program for onsite detection of low concentrations of volatile compounds. Utilizing the principle of thermal desorption used in gas chromatography for soil analysis, volatilized compounds are transferred to the surface where they are trapped on an absorbent and later desorbed into a gas chromatograph (GC) for identification and quantitation. In operation, the VOC sampler assays discrete volumes of soil by heating and desorbing the volatile compounds, then ejecting the spent sample and pushing to successive depths where additional samples may be taken. When combined with an onsite laboratory equipped with a field portable GC, the SCAPS system offers a potentially viable alternative to conventional site characterization methods.

VOC sampler performance was evaluated in the laboratory¹ in order to optimize the system and the operating conditions. Results from the initial laboratory studies were used to select operating conditions, improve the probe design prior to field trials, and identify possible long-term enhancements to probe capability.

¹ Myers, K. F., Brannon, J. M., Karn, R. A., Price, C. B., Eng, D. Y., Strong, A. B., and Cooper, S. S. (1995). "Laboratory evaluation of a volatile organic compound analysis system for the site characterization and analysis penetrometer system," Technical Report IRRP-95-3, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

Objectives

The objectives of the fiscal year 1994 (FY94) Strategic Environmental Research and Development Program and FY95 U.S. Army Environmental Quality Technology Research Program were twofold. The first objective was to improve the sampler mechanically in order to simplify operation and to evaluate additional target analytes. The second objective was to verify the mechanical and chemical functioning of the VOC sampler in the vapor and soil sampling modes and compare the sampler results with validation sample results from traditional laboratory analyses. Soil sampling was conducted above and below groundwater level, in the saturated zone, while soil vapor sampling was conducted only in the vadose zone.

2 Experimental Section

Thermal Desorption VOC Sampler Description

VOC probe

The probe design consists of a series of concentric steel cylinders with gas channels and piston chambers made tight by O-rings (Figure 1). A central actuator rod is held in place by locking lugs during the closed position. The sample chamber is heated by a nichrome-wrapped ceramic heater fitted with an inner, stainless steel protective sleeve and a thermocouple to monitor temperature. During sampling the probe is pushed to sampling depth, the locking lugs are pneumatically released, and the piston is retracted to reveal the sample chamber. The probe is then pushed an additional 1.5 to 1.75 in.¹ to sample a plug of soil of a known diameter and an estimated volume. Carrier gas is introduced through a stainless steel tube located along the inner wall of the outer housing. The gas enters the sample chamber area through four equally spaced openings above and behind the heater. The gas is preheated as it passes down the surface of the heating coil and into the bottom of the sample chamber where the gas sweeps upward over the soil plug to purge the VOCs as they are volatilized into the chamber. The gas carries the volatilized sample up through the sample exit line and into the sample collection device at the surface.

Sample transfer line

Stainless steel tubing (1/16-in.) was used for both the laboratory evaluation and the field trial. Previous studies had indicated that best recoveries were achieved through heated transfer lines. For the laboratory tests, the tubing was wrapped with 120-V heating tape and heated to 100 °C for 2 hr prior to sampling. The field trials were conducted with unheated tubing. This was possible because the site chosen for the field trials was

¹ A table of factors for converting non-SI units of measurement to SI units is presented on page vii.

