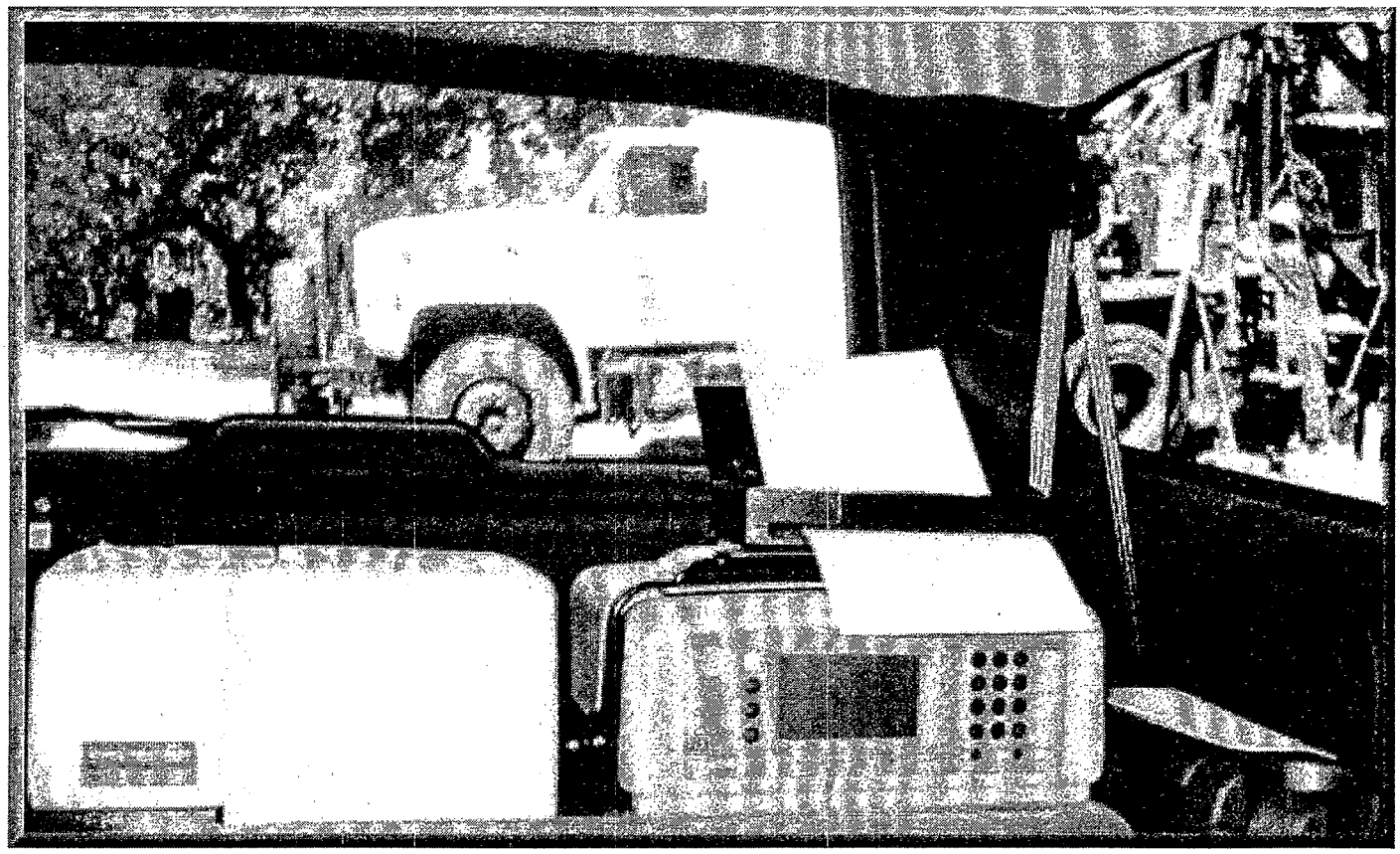
United States
Environmental Protection
Agency

Solid Waste and
Emergency Response
(5102G)

EPA 542-R-01-011
August 2001
www.epa.gov
http://cluin.org

Innovations in Site Characterization

Technology Evaluation: Real-time VOC Analysis Using a Field Portable GC/MS



EPA 542-R-01-011
August 2001

Innovations in Site Characterization Technology Evaluation:

Real-time VOC Analysis Using a Field Portable GC/MS

U.S. Environmental Protection Agency
Office of Solid Waste and Emergency Response
Technology Innovation Office
Washington, DC 20460

Notice

This material has been funded wholly by the United States Environmental Protection Agency under Contract Number 68-W0-0122. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Copies of this report are available free of charge from the National Service Center for Environmental Publications (NSCEP), PO Box 42419, Cincinnati, Ohio 45242-2419; telephone (800) 490-9198 or (513) 489-8190 (voice) or (513) 489-8695 (facsimile). Refer to document EPA 542-R-01-011, *Innovations in Site Characterization Technology Evaluation: Real-time VOC Analysis Using a Field Portable GC/MS.* This document can also be obtained through EPA's Clean Up Information (CLU-IN) System on the World Wide Web *at http://cluin.org.*

Comments or questions about this report may be directed to the United States Environmental Protection Agency, Technology Innovation Office (5102G), 1200 Pennsylvania Ave., NW, Washington, DC 20460; telephone (703) 603-9910.

Foreword

This evaluation of a field portable analytical technology is part of a series of case studies designed to provide cost and performance information for innovative tools supporting less costly and more representative site characterization. Based on actual field projects, these case studies include reports on new technologies as well as innovative applications of familiar tools in the context of more efficient work strategies. The ultimate goal of this case study series is to aid practicing site professionals to enhance the cost-effectiveness and defensibility of decisions regarding the disposition of hazardous waste sites.

Acknowledgments

This document was prepared by Science Applications International Corporation (SAIC) for the United States Environmental Protection Agency's (EPA) Technology Innovation Office under EPA contract 68-W0-0122. Special acknowledgment is given to the U.S. Army Corps of Engineers, Sacramento District, and Field-Portable Analytical, Inc. for their support in preparing this technology evaluation.

this page intentionally left blank

Table of Contents

Notice ii
Foreword iii
Acknowledgments iii
Technology Evaluation Abstract
Real-time VOC Analysis Using a Field Portable GC/MS vii
Technology Quick Reference Sheet
HAPSITE Field Portable Gas Chromatograph/Mass Spectrometer (GC/MS) ix

EXECUTIVE SUMMARY 1

SITE INFORMATION 3
Identifying Information 3
Background 3
Site Logistics/Contacts 5

MEDIA AND CONTAMINANTS 6
Matrix Identification 6
Site Geology/Stratigraphy 6
Contaminant Characterization 6
Matrix Characteristics Affecting Characterization Cost or Performance 6

SITE CHARACTERIZATION PROCESS 7
Goal of Site Characterization 7
Sampling Work Plan 7

CHARACTERIZATION TECHNOLOGIES 8
Sample Collection Technologies or Procedures 8
Field Analytical Technologies 9
Quality Assurance/Quality Control 10

PERFORMANCE EVALUATION 13
Sampling Results 13
Technology Performance–MPA Project 15
Technology Performance–ETV Evaluation 17

COST COMPARISON 19

OBSERVATIONS AND LESSONS LEARNED 20

REFERENCES 21

List of Figures

Figure 1: Location of Monterey Peninsula Airport Near Monterey, California 4
Figure 2: Extent of TCE Plume 16

List of Tables

Table 1. QC Acceptance Criteria 12
Table 2. Duplicate Analyses 12
Table 3. Surrogate Recoveries 13
Table 4. Matrix Spike Recovery and Precision 13
Table 5. HAPSITE GC/MS Analytical Results 14
Table 6. Comparison of Boring and Monitoring Well Results 15

TECHNOLOGY EVALUATION ABSTRACT

REAL-TIME VOC ANALYSIS USING A FIELD PORTABLE GC/MS

Site Name and Location: Monterey Peninsula Airport (MPA), Monterey, California	**Sampling & Analytical Technologies:** HAPSITE Portable GC/MS with Headspace Sample Introduction System	**Current Site Activities:** Continuing investigations of extent of ground water contamination
Period of Operation: MPA: 1942-1989 **Operable Unit:** Not applicable		**Analytical Service Provider:** Field-Portable Analytical, Inc. 3330 Cameron Park Dr., Suite 850 Cameron Park, CA 95682 (530) 676-6620 *http://www.fieldportable.com*
Point of Contact: Jerry Vincent U.S. Army Corps of Engineers-Sacramento District (916) 557-7452	**Media and Contaminants:** Ground water contaminated with chlorinated volatile organic compounds (VOCs)	

Number of Samples Analyzed during the Phase of the Site Investigation:
Fourteen ground water samples collected from borehole locations were quantitatively analyzed for VOCs by the HAPSITE GC/MS (EPA SW-846 Method 8260) using equilibrium headspace as the sample preparation method (EPA SW-846 Method 5021). Fifty-three QC samples were analyzed [20 calibration standards + 10 blanks + 4 MS/MSDs (2 pairs) + 9 duplicates + 10 instrument tuning standards].

Estimated Resource Savings Using Real-time Data Results:
$27,000 (26% of total projected costs) and 4 days of field time

Description:
During site investigation activities at the MPA, an on-site measurement technology (HAPSITE GC/MS) was used to determine the appropriate placement of monitoring wells to characterize the horizontal extent of a trichloroethene (TCE) plume migrating beyond site boundaries. A drill rig drilled borings from which ground water samples were collected using disposable bailers. Through the use of quantitative field analyses, real-time VOC results from the samples were used to model the plume, to guide decisions about locating additional borings, and to select which borings would be converted to permanent monitoring wells. Two years later, real-time VOC results were again successfully used, this time to characterize the vertical extent of TCE contamination. Field-Portable Analytical Inc. provided the HAPSITE GC/MS instrumentation, the associated standards and supplies, and the analytical chemist operator able to produce VOC data of the quality desired by the client.

Results:
This project illustrated the successful use of low-cost, real-time field analyses, using a technology (HAPSITE GC/MS) based on a definitive determinative method (SW-846 Method 8260), to guide real-time decision making. The data were effective for making correct decisions concerning the placement of borings and the installation of long-term monitoring wells. In the on-site area of investigation, TCE was detected in 8 downgradient borehole locations at the northeastern portion of the site. In the off-site area of investigation, TCE was detected in 8 of the 13 borehole locations along the proposed path of the TCE plume.

The analytical performance criteria in the project's quality assurance/quality control (QA/QC) protocol were satisfactorily achieved. Split sample analysis during a previous work phase at this site had established to the Corps' satisfaction that the on-site analytical service provider could use the field GC/MS to generate VOC data comparable to fixed laboratory GC/MS data. The correctness of the real-time, field decisions based on the HAPSITE VOC data was later verified by fixed laboratory analysis of ground water collected from the completed monitoring wells. The HAPSITE GC/MS was successfully used to produce low-cost, real-time data that supported real-time decision-making within a single field mobilization of 3 weeks. The use of off-site laboratory analyses instead of field analyses would have resulted in higher costs and a longer project time frame.

this page intentionally left blank

TECHNOLOGY QUICK REFERENCE SHEET

HAPSITE Field Portable Gas Chromatograph/Mass Spectrometer (GC/MS)

Technology Evaluation: On-Site VOC Analysis at Monterey Peninsula Airport (MPA) Using the HAPSITE Field Portable GC/MS

Technology Name: HAPSITE Field Portable Gas Chromatograph/Mass Spectrometer (GC/MS) with Headspace Sample Introduction System			
Summary of Technology Evaluation's Performance Information			
Project Role: Provide real-time volatile organic compound (VOC) results to model a trichloroethene (TCE) plume and guide the placement of borings and permanent monitoring wells.		**Analytical Information Provided:** Quantitative VOC results using EPA SW-846 Methods 5021 and 8260 for ten VOC target analytes.	
Total Project Cost: Approximately $75,000. Included 17 days in the field for a 3-person drilling crew, the on-site analytical team, and the USACE personnel.	**Cost Per Sample:** Not applicable. Analytical services were procured on a per day basis, not on a per sample basis. The cost was approximately $2000/day for analytical services that included the instrument and its operation, consumables, and labor costs (including second-person data review and preparation of electronic deliverables).		
Project Cost Breakdown			
Instrument Cost: Instrument was provided by analytical service provider.	**Consumables Cost:** Sample handling accessories (syringes, vials, standards, etc.): about $50/day (cost included in daily service rate).	**Labor Cost:** Included in daily service rate.	**Waste Disposal Cost:** Analytical wastes disposed with investigation-derived waste; no additional cost.
Site-Specific Precision/Accuracy Achieved: Analytical Precision: For the MPA samples, the HAPSITE instrument provided precision of 6-17 relative percent difference (RPD) for duplicate sample results (n = 5 analyte results); and 0-1 RPD for matrix spike duplicate (n = 1 MSD). Analytical Accuracy: HAPSITE accuracy ranged from 86% to 94% recovery for 3 analytes spiked into sample matrix (n = 1 matrix spike). The recovery of surrogate compounds over a 10-day project period ranged between 78 and 127% (n = 42; as 14 samples X 3 surrogate analytes each).			**Throughput Achieved:** 25-30 water samples/day [Results for water samples can be turned around in ½ - 1 hr.; gas sample results in about ½ hr.]
General Commercial Information (Information valid as of June 2001)			
Vendor Contact: 1-800-223-0633 *www.inficon.com*	**Vendor Information:** INFICON Inc. Two Technology Place East Syracuse, NY 13057	**Limitations on Performance:** GC oven temperature range is limited to 10°C above ambient (coolest temperature) to a maximum of 80°C (warmest temperature). For stack (gas) sampling, the gas stream must have less than 95% relative humidity to avoid condensation	

(continued)

TECHNOLOGY QUICK REFERENCE SHEET (continued)

HAPSITE Field Portable Gas Chromatograph/Mass Spectrometer (GC/MS)

General Commercial Information (Information Valid as of June 2001) (continued)

Availability/Rates:	Principle of Analytical Operation:	Power Requirements:	Instrument Weight and/or Footprint:
Commercially available for purchase: • Instrument without service module: $75,000 • Instrument with vacuum pump service module: $95,000 • Field portable printer: $300-$500 Leasing options may be available.	VOC concentrations in the sample equilibrate with VOC concentrations in the headspace of the sample vial. Headspace vapor is swept into the GC column using a carrier gas. The GC column separates analytes, which are then detected by MS. The MS can be programmed to identify selected compounds in either the full scan or selected ion monitoring (SIM) mode.	Either self-contained batteries (nickel-cadmium) or line (ac) power. Battery lifetime is 2-3 hours for the GC/MS, and 4-6 hours for the headspace sampling accessory.	GC/MS: 15.9 kg (with batteries), 46 cm x 43 cm x 18 cm Headspace sampling system: 6.8 kg, 36 cm x 39.5 cm x 19 cm Notebook computer: 3.6 kg Printer: 2.3 kg Complete system: 28.6 kg

General Performance Information

Known or Potential Interferences:
As with all GC/MS analyses, the coelution of non-target compounds with target analytes poses the potential for interference and/or errors in quantitation.

Applicable Media/Matrices:	Analytes Measurable with Expected Detection Limits:	Other General Accuracy/Precision Information:
Water, soils, sediments and vapors/gases (e.g., ambient air, exhaust and stack emissions, soil gas).	Volatile organic compounds (VOCs) at concentrations between 2 and 5 µg/L (using the MS in full scan mode). Detection limits of about 0.5 ppb are possible using the MS in the SIM mode.	In an EPA ETV evaluation [1], the HAPSITE GC/MS detected 100% (59 of 59) of calibrated analytes present in excess of 5 µg/L in PE samples. Correlation coefficients of HAPSITE results against reference laboratory results averaged 0.989. Across 22 target compounds, precision ranged from 2 to 28% relative standard deviation, and accuracy ranged from 1 to 33% absolute percent difference.
Wastes Generated Requiring Special Disposal: None		**Rate of Throughput:** In the EPA ETV evaluation, water samples were analyzed at a rate of 2-3 samples/hour, including periodic analysis of blanks and calibration check samples.

Note: [ ] indicates a cited reference. Cited references appear both in the text and in some section headings.

EXECUTIVE SUMMARY

This technology evaluation report describes the use of a field-based measurement technology, the portable INFICON HAPSITE gas chromatograph/mass spectrometer (GC/MS), to measure volatile organic contaminant levels, particularly trichloroethene (TCE), in ground water on a real-time basis. The results were effective for making decision-making in the field that guided characterization of the plume and optimal placement of monitoring wells. Real-time use of the technology allowed well installation at a lower cost than if more conventional technologies with a longer turnaround time for results (i.e., conventional off-site fixed laboratory analyses) had been used.

The Monterey Peninsula Airport (MPA) is located near the city of Monterey, California. Past Department of Navy (DoN) activities released TCE contamination into soil and ground water. The U.S. Army Corps of Engineers (USACE) began conducting a series of activities to characterize the extent of the TCE contamination and migration. During 1999, the USACE collected ground water samples from soil borings and monitoring wells both inside and outside the boundaries of the MPA for on-site analysis of volatile organic compounds (VOCs). The HAPSITE GC/MS instrument was used as the determinative method (i.e., the instrumentation generating the analytical result) according to the Environmental Protection Agency's (EPA's) SW-846 Method 8260 (Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry) [2]. Sample preparation and introduction (into the GC/MS instrument) was accomplished using an equilibrium headspace technique (SW-846 Method 5021) [3].

The USACE had previously used Field-Portable Analytical, Inc. in 1998 as a contracted analytical service provider to furnish on-site analysis of MPA ground water VOC samples. During this earlier work, the USACE requested split sample VOC analyses, so that the same ground water samples were run both by the on-site analytical team (using the HAPSITE GC/MS) and by a conventional fixed laboratory. This activity established that the on-site analytical service provider could generate VOC data of known and documented quality comparable to traditional VOC data on the site-specific sample matrix. During the 1999 project, ground water samples collected from the soil borings were analyzed by the HAPSITE instrument only. It was not necessary to again split samples for confirmatory analysis by an off-site laboratory because the reliability of the analytical service provider had already been demonstrated. The validity of the 1999 field-generated VOC data set was confirmed through the use of a field quality assurance/quality control (QA/QC) program specified in the project's quality assurance plan.