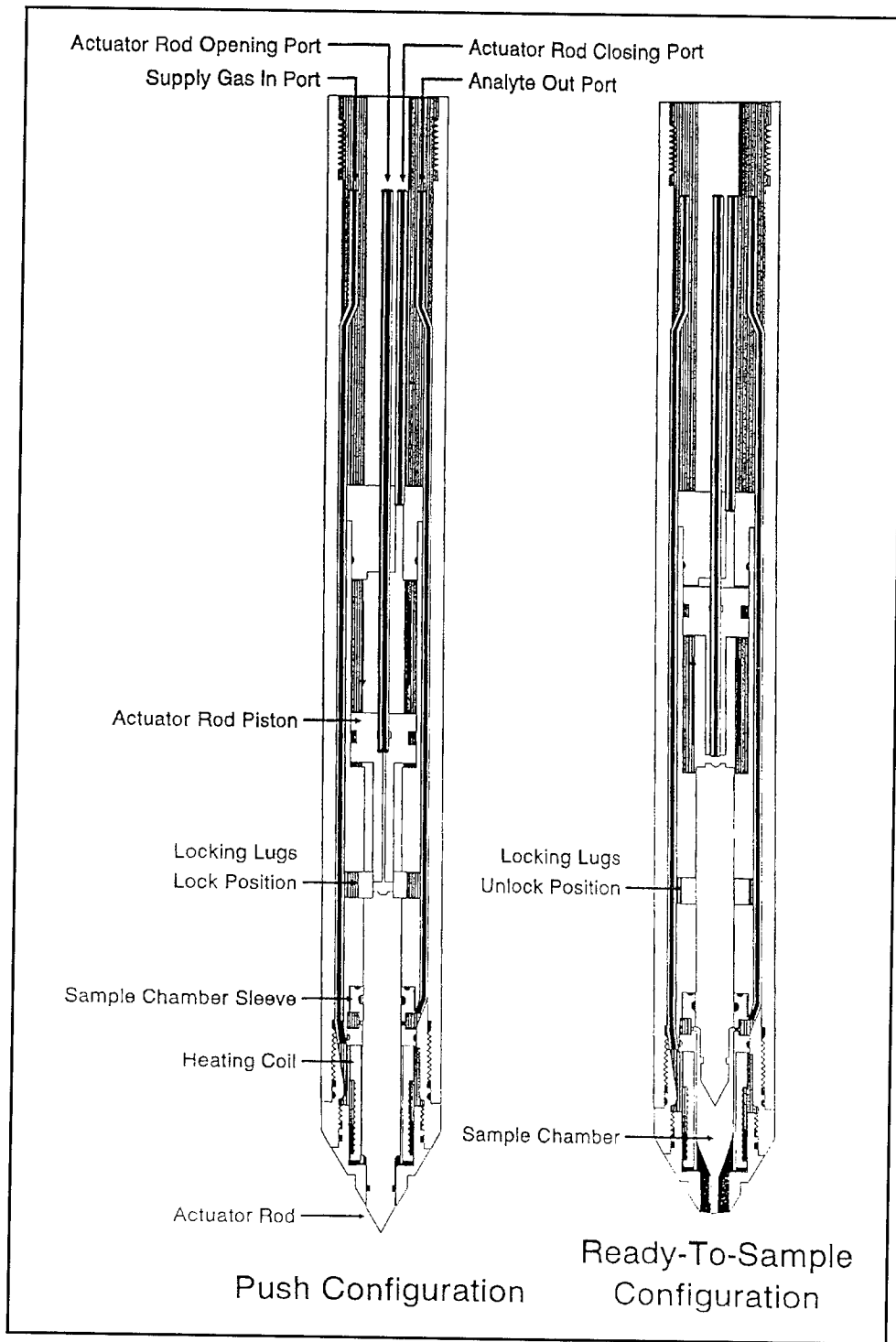


Figure 1. Thermal desorption VOC probe

known to be contaminated with BTEX (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene and *p*-xylene) and TCE (trichloroethene) compounds that have good transfer efficiencies in unheated conditions. The unheated sample transfer line, the three lines supplying carrier gas to support sampling and probe functions, and the heater and thermocouple wires were wrapped together with heat shrink plastic to form an umbilical line between the VOC probe and the SCAPS truck. The umbilical was threaded through 1-m sections of pipe that are used to advance the sampler through the soil.

Sample collection device and instrumentation

Analyses were carried out on a Hewlett Packard 5890 series II gas chromatograph interfaced to a HP 5971 Series Mass Selective Detector with an OI Analytical model 4560 purge and trap (GC/MS) or on a model 8610 portable GC (SRI Instruments, Las Vegas, NV) with a photo ionization detector (PID). Traps for sample collection were packed with tenax. For laboratory evaluation analysis, the trap in the GC/PID purge and trap sampler was replaced with a trap containing the sample collected from the VOC sampler. This trap was desorbed and the analytes quantitated against a standard curve generated using SW-846 Method 8021A.¹ For field trials, the tenax trap was desorbed with 1 mL of methanol. A portion of the resulting extract, ranging from 0.020 to 0.100 mL was added to 5 mL of American Society for Testing and Materials (ASTM) Type I water for analysis by purge and trap.

Soil samples taken for comparison and validation were analyzed by SW-846 Method 8260A² and by the methanol field extraction method³ followed by analysis by GC/MS Method 8260A.

Analytes

Twelve compounds were included in the initial laboratory evaluation:⁴ the BTEX compounds (benzene, toluene, ethylbenzene, *o*-xylene, *m*-xylene, and *p*-xylene); trichloroethene (TCE); *trans*-1,2-dichloroethene; chlorobenzene; *o*-dichlorobenzene; *m*-dichlorobenzene; and

¹ U.S. Environmental Protection Agency. (1992). "Halogenated volatiles by gas chromatography using photo ionization and electrolytic conductivity detectors in series: Capillary column technique," SW846 Method 8021A.

² U.S. Environmental Protection Agency. (1994). "Volatile organics by gas chromatography/mass spectrometry (GC/MS): Capillary column technique," SW846 Method 8260A.

³ Hewitt, A. D. (1994). "Comparison of methods for sampling vadose zone soils for determination of trichloroethylene," *Journal of AOAC International* 77, 458-63.

⁴ Myers, K. F., Brannon, J. M., Karn, R. A., Price, C. B., Eng, D. Y., Strong, A. B., and Cooper, S. S. (1995). "Laboratory evaluation of a volatile organic compound analysis system for the site characterization and analysis penetrometer system," Technical Report IRRP-95-3, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

p-dichlorobenzene. The laboratory evaluation conducted during this study included five additional compounds: 1,1-dichloroethene; *cis*-1,2-dichloroethene; tetrachloroethene (PCE); naphthalene; and 2-methylnaphthalene.

Methods

Laboratory testing

The effects of soil type and moisture were evaluated using sand, silt and clay soils mixed with organic free water to simulate moisture contents by weight of 10 and 20 percent for silt only. Temperature in the probe sample chamber was stabilized at 120 °C. Soil was packed (weight density of 1.7 g/cm³) into a 500-mL stainless steel beaker, placed on a hydraulic jack, and forced up into the sample chamber. The beaker was removed and the chamber sealed with a stainless steel plate fitted with an injection port sealed with a Teflon-lined septum. Standard solution containing the target analytes was injected into the center of the soil plug. Immediately after sealing the sample chamber with the stainless steel plate, gas flow was initiated at 40 mL/min., and vapor was collected for 30 min. on a tenax trap. All tests were conducted in triplicate. A detailed description is provided in Myers et al.¹

Field testing

The field trial was conducted at Dover Air Force Base (AFB), Dover, DE. Sampling was conducted behind Building 719 in an area adjacent to a jet wash. Sample positions are given in Figure 2. Sampling depths and a description of the type of sample taken at each depth are presented in Tables 1–3 for Holes 17, 18, and 19, respectively. Because of the water main breakage by the USEPA contractor drill rig, verification soil samples are only available from Hole 20, which corresponds to Hole 19.

¹ Myers, K. F., Brannon, J. M., Karn, R. A., Price, C. B., Eng, D. Y., Strong, A. B., and Cooper, S. S. (1995). "Laboratory evaluation of a volatile organic compound analysis system for the site characterization and analysis penetrometer system," Technical Report IRRP-95-3, U.S. Army Engineer Waterways Experiment Station, Vicksburg, MS.