Upon completion of plume definition, the HAPSITE instrument left the site, and the installation of permanent monitoring wells in selected borings was completed. After the wells had been developed by surging, bailing, and purging, ground water samples were collected and sent to a conventional laboratory for VOC analysis using Methods 5030 (purge & trap) and 8260 (GC/MS). The two sets of VOC data (on-site versus off-site laboratory) were not expected to be directly comparable because the sample sets themselves were not directly comparable (water collected from a boring versus water collected from a fully developed well). Although a comparison between the two data sets shows expected variations, there is excellent agreement between the two data sets when they are assessed according to their ability to support project decision-making.

The HAPSITE instrument was used again at the MPA in 2001 for real-time characterization of the vertical extent of TCE contamination. Although this report does not include an evaluation the data set generated in 2001, the USACE again reported complete satisfaction with the ability of the field GC/MS to provide reliable data supporting a dynamic work plan strategy that modeled vertical stratification of the TCE plume to a degree not feasible using traditional off-site analyses.

In addition to presenting the performance of the HAPSITE GC/MS in the MPA project, this report briefly reviews the HAPSITE's performance in an EPA Environmental Technology Verification (ETV)

demonstration that assessed the ability of several field portable instruments (including the HAPSITE GC/MS) to detect and measure VOCs in ground water. The ETV reports for this demonstration, including the HAPSITE report, are available through the ETV website for "Well-Head Monitoring - VOCs," which can be found on the *http://www.epa.gov/etv/verifrpt.htm#monitoring* webpage.

According to the USACE [4], the portion of the MPA site characterization effort that encompassed the summer of 1999 cost approximately $75,000. This figure included not just the HAPSITE activities, but also the drilling team and USACE personnel costs. The USACE estimates that use of the HAPSITE instrument resulted in a savings of approximately $27,000 and at least four days of field time, when compared to projected work flow assuming the fastest possible turnaround of data from an off-site laboratory.

The USACE was charged a daily rate by the analytical service provider, who provided all instrumentation, supplies and personnel as part of a turnkey service. If purchased from the instrument vendor, the HAPSITE GC/MS unit costs approximately $60,000 and the headspace sampling accessory costs approximately $15,000, for a total cost of $75,000. (A vacuum pump service module costs an additional $20,000.) Both the instrument and accessory may be available for lease. Depending on the type and number of analyses being performed, varying quantities of consumable items, such as syringes, vials, gloves, bottled gases and reagents may be required at costs ranging from $50 to $250 per day.

Instrument operation requires at least one well-trained GC/MS operator. Sample throughput can vary depending on a number of factors, including the target analyte list and the number of samples submitted for analysis, which can be up to 25 to 30 samples per day. As with all on-site analyses, comparing the cost of analytical alternatives on a "cost per sample" basis is seldom reflective of the true economic value of using field analytical technologies. The real value in using field methods is the time and labor savings realized when the ability to make accurate real-time decisions minimizes (1) the down-time of costly equipment and services (such as a subcontracted drill rig and team), and (2) repeated mobilizations back to the field to fill data gaps. In addition, the opportunity to make many more measurements in the field while the analytical equipment is available on-site provides a cost-effective means of managing the major source of data uncertainty, which is that due to sampling variability in heterogeneous environmental media [5].

The HAPSITE GC/MS and accessories provides the versatility to generate reliable, real-time, and cost-efficient data for measuring VOCs in ground water, solid media (such as soil and sediment samples), and gaseous samples (e.g., ambient air, exhaust, stack emissions, and soil gas).

SITE INFORMATION

Identifying Information

Monterey Peninsula Airport
Monterey, CA

Background [6, 7]

Physical Description: The Monterey Peninsula Airport (MPA) is located approximately two miles east of the city of Monterey, California, within the MPA District. Figure 1 illustrates the site location relative to Monterey, California. The MPA covers a total of 455 acres. One acre within the MPA's total acreage and approximately one acre off site in a residential area were of primary interest in this study.

Site Use: From 1942 to 1989, the Department of the Navy (DoN) leased the 455-acre site from the MPA District and used it as an air base. In 1946, the Federal government determined that the airport was not required for full military purposes. Consequently, the MPA District was granted joint and equal use of the landing facilities. Other MPA facilities such as parking aprons, hangers, repair shops and storage tanks continued to be solely used by the DoN. Between 1972 and 1982, the Naval Postgraduate School of the DoN at Monterey continually renewed its lease with the MPA District which included the use of underground fuel storage tanks and supporting pipelines in the cantonment area at the north end of the property. In 1989, the MPA District released DoN from its lease of the 455-acre parcel. The site is currently a municipal airport.

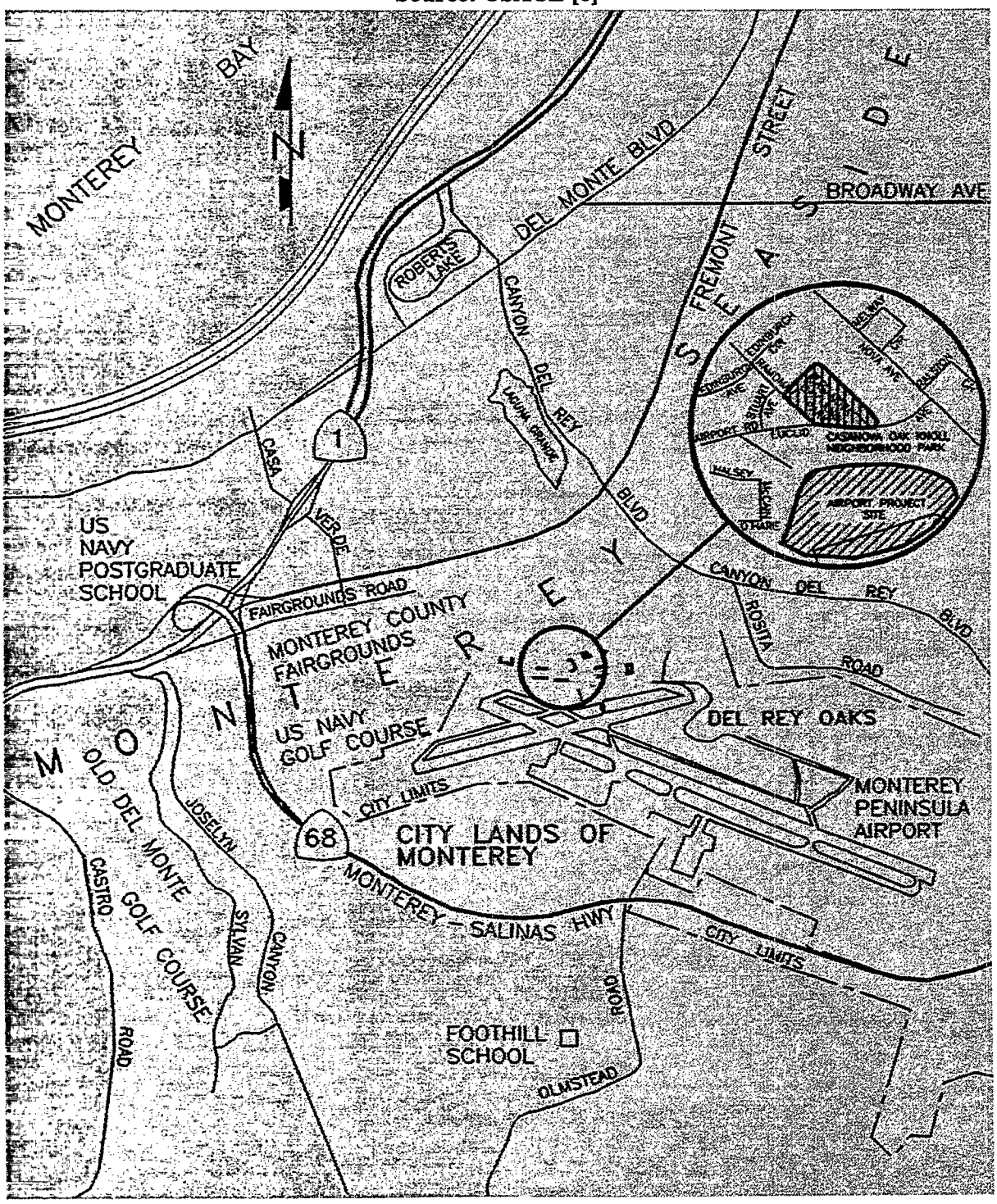
Release/Investigation History: From the 1940s to 1972, Building 17 of the MPA was used by the DoN as an engine repair facility. In this facility, aircrafts parts were cleaned by spraying them with trichloroethene (TCE). Spills were collected in a concrete sump located outside the hangar where the contents were allowed to evaporate. Reportedly, the sump was frequently clogged with organic debris causing the contents to spill unchecked down the slope. Leakage of materials may also have occurred through the bottom of the sump.