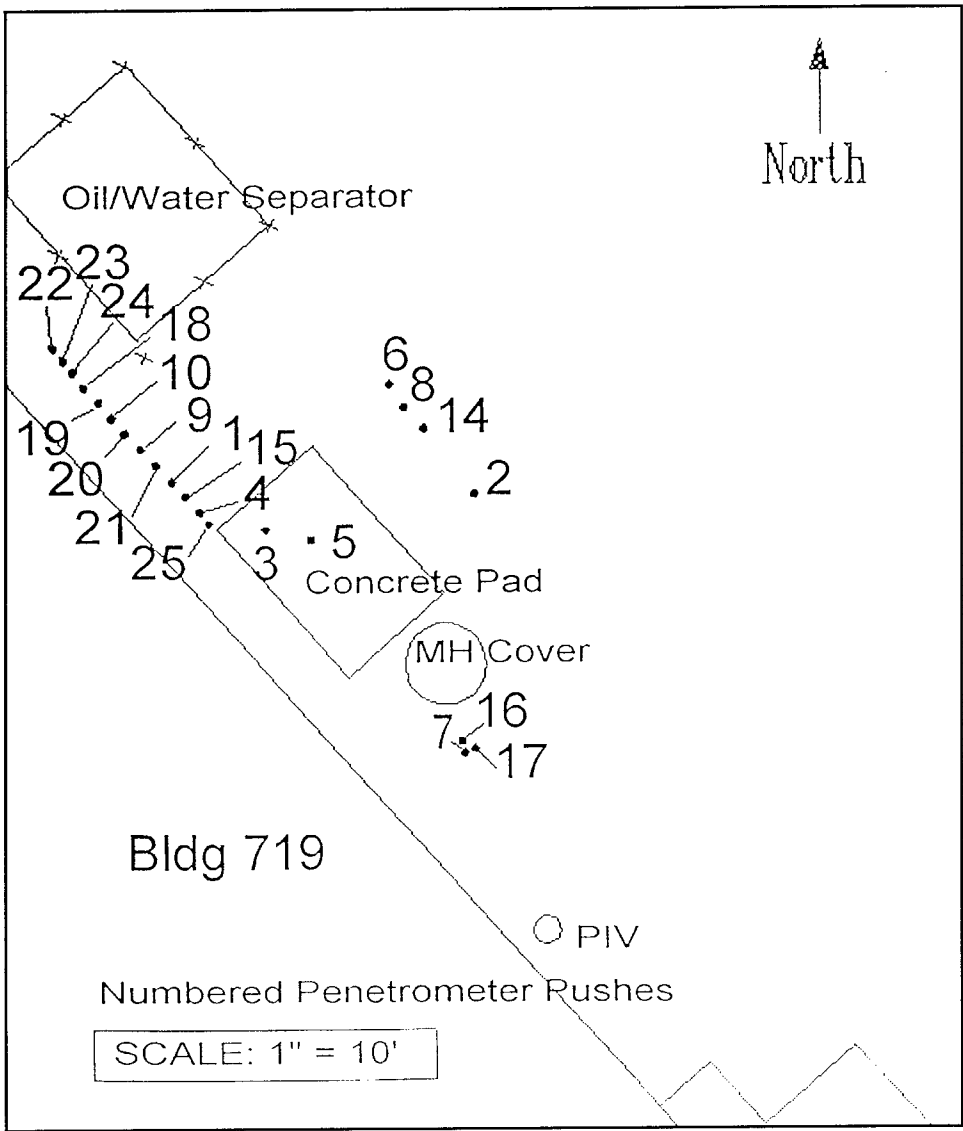


Figure 2. Sampling stations at Building 719, Dover Air Force Base

Table 1
Samples Taken in Hole 17, Dover Air
Force Base

Depth, ft	Type of Sample	Heating Time, min.
3	Soil	30
4	Soil	30
5	Soil	30
5.75	Vapor	30
6	Soil	30
7	Soil	30
8	Soil	30
8.5	Soil	30
9	Vapor	30

Table 2
Samples Taken in Hole 18, Dover Air
Force Base

Depth, ft	Type of Sample	Heating Time, min.
6	Soil	30
6.5	Vapor	30
7	Soil	30
7.5	Vapor	30
8	Soil	30

Table 3
Samples Taken in Hole 19, Dover Air Force Base

Depth, ft	Type of Sample	Heating Time, min.	Comments
4	Soil	30	
4.5	Vapor	30	With vacuum only
5	Soil	30	
5.5	Vapor	30	With vacuum only
6	Soil	11	
6.5	Vapor	30	With vacuum only
7	Soil	6	Sample ejected in hole
7.5	Vapor	30	With vacuum only
8	Soil	8	Sample ejected in hole
8.5	Vapor	30	With vacuum only
9	Soil	11	Sample ejected in hole
10 (water table)	Soil	10	Sample ejected in hole
11	Soil	10	Sample brought to surface for examination

In operation, the sampler (Figure 1) in the soil sampling mode was pushed to a desired depth in the subsurface. The sampler was then raised 0.5 in. to break contact with the soil and the actuator rod was retracted. The sampler was then pushed 1.5 in. and the temperature monitored to gauge the amount of soil in the sample chamber. If the temperature drop was not too severe (severe decreases indicated sample chamber filling with slush), the sampler was pushed an additional 0.4 in. A full 1.9-in. push resulted in a plug approximately 1 in. long in the sampler. Prior to the push, temperature in the probe desorption chamber was stabilized at 120 °C and a tenax trap placed on the surface outlet to adsorb purged contaminants from the carrier gas. Immediately after an appropriate soil sample was pushed into the probe sample chamber, gas flow was initiated at 60 mL/min. At the conclusion of a sampling event, contaminants on the tenax trap were desorbed with 1 mL of methanol, and the methanol extract was analyzed using a field portable GC/PID. When available, an ion trap MS was used to screen the methanol extracts for contaminant concentration ranges prior to GC injection or for independent verification of compounds detected by the GC/PID. At the conclusion of thermal desorption of contaminants from the in situ soil, the soil sample was expelled from the probe either at the surface or in situ (after raising the probe 1 ft), and the probe was brought to the surface where it was purged with nitrogen at a high flow rate (greater than 250 mL/min.) for 10 min. The probe actuator rod was then closed and a system blank measured with a tenax trap for

10 min. The sampler was then pushed to a new depth where the process was repeated.

Alternatively, the sampler was used as a vapor sampler in the vadose zone. In the vapor sampling mode, the sampler was pushed to the desired depth in the subsurface, raised 1.0 in. to break contact with the soil, and the actuator rod retracted. Two methods of vapor sampling were tested. The first method (Holes 17 and 18) involved flow of carrier gas (60 mL/min.) and heating (120 °C) with applied vacuum drawing the mixture of soil gas and carrier gas to the surface where the gas sample was trapped and analyzed. Vapor sampling in Hole 19 was conducted in the same manner except that the flow of carrier gas was not initiated and soil gas was brought to the surface by vacuum only.

3 Results and Discussion

Laboratory Results

Recoveries of higher molecular weight, higher boiling VOCs (tetrachlorethene, naphthalene, 2-methylnaphthalene) from soils ranged from 75 to 94 percent (Table 4). These results compared favorably with recoveries of the 12 compounds initially investigated (Table 5). The 1,1-dichloroethene and *cis*-1,2-dichlorethene gave poor recoveries for all soil types and moisture contents as did the *trans*-1,2-dichlorethene. These recoveries are due to the poor trapping efficiency of tenax for these compounds. This can be remedied as site conditions warrant by changing the trap material or by placing an additional trap containing a different adsorbent in series to increase the trapping efficiencies of these compounds. Recoveries for tetrachloroethene are similar to those of trichloroethene. The remaining compounds, naphthalene and 2-methylnaphthalene, are two of the more volatile polyaromatic hydrocarbons (PAHs) that might be found as contaminants onsite. Comparison of recoveries of the expanded target compounds from the unheated tubing studies (Table 6) to recoveries from the silt at 10-percent moisture suggests that heated tubing may improve transfer efficiency for tetrachlorethene, naphthalene, and 2-methylnaphthalene.

Table 4
Percent Recoveries (R) of Expanded Target Compound List From
Soils at 10 and 20 Percent Moisture (M)

Compound	R (SE), % ¹			
	Silt 10% M	Silt 20% M	Sand 10% M	Clay 10% M
1,1-Dichloroethene	3.0 (0.2)	2.0 (1.2)	4.0 (0.1)	2.0 (0.9)
<i>cis</i> -1,2-Dichloroethene	2.0 (0.5)	6.0 (2.9)	2.0 (0.7)	3.0 (1.4)
Tetrachloroethene	94.0 (0.7)	78.0 (1.0)	88.0 (0.4)	75.0 (1.6)
Naphthalene	92.0 (0.1)	90.0 (3.2)	92.0 (1.1)	93.0 (0.5)
2-Methylnaphthalene	90.0 (2.1)	89.0 (2.9)	89.0 (0.5)	91.0 (2.1)

Note: Tubing was 1/16-in. stainless steel heated to 100 °C. Probe temperature was 100 °C with a flow rate of 40 mL/min.

¹ Standard error of the mean of three replicate samples.

Table 5
Percent Recoveries (R) of Original Target Compound List From
Soils at 10 and 20 Percent Moisture (M)

Compound	R (SE), % ¹			
	Silt 10% M	Silt 20% M	Sand 10% M	Clay 10% M
<i>trans</i> -1,2-Dichloroethene	0.0 (0.0)	1.4 (0.2)	2.7 (0.6)	1.8 (0.6)
Benzene	96.5 (2.0)	69.3 (0.8)	92.6 (2.1)	87.8 (2.0)
Trichloroethene	93.4 (1.2)	89.5 (2.5)	86.8 (1.6)	77.7 (7.3)
Toluene	102 (2.8)	94.1 (2.9)	95.9 (1.0)	88.3 (1.3)
Chlorobenzene	95.7 (1.0)	87.8 (3.2)	92.3 (0.1)	81.7 (0.3)
Ethylbenzene	92.9 (1.2)	93.9 (1.9)	91.2 (2.9)	81.7 (0.3)
<i>m</i> - & <i>p</i> -Xylenes	101 (1.3)	90.5 (4.2)	96.8 (0.7)	90.0 (1.0)
<i>o</i> -Xylene	100 (1.3)	89.0 (1.0)	96.3 (0.6)	86.8 (0.5)
<i>m</i> - & <i>p</i> -Dichlorobenzene	93.1 (2.1)	81.3 (3.8)	86.5 (0.7)	79.1 (2.9)
<i>o</i> -Dichlorobenzene	125 (8.2)	88.2 (1.8)	108 (10.3)	98.7 (7.4)

Note: Tubing was 1/16-in. stainless steel heated to 100 °C. Probe temperature was 100 °C with a flow rate of 40 mL/min.

¹ Standard error of the mean of three replicate samples.

Table 6 Percent Recoveries (Standard Error) From 500-ng Spikes After 30 min of Sampling (GC Method 8021A) From the Tube Evaluation Test	
Expanded Target Compounds	1/16-in. Stainless Steel
1,1-Dichloroethene	1.3 (1.4)
<i>cis</i> -1,2-Dichloroethene	3.0 (0.6)
Tetrachloroethene	84.3 (2.4)
Naphthalene	86.0 (4.2)
2-Methylnaphthalene	85.0 (1.6)
Note: Tube temperature was 25 °C with a flow rate of 40 mL/min.	

Field Results

Mechanical functioning

During the field test, various aspects of mechanical functioning were tested. On Hole 17, difficulties were encountered in determining when the probe was opened or closed. This led to the lack of samples between 6 and 8.5 ft in Hole 17. Lifting the probe 0.5 in. prior to retracting the actuator rod resulted in sufficient flow drop to determine whether the probe had opened prior to obtaining a soil or vapor sample.

The soil and fill material at Dover posed severe operating problems for the probe piston. When dried, the material tended to disintegrate and cake at the bottom of the sample chamber during ejection, preventing the actuator rod from completely descending and closing the probe. An alternative sampling scheme was devised to reduce the occurrence of caking and improve the probe's closure rate. Laboratory testing had shown that soil contaminant desorption was complete when the soil was completely dry and the temperature in the sample chamber returned to presampling conditions. Thus, the thermal desorption sampling time for Hole 19 was reduced to the minimum time necessary to dry the sample by monitoring the rise in thermocouple temperature. Sampling times were reduced to 6 to 11 min, greatly improving probe functioning in this soil. Improved probe operation resulted from the lack of overbaking the soil, resulting in greater cohesion and reducing the powdery material that could cake and pack preventing probe closure.

Soil sampling

The major contaminants detected in soil in Hole 19 (Table 7) were *cis*-1,2-dichloroethene, 1,1,1-trichloroethane, trichloroethene, tetrachloroethene, ethylbenzene, and total xylenes. In general, concentrations of these compounds increased with depth as illustrated by the chromatograms obtained in the field (Figure 3). For most compounds with concentrations reported above the detection limit for the method of analysis, correspondence between the data from the VOC sampler (Table 7, Column a), the verification sample laboratory extract (Table 7, Column b), and the verification sample field methanol extract (Table 7, Column c) was good. Although present in the soil samples, 1,1,1-trichloroethane is not detected by GC/PID and does not appear in Table 7, Column a. The compound detected by GC/PID entitled "unresolved hydrocarbons" is a mass of hydrocarbons that could not be resolved by the chromatographic method. By GC/MS, these unresolved compounds were tentatively identified as branched and straight-chain hydrocarbon compounds. These unresolved compounds possessed high-peak areas in most samples, indicating presence at high concentrations. The field extract by GC/MS for the 9-ft sample from Hole 20 arrived at the laboratory with a methanol volume that was less than the other methanol field extracts. Data from this sample may be erroneously high.