In March and April of 1997, the U.S. Army Corps of Engineers (USACE), Sacramento District, conducted an investigation to characterize and determine the extent of soil and ground water contamination released from two 50,000-gallon underground storage tanks (USTs), and to remove five smaller USTs ranging in size from 300 to 700 gallons. In addition, three 2,500-gallon USTs were removed from locations directly downgradient from the 50,000-gallon USTs. Soil contamination from released fuel was evident at the locations of all USTs.

In January 1998, the Sacramento District of the USACE conducted a supplemental investigation that continued the on-site characterization of the petroleum plume initiated in 1997 at the MPA, and extended the investigation off-site into the residential neighborhood north of the airport. The petroleum plume was being delineated using the field-portable HAPSITE GC/MS, when the GC/MS unexpectedly showed that TCE was also present in the ground water. The on-site availability of the GC/MS made it possible to modify the project work plan to accommodate a preliminary assessment of the TCE plume at that time. A more thorough investigation of the TCE plume extent for the purpose of installing a TCE monitoring well network was conducted in 1999, again using the HAPSITE GC/MS. The 1999 investigation forms the basis of this technology evaluation report.

SITE INFORMATION (continued)

FIGURE 1: LOCATION OF MONTEREY PENINSULA AIRPORT NEAR MONTEREY, CALIFORNIA, SCALE: 1" = 1000'
Source: USACE [6]



SITE INFORMATION (continued)

Regulatory Context [8]: Monterey Peninsula Airport is being addressed under the military's Formerly Used Defense Site (FUDS) Program. At MPA, FUDS oversight includes two 50,000-gallon, concrete, underground storage tanks (USTs), Building 17, a fire fighting training facility, and numerous smaller UST sites. Chemicals of concern include petroleum products and their associated compounds, and chlorinated solvents (e.g., TCE). Site assessment activities to date have determined the extent and degree of ground water impacts associated with the two 50,000-gallon fuel tanks. The USACE is monitoring the site for UST/petroleum hydrocarbon impacts on a quarterly basis pending design of a remediation system. Ground water assessment activities in 1998 associated with the two former 50,000-gallon diesel tanks near Building 17 unexpectedly revealed significant concentrations of TCE in ground water (up to 1,400 ppb near the source).

Investigation activities at this site began slowly, but became more intense during the latter part of year 2000 due to regulator concern over potential contamination of private wells by TCE. Identifying all private wells in the area of the TCE plume thus became a priority. The area is supplied by a municipal water system, however, some residents use private wells for irrigation. The municipal system was recently tested at several of the resident's outdoor faucets to confirm the integrity of local water supply lines, and contamination was not detected. However, some private wells have been found to contain TCE, while it has been shown that other private wells do not contain TCE contamination. Regulatory staff coordinated efforts with neighborhood representatives to encourage residents to come forward with information regarding historic practices by the military or others that may be causing environmental problems.

National Priority List (NPL) listing: None

Enforcement Dates: A Notice of Violation was issued July 24, 2000, by the California Regional Water Quality Control Board. It contained a schedule for compliance with Cleanup or Abatement Order (CAO) 99-005. CAO 99-005 concerns the cleanup of the contaminated areas at MPA.

Site Logistics/Contacts

Lead Regulatory Agency Contact:
Grant Himebaugh
California Regional Water Quality Control Board
Central Coast Region
San Luis Obispo, CA
(805) 542-4636

USACE Quality Assurance Contact:
Pam Wehrmann
U.S. Army Corps of Engineers
Environmental Chemistry Section
Sacramento District
(916) 557-6662

USACE Project Geologist:
Pat Cantrell
U.S. Army Corps of Engineers
Environmental Design Section
Sacramento District
(916) 557-5371

USACE Project Manager:
Jerry Vincent
U.S. Army Corps of Engineers
Programs & Project Management Division
Sacramento District
(916) 557-7452

Analytical Service Provider:
Field-Portable Analytical, Inc.
3330 Cameron Park Dr. Suite 850
Cameron Park, CA 95682
(530) 676-6620
http://www.fieldportable.com

MEDIA AND CONTAMINANTS

Matrix Identification

Type of Matrix Sampled and Analyzed: Ground water

Site Geology/Stratigraphy [6]

The surficial geological units mapped in the vicinity of MPA are Pleistocene to Holocene alluvium, Pleistocene Aromas sand, Pleistocene dune deposits, and the Miocene Monterey Formation, which consists of siliceous mudstone. A cross section through the central portion of the airport shows that the Aromas sand and the older alluvium are underlain by the Monterey Formation. Lithologic logs from ground water monitoring wells at the MPA indicate that the underlying alluvial deposits consist primarily of sand lenses of variable thickness interbedded with minor lenses of clay.

The MPA is located in the Carmel sub-basin, which enclosed two ground water systems: the Carmel Valley aquifer and the Canyon del Rey aquifer. The Carmel Valley aquifer is composed mostly of alluvium and terrace deposits. Ground water moves northwest down the valley and discharges into Carmel Bay. The Canyon del Rey aquifer consists of recent sand dunes and underlying unconsolidated sediments. In the airport vicinity, movement of the Chupines fault has elevated the Monterey Formation and led to the erosion and removal of the main water-bearing formations. What remains of the airport aquifer is primarily older alluvium and the Aromas sand. Ground water movement is northwest toward Monterey Bay.

Contaminant Characterization

Primary Contaminant Groups at the Site: Volatile organic compounds (VOCs), primarily benzene, toluene, ethylbenzene, and xylenes (BTEX) and trichloroethene (TCE).

Matrix Characteristics Affecting Characterization Cost or Performance

There were no matrix characteristics that adversely affected either characterization costs or performance when using the HAPSITE GC/MS.

SITE CHARACTERIZATION PROCESS

Goal of Site Characterization

The goal of the 1999 ground water investigation at the Monterey Peninsula Airport was to quantitatively characterize the horizontal extent of TCE contamination due to the DoN activities at Building 17, the former engine repair facility, in the ground water on-site and off-site of the Monterey Peninsula Airport. The field-portable gas chromatograph/mass spectrometer (HAPSITE GC/MS) was used to provide real-time, low-cost data to guide optimal placement of permanent monitoring wells in a timely manner.

In addition to the 1999 horizontal characterization of the plume, the HAPSITE GC/MS was used during the early part of 2001 to vertically characterize TCE levels within the plume. The purpose in 2001 was to determine the full extent of contamination and whether TCE stratification was occurring within the subsurface aquifer formation.

Sampling Work Plan [6, 7]

In March 1999, the USACE developed a field sampling plan (FSP) for the summer of 1999 TCE ground water investigation at the MPA (the subject of this report). The FSP addressed the forthcoming ground water investigation and the location of proposed borings and temporary wells and soil and ground water sample collection from each boring and subsequent laboratory analysis of the samples. The FSP specified that ground water samples would be collected for analysis by both an "on-site laboratory" and a "conventional laboratory," and that the samples collected for analysis by the on-site laboratory would use EPA SW-846 Method 8260 to analyze for VOC contamination.

The field-portable HAPSITE GC/MS was selected for the 1999 investigation since the HAPSITE had been instrumental in the 1998 investigation that initially discovered and partially delineated the TCE plume. Split sample analyses during the 1998 investigation established to the satisfaction of the USACE project team that Field-Portable Analytical, Inc. was fully capable of using the HAPSITE instrument to produce data of known and documented quality for VOC analytes in the site's ground water matrix. The results of the 1998 investigation also formed the basis for selecting the initial 1999 sampling locations. Based on the VOC results from each boring, decisions would be made in the field about whether additional borings were required to adequately characterize the plume and where those locations would be. Decisions would also be made about whether a particular boring would be converted to a permanent monitoring well, or back-filled and sealed. After a boring was drilled, ground water samples were collected from the open borings using disposable bailers, and the samples were analyzed for VOCs by the HAPSITE GC/MS instrument using the equivalent of SW-846 Method 8260 [2].

For the on-site investigation, 9 soil borings (MPA-B7, -B7A, -B8, -B9, -B10, -B11, -B12, -B18, and -B19) were drilled at representative locations within the light industrial area. Five of these 9 borings were later converted to monitoring wells (MPA-MW9, -MW10, -MW11, -MW12, -MW13). One well was installed north of Building 17, three were located downgradient, and one upgradient from the source of contamination. For the off-site investigation in the residential area, 5 soil borings (MPA-B13, -B14,-B16, -B17, and -B20) were drilled at representative locations within the boundaries of the city park and two adjacent streets. Three of these 5 borings were later converted to monitoring wells (MPA-MW14, -MW15, and -MW16). Two additional borings (MPA-B15 and MPA-B15A) yielded no water and therefore no analyses were performed.

Sample Collection Technologies or Procedures [6, 7]

Ground water samples were collected from open borings using disposable bailers and transferred to 40-mL VOA vials. Only one sample was taken from the bottom of each borehole. (Collection at multiple intervals within the boring was not possible since hollow-stem auger drilling was used.) Within minutes after collection, the VOA vials were handed to the HAPSITE GC/MS operator, who poured the VOA vial's contents into a 50-mL gas tight syringe. Using the syringe, exactly 20 mL of sample was introduced into a headspace vial and sealed. A measured amount of internal standard/surrogate solution or matrix spike solution was then injected into the sealed headspace vial through the septum. Because sample analysis was nearly immediate, neither chemical nor physical means of sample preservation was required. The USACE used the VOC results on a real-time basis to determine whether the boring should be filled and sealed or converted into a monitoring well. When monitoring wells were installed, they were developed prior to further sampling by surging, bailing, and purging.