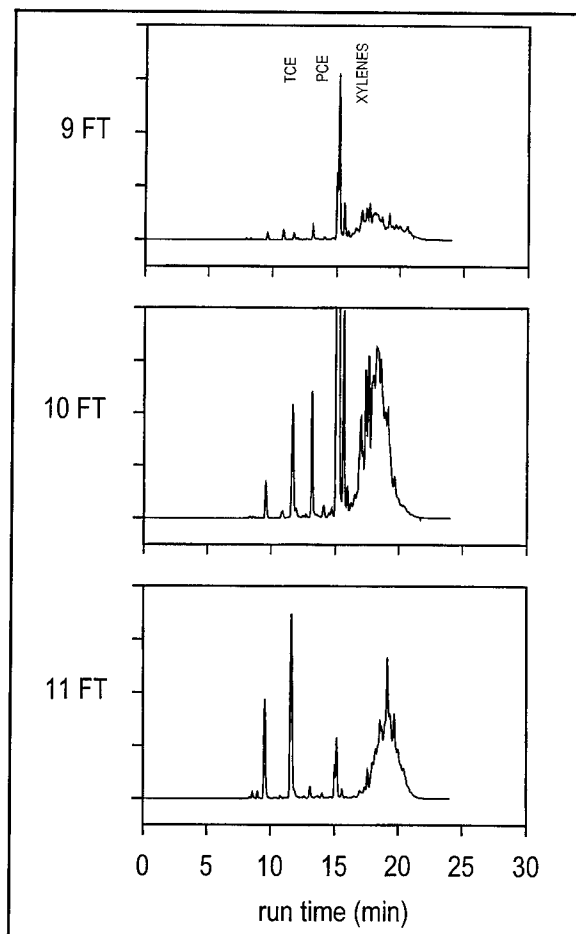


Figure 3. Thermal desorption VOC system chromatographs for soil samples from Hole 19

Soil concentrations from Hole 19 (Table 8, Columns a and b) obtained from the VOC sampler were in some cases comparable, but were generally lower than soil concentrations from validation samples of corresponding depth from Hole 20 (Table 8, Columns c and d). The lower concentrations obtained with the VOC sampler were probably a result of losses of carrier gas and contaminant occurring from the opening in the probe in the sandy soils at Dover. This source of loss will be rectified in a new manifold that has mass flow meters for carrier gas going down the probe and gas going to the trap so that flows can be balanced and prevent losses to the surrounding soil environment.

Table 7
Dover AFB VOC Sampler Field Soil Desorption Concentrations for Hole 19 (a) Compared
with Laboratory Soil Extractions by EPA Method 8260 (b) and to Field Methanol
Extractions Analyzed by EPA Method 8260 (c) for Verification Hole 20

Compound	(a) SCAPS GC/PID µg/g	(b) 8260 GC/MS µg/g	(c) Methanol GC/MS µg/g	(a) SCAPS GC/PID µg/g	(b) 8260 GC/MS µg/g	(c) Methanol GC/MS µg/g	(a) SCAPS GC/PID µg/g	(b) 8260 GC/MS µg/g	(c) Methanol GC/MS µg/g
	4 Ft			5 Ft			6 Ft		
1,1-Dichloroethene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 0.59	< 5.0	< 0.0625	< 5.8	< 5.0
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 0.59	< 5.0	< 0.0625	< 5.8	< 5.0
<i>cis</i> -1,2-Dichloroethene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 0.59	< 5.0	0.05	< 5.8	< 5.0
Benzene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 0.59	< 5.0	< 0.0625	< 5.8	< 5.0
Trichloroethene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 5.9	< 5.0	0.035	< 5.8	< 5.0
1,1,1-Trichloroethane	NA	< 5.9	4.6	NA	0.28	< 5.0	NA	1.8	1.3
Toluene	0.0075	< 5.9	< 5.0	0.0225	< 0.59	< 5.0	0.0225	< 5.8	< 5.0
Tetrachloroethene	< 0.0625	< 5.9	< 5.0	< 0.0625	< 0.59	< 5.0	< 0.0625	< 5.8	< 5.0
Chlorobenzene	0.005	< 5.9	< 5.0	0.015	< 0.59	< 5.0	0.0075	< 5.8	< 5.0
Ethylbenzene	< 0.0625	< 5.9	< 5.0	0.1375	0.17	< 5.0	0.1375	0.77	0.31
Total Xylenes	0.01	< 5.9	< 5.0	0.53	0.44	< 5.0	0.54	1.7	1.2
Unresolved hydrocarbons ¹	1612873	NA	NA	2623399	NA	NA	1348186	NA	NA
	7 Ft			8 Ft			9 Ft		
1,1-Dichloroethene	< 0.0625	< 5.8	< 5.0	0.045	< 5.6	< 5.0	< 0.0625	< 28	< 25
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 5.8	< 5.0	< 0.0625	< 5.6	< 5.0	< 0.0625	< 28	< 25
<i>cis</i> -1,2-Dichloroethene	0.0448	< 5.8	2.1	0.2975	3	16	0.14	3.1	160
Benzene	< 0.0625	< 5.8	< 5.0	< 0.0625	< 5.6	< 5.0	0.005	< 28	< 25
Trichloroethene	< 0.0625	4.4	3.7	0.135	4.8	13	0.1425	1.6	500
1,1,1-Trichloroethane	NA	29.0	51.0	NA	92	230	NA	90	660
Toluene	0.0102	< 5.8	< 5.0	0.0975	0.67	1.6	0.145	< 28	< 25
Tetrachloroethene	< 0.0625	< 5.8	0.76	0.0225	< 5.6	< 5.0	0.0725	< 28	< 25
Chlorobenzene	< 0.0625	< 5.8	< 5.0	0.0075	< 5.6	< 5.0	0.0225	< 28	< 25
Ethylbenzene	< 0.0625	1.6	1.8	0.085	4.8	8	0.81	3.2	15
Total Xylenes	< 0.0625	3.1	5.8	0.1925	8.9	26	3.06	6.4	52
Unresolved hydrocarbons ¹	63040	NA	NA	6416	NA	NA	654299	NA	NA

(Continued)

Table 7 (Concluded)

Compound	(a)	(b)	(c)	(a)	(b)	(c)
	SCAPS GC/PID µg/g	8260 GC/MS µg/g	Methanol GC/MS µg/g	SCAPS GC/PID µg/g	8260 GC/MS µg/g	Methanol GC/MS µg/g
	10 Ft			11 Ft		
1,1-Dichloroethene	< 0.0625	< 29	< 25	0.845	< 29	< 25
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 29	< 25	0.43	< 29	< 25
<i>cis</i> -1,2-Dichloroethene	0.3375	2.6	51	31.6	53	100
Benzene	0.01	< 29	< 25	0.015	< 29	< 25
Trichloroethene	9.875	< 29	5.1	19.4	150	290
1,1,1-Trichloroethane	NA	140	370	NA	320	410
Toluene	1.8225	1.5	2.2	0.825	2.5	< 25
Tetrachloroethene	0.3975	< 29	4.9	0.200	< 29	4.4
Chlorobenzene	0.1	< 29	< 25	0.025	< 29	< 25
Ethylbenzene	8.0225	7.5	9.8	0.765	8	9
Total Xylenes	15.88	12	43	1.263	12	39
Unresolved hydrocarbons ¹	1975525	NA	NA	1081003	NA	NA

Note: NA = Not available

¹ Unresolved hydrocarbons expressed as area.