One of the values of on-site analysis becomes evident when one contrasts this sampling sequence, which takes the sample from bailer to the analytical instrument in a matter of a few minutes, to a more traditional sampling and analysis sequence, in which up to 14 days can pass between collection and analysis. In addition to the expense and inconvenience of waiting for days or weeks for data, the longer the elapsed time between sample collection and analysis, the greater the likelihood that target analytes will be lost. Furthermore, a traditional sampling and analysis sequence requires the addition of chemical preservatives (acid to retard the growth of organisms, and sodium thiosulfate when the presence of free chlorine is suspected) which increases the likelihood of sample contamination and/or analyte loss through chemical reaction. Sample handling and transport provides additional opportunities for sample contamination or compromise through proximity to higher concentration wastes, loss of volatile analytes when temperatures exceed 4°C, or a complete loss of the sample through container breakage.

A comparison of the analytical results for samples obtained from the boreholes using the field-portable HAPSITE GC/MS and those for samples from the monitoring wells using fixed laboratory analyses shows that the data are in agreement (see Table 6 under "Performance Evaluation" section). In other words, both data sets support the same conclusions about the nature and extent on TCE contamination. However, differences in the numerical results do, of course, exist because the samples were collected at different times under different conditions. There are a number of factors related to sample support (i.e., the physical characteristics of the sample, such as the volume of ground water withdrawn from the aquifer, the degree of physical mixing between chemically stratified zones, etc.) and sample collection that could contribute to any observed differences, including:

- Random temporal variability within a boring/monitoring well location might explain differences between constituent concentrations found at the time the boring sample was collected versus the time the sample was collected from the permanent monitoring well.

- Samples obtained from an open borehole represent ground water from saturated zones throughout the depth of the borehole, whereas samples obtained from a permanent monitoring well represent ground water entering the well from the screened interval.

- Drilling techniques such as the use of augers cause disturbance to the subsurface and ground water immediately adjacent to the borehole. Disturbances due to drilling activities may cause the loss of volatiles or increased turbidity in the borehole samples. Development of the permanent monitoring wells, however, decreases the impact of drilling activities on the samples obtained from the monitoring wells.

In addition to the 1999 horizontal characterization of the contaminant plume at the MPA, the USACE again used the HAPSITE GC/MS during early 2001 to further characterize the vertical and horizontal extent of TCE levels within the plume. Although the 2001 characterization effort is not the primary subject of this report, it provides an excellent example of how field measurement instrumentation supports better and faster decision-making at low cost. The 2001 characterization effort involved collecting a series of ground water samples at 5-foot intervals while moving deeper into the aquifer. After submission to the on-site analytical service provider, VOC results were made available to the project team within 30 minutes to 1 hour. A cone penetrometer (CPT) rig was used during this characterization to permit collection of samples at multiple intervals. Once sample analyses provided "non-detect" at two consecutive depths, sample collection at that location ceased and the testing operation moved to a different location. Given that this characterization did not experience the time lag associated with off-site laboratory analyses, the USACE saved both time and money by using a real-time approach. In fact, the USACE may not have considered conducting the vertical characterization without the ability to provide real-time data results to guide the procedure. The USACE found discernable degrees of TCE stratification throughout the plume in as little as a 5-foot change in depth. This fact will greatly influence the planning and design of follow-up remedial and monitoring activities.

Field Analytical Technologies [7, 9, 10]

The INFICON HAPSITE GC/MS is a full featured quadrapole GC/MS, equipped with a 27-m SPB-1 column and a 3-m blackflush column [11]. The interface between the GC and the MS is a 70% dimethyl silicone/30% polycarbonate membrane that allows organic constituents to migrate into the MS, while keeping inorganic constituents out of the MS. The instrument utilizes a chemical "getter" pump to maintain adequate vacuum for weeks at a time, although the getter pump must be periodically replaced as a consumable item. The optional service module serves as a rough/turbo vacuum pump that initially develops the vacuum within the MS after change-out of the getter pump. Vacuum is then maintained by the getter pump. If sufficient power is readily available, the MS may be run directly using the turbo vacuum pump during routine instrument operation so that the life of the getter pump is extended.

For the investigation at the MPA, the instrument was transported and operated in the back of a van (see cover photo). Standards were stored in the van on ice. The HAPSITE GC/MS was connected to a headspace sampling accessory that uses the equilibrium headspace method for introduction of samples into the GC. Precisely measured samples (20 mL) were loaded into headspace vials (40-mL screw cap VOA vials), then sealed with a PTFE coated septum. An internal standard/surrogate solution was injected into each sample, blank, and standard. The vials were then placed in an pre-heated (60°C) oven and allowed to equilibrate for a minimum of 20 minutes. As the samples were heated, volatile constituents were driven from the water sample into the vapor phase above the sample (headspace). When equilibrium was established, the headspace in the vial was swept into the HAPSITE GC/MS using a nitrogen carrier gas.

Target analytes were identified based on comparison of chromatographic retention time to that of standards, and on the relative abundance of characteristic ions in the resulting mass spectrum. Because the partition coefficient of each target analyte between a specified volume of water and volume of headspace is characteristic of that compound, the concentrations of target analytes were quantitated based on direct comparison with a standard curve. Note that although the principles behind the equilibrium headspace sample preparation method used for the field technique (SW-846 Method 5021) are somewhat different from those for purge & trap (SW-846 Method 5030, the most commonly used fixed laboratory method), the numerical results from the HAPSITE GC/MS should be directly comparable to fixed laboratory GC/MS analysis if other sampling and analytical factors are also comparable.

Quality Assurance/Quality Control [7, 10]

All quantitative analyses, whether conducted in a fixed laboratory or in the field with portable instrumentation, require quality control (QC) measurements that document the quality of the analytical results. Quality control results are evaluated against acceptance criteria determined both by the method (to ensure that the method is being implemented properly) and by the project's data quality needs (to ensure that the analytical results are adequate for their intended purpose). When project personnel plan for using a field-portable analytical technology such as the HAPSITE GC/MS, it is important to draw upon the expertise of an analytical chemist so that selection and usage of the technology will be appropriate to the project goals. The chemist will also design a QC protocol that is sufficient to ensure that the resulting data will be of known quality commensurate with its intended use. If needed to meet project goals, the same types of QC activities used in a fixed laboratory can be applied to field analyses.

The QC activities required for quantitative analysis of VOCs by both field and fixed laboratory GC/MS instrumentation include:

- Initial calibration - A calibration curve is prepared by analyzing standards at a minimum of 5 different concentrations. The mathematical expression of a line defined by the response of the instrument to these standards is used to calculate the concentration of target analyte(s) present in the samples. A complete standard curve must be prepared and analyzed for each target analyte that is reported quantitatively. The analytes quantitated during the MPA on-site VOC analyses were:

vinyl chloride	trichloroethene	ethyl benzene
trans-1,2-dichloroethene	toluene	*m,p*-xylene
cis-1,2,-dichloroethene	tetrachloroethene	*o*-xylene
benzene		

  Reported sample results must be within the range defined by the lowest and highest concentration standards used in the calibration curve. Samples with concentrations higher than the highest standard must be diluted to bring them within the range. Samples with results below the lowest standard are reported as less than some reporting limit.

- Instrument tune - This involved analysis of a solution of a standard compound resulting in a mass spectrum that meets very specific criteria. This ensures that subsequent mass spectra will be characteristic of the target analytes and reproducible, allowing accurate qualitative identification of compounds. In the case of VOC analyses (both field and fixed lab analyses), the tune compound commonly used is bromofluorobenzene (BFB). Alternatively, the HAPSITE manufacturer provides guidelines for a mass calibration procedure that will yield standard spectra. The use of this procedure to tune the mass spectrometer, rather then tuning using BFB, may be an acceptable alternative for some projects.

- Continuing calibration check - Once a calibration curve is established, the analyst must ensure that the instrument response does not vary significantly over time. This is accomplished by the analysis of a single calibration standard at a concentration near the mid-point of the calibrated range. The continuing calibration check (CCC) is analyzed at the beginning of each analytical shift.

- End calibration check - Functioning much like the CCC, a calibration check sample was analyzed at the end of each analytical shift, ensuring the instrument response did not vary significantly during the time period over which environmental samples were being analyzed. Similar to a CCC, the end calibration check is comprised of a mid-point calibration standard. This QC check is commonly requested as part of the QA package for USACE projects.

- Duplicates - The precision, or reproducibility, of a measurement system is evaluated by measuring the same variable in two samples that are expected to yield closely similar results, and then mathematically determining how close the results are. Usually two repeat measurements are compared (duplicates), although more than two repeat analyses are sometimes desirable (referred to as replicates). The results of duplicate analyses can sometimes be difficult to evaluate because many variables from both the sample collection and the sample analysis processes can be involved. The project planning team should carefully consider which analytical or sampling variable(s) they want to evaluate for precision before deciding on the types and numbers of duplicate analyses to be performed [12]. Relative percent difference (RPD) is a common means of mathematically calculating the closeness of duplicate results.

- Method blanks - The possibility of extraneous contamination, through improper sample handling or contaminated reagents and glassware, must be evaluated to ensure that the concentrations reported are those occurring in the original sample. Method blanks are prepared and analyzed along with each group of samples by carrying samples of reagent-grade water through the entire analytical process.

- Surrogates - All samples, blanks, and standards are spiked with known concentrations of compounds that are chemically similar to the target analytes of interest, but are known not to be present in the samples. The surrogate compounds used for the MPA VOC analyses were dibromofluoromethane, deuterated toluene, and bromofluorobenzene. The recovered concentration of these compounds is used to evaluate the effectiveness of the analytical process. Recoveries significantly lower than 100% may mean that the sample preparation or extraction process used was ineffective, that samples were handled improperly, that the instrument was calibrated improperly, or one of a myriad other problems. Recoveries significantly greater than 100% may mean that the analytical method is inaccurate or imprecise for that sample matrix, that the instrument was calibrated incorrectly, or that the instrument response is changing over time. In any case, surrogate recoveries outside of pre-defined acceptance criteria signal an analytical problem that requires immediate corrective action on the part of the analyst.

Table 1 provides the QC acceptance criteria used for the analysis of VOCs for the MPA project. Both the field analytical service provider (using the HAPSITE GC/MS) and the fixed laboratory (using purge-and-trap GC/MS) utilized the same acceptance criteria for their QC programs. Results of the field QC analyses are provided in Tables 2 through 4. These data demonstrate stable performance that met the needs of the project in terms of sensitivity, precision, and bias. The generation of analytical data can be most cost-effective if the QC acceptance criteria are derived to accommodate the specific sensitivity, precision, and bias needed to meet the decision-making needs of the project. Depending on the rigor of data needed for a particular project, QA acceptance criteria might be chosen that are "tighter" or "looser" than those used for this particular project. This is in accordance with the guidance provided in the SW-846 manual (see section 2.0 of Chapter Two, page TWO-1) [13].

TABLE 1. QC ACCEPTANCE CRITERIA

Quality Control Check/Frequency	Acceptance Criteria
Initial Calibration: Five-point (minimum) calibration	Percent Relative Standard Deviation (%RSD) of ≤ 30%
Instrument Tune Using BFB: Once per 12-hour shift	Ion abundance criteria as described in EPA Method 8260
Continuing Calibration Check: Beginning of each day	Difference of the expected concentration for the CCC compounds of ± 25%
End Calibration Checks: End of each day	Relative Percent Difference (RPD) from the beginning CCC of ± 25%
Duplicates: 10% of the samples	RPD of ≤ 30% between duplicate samples
Method Blanks: After beginning of the day's CCC	Concentrations for all calibrated compounds < Reporting Limit
Surrogates: Each sample, spike, standard, and reagent blank	Recovery for each surrogate must be between 75 to 125%

TABLE 2. DUPLICATE ANALYSES

	cis-1,2-Dichloroethene (µg/L)	RPD (%)	Trichloroethene (µg/L)	RPD (%)
MPA-B7-GW	100	10	160	6
MPA-B7-GW Duplicate	110		170	
MPA-B10-GW	< 5	-	25	17
MPA-B10-GW Duplicate	< 5		21	
MPA-B11-GW	< 5	-	490	10
MPA-B11-GW Duplicate	6.8		540	
MPA-B12-GW	< 5	-	52	6
MPA-B12-GW Duplicate	< 5		55	

CHARACTERIZATION TECHNOLOGIES (continued)

TABLE 3. SURROGATE RECOVERIES

	DBF (%)	Toluene -D8 (%)	BFB (%)	Run Date
MPA-B7-GW	109	92.5	120	6/18/99
MPA-B7-GW Duplicate	114	96.6	127	6/18/99
MPA-B7A-GW	117	91.8	103	6/18/99
MPA-B8-GW	91.3	101	93.2	6/8/99
MPA-B9-GW	111	91.8	83	6/14/99
MPA-B10-GW	78.7	104	105	6/8/99
MPA-B10-GW Duplicate	82.2	95.3	81.3	6/8/99
MPA-B11-GW	86	93.5	80.9	6/10/99
MPA-B11-GW Duplicate	87	99.4	89.7	6/10/99
MPA-B12-GW	94.1	99	84.6	6/9/99
MPA-B12-GW Duplicate	85.2	94.1	97.7	6/9/99
MPA-B13-GW	120	95.5	112	6/15/99
MPA-B715-GW	111	97.7	112	6/16/99
MPA-B18-GW	116	94.2	118	6/16/99

TABLE 4. MATRIX SPIKE RECOVERY AND PRECISION

	Trichloroethene (µg/L)	RPD	Benzene (µg/L)	RPD	Toluene (µg/L)	RPD
MPA-B12-MSD	**164 (89.6%)**	**1%**	**117 (93.6%)**	**1%**	**108 (86.4%)**	**0%**
MPA-B12-MS	**162 (88%)**		**116 (92.8%)**		**108 (86.4%)**	

PERFORMANCE EVALUATION

Sampling Results [7]

Table 5 shows the analytical results for all the samples analyzed using the HAPSITE GC/MS. A total of 14 samples were analyzed from on- and off-site boring locations. Eight samples were also analyzed from eight temporary off-site monitoring wells. Of the nine on-site samples, one boring (MPA-B7) was sited in a perched water table, so a second boring (MPA-B7A) was placed nearby and also sampled. TCE was detected in 8 sampling locations downgradient from Building 17 at the northeastern portion of the site, with concentrations ranging from 10 µg/L to 890 µg/L. In addition, *cis*-1,2-dichloroethene was

detected in 6 of the on-site boring samples, at concentrations ranging from 4.5 µg/L (estimated) to 100 µg/L. A single detection of tetrachloroethene was found in one on-site boring, at 4.1 µg/L. Of the 13 off-site locations, TCE was detected in 7 of the 13 sampling points located along the proposed path of the TCE plume.

TABLE 5. HAPSITE GC/MS ANALYTICAL RESULTS

Sample Number and Location	cis-1,2-Dichloroethene (µg/L)	Trichloroethene (µg/L)
Borings (Monitoring Wells)		
MPA-B7*, On-site	100	5
MPA-B7A (MPA-MW11), On-site	55	330
MPA-B8, On-site	4.5 (estimated)	10
MPA-B9, On-site	11	610
MPA-B10 (MPA-MW10), On-site	< 5	25
MPA-B11, On-site	< 5	490
MPA-B12 (MPA-MW9), On-site	< 5	52
MPA-B13 (MPA-MW14), Off-site	< 5	17
MPA-B14, Off-site	< 5	29
MPA-B16, Off-site	< 5	50
MPA-B17 (MPA-MW16), Off-site	7.1	170
MPA-B18 (MPA-MW12), On-site	32	890
MPA-B19 (MPA-MW13), On-site	< 5	< 5
MPA-B20 (MPA-MW15), Off-site	< 5	< 5
Temporary Wells		
MPA-HP5, Off-site	< 5	8.2
MPA-HP7, Off-site	< 5	66
MPA-HP8, Off-site	< 5	3.4 (estimated)
MPA-HP9, Off-site	< 5	< 5
MPA-HP10, Off-site	< 5	< 5
MPA-HP11, Off-site	< 5	< 5
MPA-HP12, Off-site	< 5	< 5
MPA-HP13, Off-site	< 5	< 5

* Perched ground water HP = temporary well B = soil boring -MW = Monitoring well

Technology Performance–MPA Project

Technology performance should be evaluated by assessing whether the analytical technology produced data of known quality that are effective for making the intended project decisions. The preceding Quality Assurance/Quality Control section demonstrated that the HAPSITE instrument performed well within accepted limits for precision and bias across the sample preparation (i.e., equilibrium headspace) and analyte determination (GC/MS) method chain. Precision for the entire sample collection and analysis chain can be assessed through the comparison of separately collected duplicate samples (which ranged from 6 to 17% RPD; see Table 2), and through the comparison of matrix spike duplicate (MSD) to the matrix spike (MS) results (which ranged from 0 to 1% RPD; see Table 4). Potential bias introduced by the sample matrix can be assessed through sample surrogate recoveries (which ranged between 78 and 127% recovery; see Table 3), and through matrix spike/matrix spike duplicate recoveries (which ranged between 86 and 94% recovery; see Table 4).

The goal of the sampling and analysis program at the Monterey Peninsula Airport was to characterize a ground water contaminant plume, and the on-site generated QC data established that the HAPSITE GC/MS data were of known quality entirely adequate to guide plume delineation and monitoring well placement. Since the field method (using SW-846 Methods 5021 and 8260) can be expected to generate data that are directly comparable to data from the fixed laboratory (using SW-846 Methods 5030 and Method 8260) when all other factors are equivalent, and all QC criteria for the field method were well within the project's acceptance limits, the collection of split-sample data to establish the comparability of the field-portable GC/MS results to fixed laboratory GC/MS results was unnecessary.