² Sample had low methanol volume when it reached the lab.

Table 8
VOC Concentration Comparisons From Hole 19 (SCAPS GC/PID and GC/MS) and Hole 20 (EPA Method 8260 and Methanol Extract)

Compound	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)	(a)	(b)	(c)	(d)
	SCAPS GC/PID µg/g	SCAPS GC/MS µg/g	8260 GC/MS µg/g	Meth. GC/MS µg/g ¹	SCAPS GC/PID µg/g	SCAPS GC/MS µg/g	8260 GC/MS µg/g	Meth. GC/MS µg/g	SCAPS GC/PID µg/g	SCAPS GC/MS µg/g	8260 GC/MS µg/g	Meth. GC/MS µg/g
	9 Ft				10 Ft				11 Ft			
1,1-Dichloroethene	< 0.0625	< 0.31	< 28	< 25	< 0.0625	< 0.62	< 29	< 25	0.845	< 0.83	< 29	< 25
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 0.31	< 28	< 25	< 0.0625	< 0.62	< 29	< 25	0.43	< 0.83	< 29	< 25
<i>cis</i> -1,2-Dichloroethene	0.14	0.13	3.1	160	0.34	7.47	2.6	51	31.6	31.3	53	100
Benzene	0.005	< 0.31	< 28	< 25	0.01	0.24	< 29	< 25	0.015	< 0.83	< 29	< 25
Trichloroethene	0.142	0.15	1.6	500	9.88	9.71	< 29	5.1	19.4	82.7	150	290
1,1,1-Trichloroethane	NA	1.75	90	660	NA	34.7	140	370	NA	60.6	320	410
Toluene	0.145	0.14	< 28	< 25	1.82	1.67	1.5	2.2	0.825	0.47	2.5	< 25
Tetrachloroethene	0.072	< 0.31	< 28	< 25	0.4	0.38	< 29	4.9	0.2	0.1	< 29	4.4
Chlorobenzene	0.022	< 0.31	< 28	< 25	0.1	< 0.62	< 29	< 25	0.025	< 0.83	< 29	< 25
Ethylbenzene	0.81	0.98	3.2	15	8.02	8.33	7.5	9.8	0.765	0.47	8	9
Total Xylenes	3.06	2.97	6.4	52	15.9	23.1	12	43	1.26	1.06	12	39
Unresolved hydrocarbons ²	654299	NA	NA	NA	1975525	NA	NA	NA	1081003	NA	NA	NA

Note: NA = Not available.

¹ Sample had low methanol volume when it reached the laboratory.

² Unresolved hydrocarbons are expressed as area.

The methanol soil extracts taken in the field (Table 8, Column d) from Hole 20 were generally higher in concentration than soils taken in the field and shipped to the laboratory for extraction and analysis by conventional methods (Column c). Extraction into methanol preserves the volatile compounds at concentrations more representative of the true field concentrations.¹ Data obtained by the conventional EPA laboratory soil extract (Column c) probably showed lower concentrations because of compound loss during storage and handling. Detection limits for the three methods reflect the type of detector and the dilution factor required during analysis.

Archived VOC sampler extracts from the 9-, 10-, and 11-ft depths of Hole 19 were analyzed by GC/MS (Table 8, Column b) to determine TCA concentrations and to evaluate the accuracy of the field GC/PID concentrations (Table 8, Column a). TCA concentrations determined in the laboratory by GC/MS generally compared well with data from soil samples from Hole 20 (Columns c and d), although concentrations were lower from the VOC sampler extracts. Concentrations of the other compounds found in the archived extracts (Columns a and b), determined in the field by GC/PID and in the laboratory by GC/MS, compared well.

In all cases in which the soil from the validation sample (Hole 20) contained measurable concentrations of contaminant by GC/MS, the VOC sampler detected the presence of that contaminant. However, recoveries were generally low, probably because of unbalanced flow of carrier and analyte gas leading to losses through the mouth of the probe.

Concentrations of VOCs detected in soil from Hole 17 were generally low or below detection limits (Table 9). Only the 8.5-ft depth sample showed the unresolved hydrocarbons that were so much a feature of Hole 19. Conversely, more detectable VOC concentrations were found in soil samples from Hole 18 (Table 10). Unresolved hydrocarbons were found at all sampled depths.

Vapor sampling

Table 11 presents soil gas data taken with the VOC sampler (Column a) in Hole 19 and verification soil samples taken from Hole 20 (Columns b and c). As observed in Table 7, soil concentrations and the number of detects in the soil vapor increased with depth of sample. The VOC sampler detected increasingly high peak areas of unresolved hydrocarbons. Concentrations for the soil gas are expressed in micrograms/liter of gas pulled through the tenax trap by vacuum. Because the trapping efficiency of tenax for 1,1-dichloroethene, *cis*-1,2-dichloroethene, and *trans*-1,2-dichloroethene is less than 20 percent, comparison results were poor

¹ Hewitt, A. D. (1994). "Comparison of methods for sampling vadose zone soils for determination of tetrachloroethylene," *Journal of AOAC International* 77, 458-63.

Table 9
Concentrations of VOCs Desorbed From Soils From Hole 17 Using the VOC Sampler
and Analyzed by GC/PID

Compound	3 Ft µg/g	4 Ft µg/g	5 Ft µg/g	6 Ft µg/g ¹	7 Ft µg/g	8 Ft µg/g	8.5 Ft µg/g
1,1-Dichloroethene	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
<i>cis</i> -1,2-Dichloroethene	< 0.0625	0.02	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Benzene	0.005	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Trichloroethene	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Toluene	0.0225	0.028	0.119	< 0.0625	< 0.0625	0.01	0.005
Tetrachloroethene	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Chlorobenzene	0.005	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Ethylbenzene	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Total Xylenes	0.016	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625	< 0.0625
Hydrocarbon Area ¹	0	0	0	0	0	0	164339

¹ Unresolved hydrocarbons are expressed as area.

Table 10
Concentrations of VOCs Desorbed From Soils From Hole 18 Using the VOC Sampler
and Analyzed by GC/PID

Compound	6 Ft µg/g	7 Ft µg/g	8 Ft µg/g
1,1-Dichloroethene	< 0.0625	< 0.0625	0.058
<i>trans</i> -1,2-Dichloroethene	< 0.0625	< 0.0625	< 0.0625
<i>cis</i> -1,2-Dichloroethene	0.01	0.0275	0.332
Benzene	< 0.0625	< 0.0625	0.005
Trichloroethene	0.0925	0.0600	0.16
Toluene	0.045	0.0300	0.102
Tetrachloroethene	0.040	0.0225	0.0375
Chlorobenzene	0.005	0.0075	0.015
Ethylbenzene	0.305	0.1475	0.3325
Total Xylenes	1.11	0.502	1.14
Unresolved Hydrocarbons ¹	1410821	743062	488661

¹ Unresolved hydrocarbons are expressed as area.

Table 11
Comparison of VOC Sampler Soil Gas Concentrations ($\mu\text{g/L}$ vapor) From Hole 19 (a) to Laboratory Soil Extractions by GC/MS (EPA Method 8260) (b) and to Methanol Soil Field Extractions Analyzed by EPA Method 8260 From Hole 20 (c)

Compound	(a) SCAPS GC/PID $\mu\text{g/L}$ (V)	(b) 8260 GC/MS $\mu\text{g/g}$	(c) Methanol GC/MS $\mu\text{g/g}$	(a) SCAPS GC/PID $\mu\text{g/L}$ (V)	(b) 8260 GC/MS $\mu\text{g/g}$	(c) Methanol GC/MS $\mu\text{g/g}$
	5.5 Ft			6.5 Ft		
1,1-Dichloroethene	< 6.67	< 5.7	< 5	< 33.3	< 5.6	< 5
<i>trans</i> -1,2-Dichloroethene	< 6.67	< 5.7	< 5	< 33.3	< 5.6	< 5
<i>cis</i> -1,2-Dichloroethene	< 6.67	< 5.7	< 5	< 33.3	4.2	0.42
Benzene	< 6.67	< 5.7	< 5	< 33.3	< 5.6	< 5
Trichloroethene	< 6.67	< 5.7	< 5	trace	13	1.3
1,1,1-Trichloroethane	NA	< 5.7	< 5	NA	33	30
Toluene	< 6.67	< 5.7	< 5	1	< 5.6	< 5
Tetrachloroethene	< 6.67	< 5.7	< 5	< 33.3	< 5.6	< 5
Chlorobenzene	< 6.67	< 5.7	< 5	< 33.3	< 5.6	< 5
Ethylbenzene	< 6.67	< 5.7	< 5	trace	1.9	1.7
Total Xylenes	< 6.67	0.99	2.8	1.667	3.8	5.8
Unresolved Hydrocarbons ¹	0.00	NA	NA	0.00	NA	NA
	7.5 Ft (5137#19)			8.5 Ft (5137#19)		
1,1-Dichloroethene	< 33.3	< 5.5	< 5	< 33.3	< 28	< 25
<i>trans</i> -1,2-Dichloroethene	< 33.3	< 5.5	< 5	< 33.3	< 28	< 25
<i>cis</i> -1,2-Dichloroethene	< 33.3	< 5.5	1.9	< 33.3	3.1	7.4
Benzene	< 33.3	< 5.5	< 5	< 33.3	< 28	< 25
Trichloroethene	< 33.3	3.4	3.3	trace	2.7	4.7
1,1,1-Trichloroethane	NA	48	49	NA	110	100
Toluene	0.67	< 5.5	< 5	1	< 28	0.82
Tetrachloroethene	< 33.3	< 5.5	2.9	< 33.3	< 28	0.51
Chlorobenzene	< 33.3	< 5.5	< 5	< 33.3	< 28	< 25
Ethylbenzene	trace	2.8	1.5	2	4.7	4.1
Total Xylenes	1	5.4	6	8	8	14
Unresolved Hydrocarbons ¹	165054	NA	NA	1077506	NA	NA

Note: NA = Not available.

¹ Unresolved hydrocarbons are expressed as area.

between the VOC sampler results (Column a) and soil sample results (Columns b and c). Correspondence was much better for compounds such as ethylbenzene and total xylenes.

Vapor samples from Holes 17 and 18 (Table 12) showed much the same trends as did VOC sampler soil concentrations from the same holes (Tables 9 and 10). Soil VOC sampler results (Table 9) showed low concentrations of chlorobenzene and toluene in shallow soils and did not detect the unresolved hydrocarbons until the 8.5-ft sample, mirroring the performance of the sampler in the vapor mode for Hole 17 (Table 12). The two vapor samples from Hole 18 (Table 12) also mirrored the VOC sampler soil data (Table 10), although the soil mode resulted in more compounds detected than in the vapor mode. Figure 4 is a vapor sample chromatograph from Hole 17 showing the presence of small levels of contaminants, but no unresolved hydrocarbon contamination.

Table 12
Vapor Samples From Holes 17 and 18 by Field GC/PID

Compound	#17 - 5 Ft µg/L	#17 - 9 Ft µg/L	#18 - 6 Ft µg/L	#18 - 6 Ft µg/L
1,1-Dichloroethene	< 0.37	< 3.3	< 3.3	0.6
<i>trans</i> -1,2-Dichloroethene	< 0.37	< 3.3	< 3.3	0.1
<i>cis</i> -1,2-Dichloroethene	< 0.37	0.167	< 3.3	0.267
Benzene	< 0.37	< 3.3	< 3.3	0.167
Trichloroethene	< 0.37	0.5	< 3.3	0.367
Toluene	0.037	0.2	< 3.3	0.967
Tetrachloroethene	< 0.37	< 3.3	< 3.3	< 3.3
Chlorobenzene	0.007	< 3.3	< 3.3	< 3.3
Ethylbenzene	< 0.37	< 3.3	< 3.3	0.167
Total Xylenes	0.007	< 3.3	< 3.3	0.867
Unresolved Hydrocarbons ¹	0	308710	535960	488661

¹ Unresolved hydrocarbons are expressed as area.