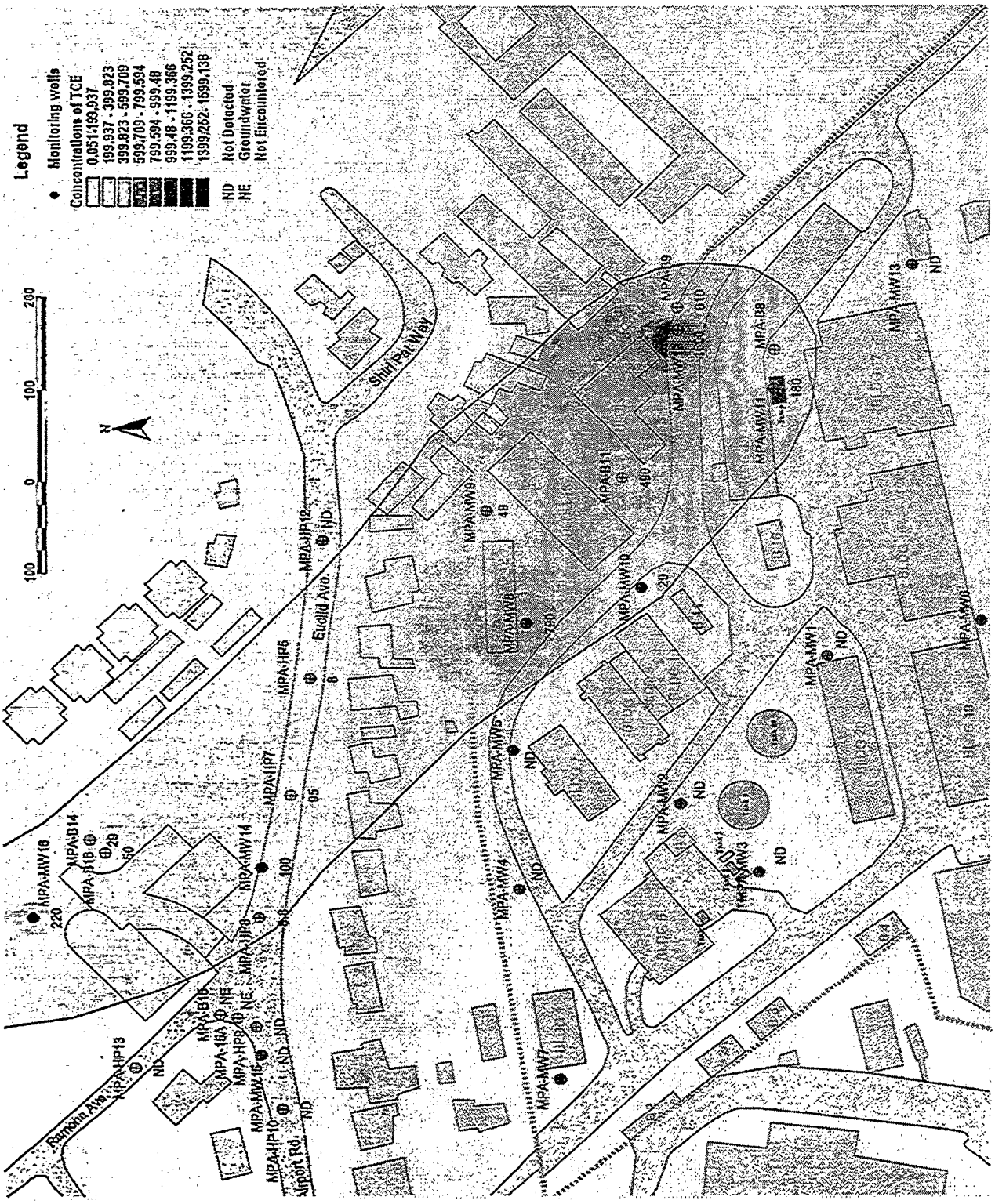
After monitoring wells were installed and fully developed in selected borings, ground water samples were collected from the wells for VOC analysis in a fixed laboratory. Because monitoring well installation and development produces mixing of ground water within the screened interval and yields ground water samples with a different physical nature (i.e., a different sample support) from samples obtained from borings, variation between the boring ground water data set (generated by the HAPSITE) and the monitoring well data set (generated by the fixed laboratory) is expected. Nonetheless, there is surprising similarity between these two data sets, as shown in Table 6. Many of the paired data results are within 50% of each other, demonstrating that the analysis of boring-derived ground water can yield data that are adequate for the purpose of identifying candidate locations for placement of permanent monitoring wells intended to monitor an existing contaminant plume.

TABLE 6. COMPARISON OF BORING AND MONITORING WELL RESULTS

Boring / Monitoring Well Location	*cis*-1,2-Dichloroethene (µg/L)		Trichloroethene (µg/L)	
	Boring (HAPSITE)	Well (Fixed Lab)	Boring (HAPSITE)	Well (Fixed Lab)
MPA-B7A / MPA-MW11	55	18	330	350
MPA-B10 / MPA-MW10	<5	0.8 (estimated)	25	48
MPA-B12 / MPA-MW9	<5	1	52	58
MPA-B13 / MPA-MW14	<5	1.8	17	110
MPA-B17 / MPA-MW16	7.1	6.9	170	220
MPA-B18 / MPA-MW12	32	110	890	1300

Figure 2 provides a graphic representation of the TCE plume, showing placement of the soil borings, monitoring wells, and temporary wells.

FIGURE 2: EXTENT OF TCE PLUME
Source: USACE [7]



Technology Performance–ETV Evaluation [1]

In addition to the HAPSITE performance as reported here from the MPA investigation, the technology's performance was also evaluated through EPA's Environmental Technology Verification (ETV) Site Characterization and Monitoring program. Partnering with DOE's Sandia National Laboratory, the EPA National Exposure Research Laboratory conducted a field demonstration of the HAPSITE field-portable GC/MS in September, 1997. The demonstration was designed to assess the instrument's ability to detect and measure chlorinated VOCs in ground water at two contaminated sites; namely, the Department of Energy's Savannah River Site, near Aiken, South Carolina, and the McClellan Air Force Base, near Sacramento, California. Ground water samples from each site were supplemented with performance evaluation (PE) samples of known composition. Both sample types were used to assess instrument accuracy, precision, sample throughput, and comparability to reference laboratory results. The primary target compounds at the Savannah River Site were trichloroethene and tetrachloroethene. At McClellan Air Force Base, the target compounds were trichloroethene, tetrachloroethene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, and *trans*-1,3-dichloropropene. The full ETV Report for the 1997 HAPSITE evaluation can be accessed through the ETV website [1]. The results for the ETV evaluation are summarized here:

Sample Throughput: Throughput was approximately two to three water samples per hour. This rate includes the periodic analysis of blanks and calibration check samples.

Completeness: The HAPSITE reported results for all but one of the 166 PE and ground water samples provided for analysis at the two demonstration sites. Operator error (sample was dropped during preparation), not instrument problems, accounted for the missing sample result.

Analytical Versatility: The HAPSITE detected all of the compounds in the PE samples for which it was calibrated. For the ETV demonstration project, the instrument was calibrated to include 84% (27 of 32) of all chlorinated and nonchlorinated volatile hydrocarbon compounds included in the PE samples using in the demonstration. Additional compounds could have been detected had the operator elected to have a longer GC/MS run time, a wider set of calibration compounds, and a reduced sample throughput. The HAPSITE detected all (59 of 59) of the ground water contaminants that were present in excess of 5 µg/L (as reported by the reference laboratory). [A total of 68 contaminants, at concentration levels of 1 µg/L or higher, were detected by the reference laboratory in all ground water samples.]

Precision: Precision was determined by analyzing sets of four replicate samples from a variety of PE mixtures containing known concentrations of chlorinated VOCs. The results are reported as the relative standard deviation (RSD) for the four replicates. The RSDs compiled for all reported PE compounds from both sites had a median value of 12% and a 95th percentile value of 29%. By comparison, the compiled RSDs from the reference laboratory had a median value of 7% and a 95th percentile value of 25%. The ranges of HAPSITE RSD values for selected target compounds were as follows:

- Trichloroethene 7 to 18%
- Tetrachloroethene, 6 to 22%
- 1,2-Dichloroethane, 2 to 12%
- 1,1,2-Trichloroethane, 8 to 28%
- 1,2-Dichloropropane, 7 to 21%
- *trans*-1,3-Dichloropropene, 7 to 17%

PERFORMANCE EVALUATION (continued)

Accuracy: Instrument accuracy was evaluated by comparing HAPSITE results with the known concentrations of chlorinated organic compounds in PE mixtures. Absolute percent difference (APD) values from both sites were calculated for all analytes in the PE mixtures. The APDs for all reported compounds from both sites had a median value of 8% and a 95th percentile value of 27%. By comparison, the compiled APDs from the reference laboratory had a median value of 7% and a 95th percentile value of 24%. The ranges of HAPSITE APD values for selected target compounds were as follows:

- Trichloroethene, 1 to 20%
- Tetrachloroethene, 6 to 33%
- 1,2-Dichloroethane, 2 to 20%
- 1,1,2-Trichloroethane 1 to 21%
- 1,2-Dichloropropane, 3 to 21%
- *trans*-1,3-Dichloropropene, 1 to 15%

Comparability: A comparison of HAPSITE and reference laboratory data was based on 33 ground water samples analyzed at each site. The correlation coefficients (r) for all compounds detected by both the HAPSITE and laboratory at or below 100 µg/L concentration levels were 0.983 at Savannah River and 0.978 at McClellan. The r values for compounds detected at concentration levels in excess of 100 µg/L were 0.996 for Savannah River and 1.000 for McClellan. These correlation coefficients reveal a highly linear comparability relationship between HAPSITE and laboratory data. This is not surprising since the determinative analytical method, namely, GC/MS, is the same for both data sets. The median absolute percent difference between ground water compounds mutually detected by the HAPSITE and reference laboratory was 13%, with a 95th percentile value of 60%.