Lab name : SCAPS field trial DOVER DE
 Analysis date : 05/15/1995 07:22:42
 Data file : P5135_5.CHR (c:\peak3\data1)
 Sample : 17-5vt28 vap-5.75 ft tp11
 Comments : VAPOR SAMPLE, 30 MINUTES
 : HOLE # 17, 5.75 FT
 : CONCENTRATION IN NG MASS ON TRAP
 :
 :

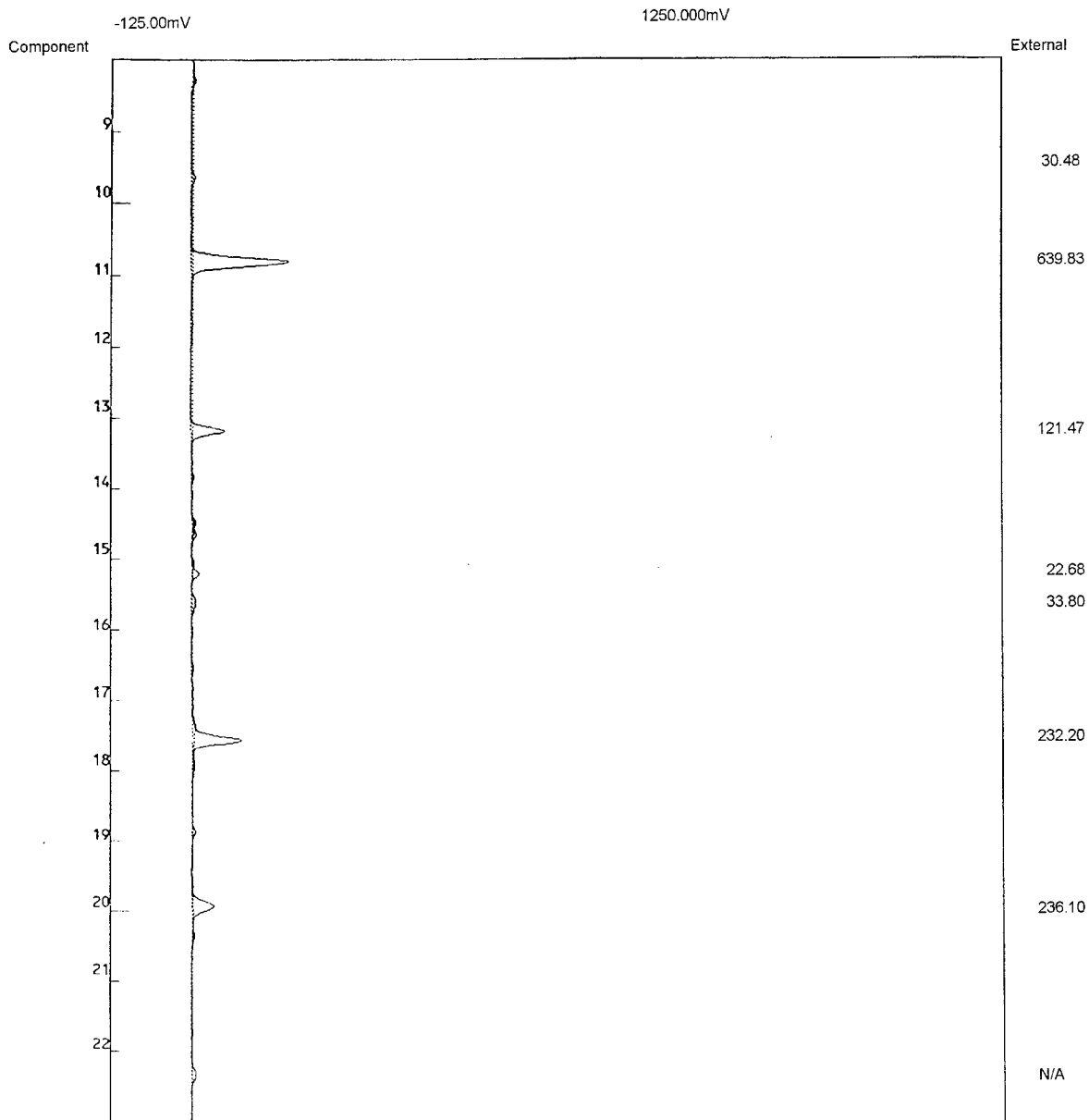


Figure 4. Chromatogram of soil vapor sample from Hole 17 obtained with the thermal desorption VOC system

4 Conclusions

Laboratory testing showed that the probe was capable of attaining adequate recoveries of the five additional compounds including the higher boiling VOCs. However, heating of the analyte line improved recoveries of the higher boiling compounds. Compounds not trapped by tenax require different trapping materials or a different trap in series.

Field testing showed that mechanically the probe functioned well, proving reliable and sturdy. Ejection of soil samples and closing of the probe below the surface was demonstrated. Vapor sampling was also demonstrated, as was soil sampling above and below the water table in the vadose and saturated zones. However, both soil and vapor sampling results indicated the need for improved flow control during soil sampling and for improved flowmetering to measure flow during soil gas sampling. Interface of the sampler and the ion trap MS could not be demonstrated because of problems with the ion trap MS. The need for an indicator to show when the probe was open or closed was also confirmed.

Chemically, the probe functioned well in an area of high contamination, worst case conditions for the probe. Carryover of contaminants between samples did not present insurmountable problems. However, the purge cycle with high backflow of nitrogen down the stainless steel analyte line requires that the probe be brought above ground for 10 min. Alternative line cleaning methods involving nitrogen saturated with methanol are being explored but this technology is not sufficiently mature for incorporation into current VOC sampler operation.

In the soil sampling mode, the sampler detected the contaminants present in the soil. However, recoveries were generally low, probably because of losses of carrier gas and contaminants through the open mouth of the probe during sampling. Better carrier gas flow control and mass flow meters on both the carrier gas and analyte lines should rectify this problem.

At the current stage of development, the thermal desorption VOC sampler is capable of conducting screening level (presence or absence and relative concentration) evaluations for VOCs in soils above and below groundwater. Screening analyses for VOCs can also be conducted using vapor sampling in the vadose zone. Field detection limits using methanol extracts of traps were as expected from the laboratory evaluation.

REPORT DOCUMENTATION PAGE

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