Deployment: The system was ready to analyze samples within 30 minutes of arrival at the ETV test sites. At both ETV demonstration sites, the instrument was transported in a minivan and was operated in its rear luggage compartment. The instrument was powered by self-contained batteries or from line ac power. The recommended training interval for routine sample processing is about 3 days for a chemist with limited GC/MS experience. Method development and analysis of very complex samples requires a higher level of operator training and experience in GC/MS data interpretation.

COST COMPARISON

The USACE estimated that using on-site GC/MS analyses to determine optimal placement of monitoring wells resulted in a cost savings of approximately $27,000. It also resulted in time savings since the drill team and USACE staff spent 4 fewer days in the field. These comparisons were developed by the USACE by assuming that samples would have to be shipped to a fixed laboratory for short-turn around analysis to achieve the same project outcome if on-site analysis had not been used [4]. The analytical service provider, Field-Portable Analytical, Inc., charged the USACE a daily rate, which included providing the HAPSITE GC/MS and all consumables, as well as analytical operators. According to the USACE, the actual combined costs for drilling and on-site analytical activities, plus USACE personnel, was approximately $75,000. This covered 17 days spent in the field with a 3-person drilling crew to

- Drill 15 borings and collect ground water samples from each boring for analysis,
- Convert 8 borings into monitoring wells and develop each well,
- Backfill borings not converted to monitoring wells based on analytical results,
- Contain all investigation-derived waste in 55-gallon drums, and
- Move all drums to designated storage on a daily basis.

Geologic conditions on-site dictated that ground water samples would be collected from open borings in order to reduce the amount of sediment in the samples. Due to certain geological conditions (flowing sands) augers could not be removed from the borings while waiting for analytical results because the holes would collapse. If the samples were sent to a stationary laboratory for analysis on a 24-hour turnaround basis, each boring would have held a drill rig captive for at least one full day before knowing if the boring would be backfilled or converted into a monitoring well. The USACE estimated that the drilling operations would have taken at least 21 days at a projected cost of $102,000 had they not been able to make real-time decisions about well placement, instead of the $75,000 actually incurred. Additionally, the on-site analyses resulted in a logistically smoother project because off-site drilling was conducted in a city park, which required tight scheduling and restricted hours.

While one could make some educated assumptions and calculate a per-sample cost for on-site GC/MS analyses, it cannot be overstated that the value in on-site analyses may not be realized as a cost savings in dollars and cents saved per sample, but rather as:

- Reducing down-time of costly equipment and services (such as a subcontracted drill rig and team) while waiting for laboratory results,
- Fewer mobilizations back to the field to fill data gaps, and
- The ability to make decisions in real-time, based on immediately available analytical results.

In addition, one must consider the enormous potential value to be gained by increasing sample density, thereby improving decision quality by controlling sampling uncertainty. Given the relatively fixed costs for an 8-hour on-site analytical shift, one can elect to make many measurements within that time frame, greatly increasing the information value of the data set, without increasing the analytical expense.

A HAPSITE GC/MS costs $60,000, with an additional $15,000 for the headspace sampling accessory. The cost of consumable analytical supplies, such as syringes, sample vials, gloves, bottled gases, standards and surrogate compounds will vary depending on the sample medium (air/gas, water, or solids), the target analyte list, desired analytical data quality, number of samples, and sample throughput. Consumable costs may range from $50 per day to $250 per day. Analysis also requires at least one well-trained GC/MS operator, and some projects may require two operators, again depending on sampling and analytical complexity and throughput.

OBSERVATIONS AND LESSONS LEARNED

The results of this MPA investigation and the EPA ETV demonstration show that the field-portable HAPSITE GC/MS can provide useful, cost-effective data for on-site and real-time monitoring of volatile organic compounds. Characterizations can be done more quickly than using more conventional approaches, while supporting the generation of more reliable data sets because the nature of field analysis supports better management of sampling uncertainties. This, in turn, leads to more confidence in project decision-making. The HAPSITE instrument can be employed in a variety of applications, ranging from producing rapid analytical results in screening investigations (such as aiding monitoring well placement) to producing accurate and precise data sets that are directly comparable with those obtained from an off-site laboratory. The rigor of the QA/QC protocol should be matched to the rigor of data needed to support the project's objectives (i.e., the project DQOs).

The successful use of the HAPSITE GC/MS at the MPA to generate the definitive, high quality data requested by the USACE emphasizes several points regarding the advantages of field measurement technologies. For example, the number of samples need not be the limiting cost factor to the same degree as it is for conventional fixed laboratory analyses, particular when field laboratory operator rates are charged on a per time (rather than per sample) basis. This permits additional sampling to generate more data points than might otherwise be practical. Real-time results also permit better decision-making regarding whether additional samples are even necessary. This promotes reaching the most appropriate data density that supports defensible environmental decisions despite matrix heterogeneity.

Real-time, reliable results may also permit fewer days in the field, such as occurred at the MPA, because monitoring well location selection and development can occur on the same day as boring sample collection and analysis. The project management team did not have to arrange a return of the drilling rig days or weeks later while awaiting the receipt and evaluation of fixed laboratory results. This advantage was particularly appreciated during the MPA investigation given that the off-site sampling locations were performed in city streets and a neighborhood park. Access to the park grounds was limited to periods when no children were present at a near-by day care facility and on the provision that all drilling activities were to be completed within one day. These schedule limitations were accommodated through use of the field analytical technology.

Another benefit of field analysis is that sample handling, preservation, and storage impacts are minimized. It is well known that the greatest risk for non-representative data (i.e., results that do not accurately reflect true site conditions) occurs during sample selection, collection, and handling. Matrix heterogeneity may cause samples to miss contamination. There are multiple opportunities for VOC analyte loss from environmental samples through volatilization, and biological or chemical degradation as a consequence of repeated sample handling, transportation and undesirable side effects of sample preservation. For example, although acidification is a common preservation technique to minimize loss VOCs biodegradation losses, EPA SW-846 Method 5035 warns that acidification can cause effervescence in samples containing carbonates, resulting in severe loss of VOCs [14]. The need for preservation and its artifacts can be avoided when samples can be analyzed immediately.

Given the above advantages, the use of field measurement technologies such as the HAPSITE GC/MS is well-suited for instituting a dynamic work plan strategy, which relies on real-time data to guide real-time decision-making and allow complete characterization with fewer site mobilizations than conventional work strategies [15]. Unexpected results can be evaluated and resolved immediately, eliminating difficult decisions later about whether to exclude data of questionable validity, or whether to remobilize to the site to resolve uncertainties with additional data. Samples can be rerun or recollected immediately at low cost to verify unexpected results [16]. This can significantly reduce site characterization and cleanup costs, project time frames, and disputes over data reliability or completeness.

OBSERVATIONS AND LESSONS LEARNED (continued)

However, the use of field analysis is not without caveats. Trained technicians may be suitable to *operate* on-site analytical equipment under supervision, however, experienced analytical chemistry expertise is vital to the appropriate *selection* of field analytical equipment and methods and the *design* of a project's standard operating procedures (SOPs) and QC procedures. Project-specific decision goals and site conditions (such as matrix interferences) may indicate that modification of "off-the-shelf" methods is desirable or necessary to ensure that the data generated will match its intended use. A chemist who understands the project goals and the anticipated sampling design should be involved during project planning so he/she can use that knowledge to design an appropriate analytical program. If a technician is used to implement the analytical SOPs in the field, the chemist should be available to offer technical support. Field personnel should be able to access the chemist for assistance in interpretation of the data being generated, troubleshooting any problems that arise, and guiding site personnel regarding the proper use of the results.

Two points should be kept in mind when operating a HAPSITE GC/MS in a field situation [16]:

- When the instrument is calibrated for its standard range of compounds, it is possible to detect and quantitate unexpected analytes. For example, at the initial 1998 investigation at the MPA, the field team expected to characterize a petroleum plume, and the instrument also showed that TCE was present. While such discoveries may not disturb a regulator, it may be initially disconcerting to the project team or a site owner. There is benefit, however, in making such a discovery while the project team is in the field, because if desired the work plan can be adjusted to account for the new analytes in a cost-effective manner.

- The instrument operator, as a member of the team, should resist reporting preliminary results, or data that may appear to be unreliable. Although a GC/MS method (e.g., SW-846 Method 8260) is highly regarded as supplying credible data, operator error can still produce inaccurate results. Fortunately, as noted above, the flexibility inherent in field measurement technologies permits immediate investigation of any questionable result. The operator should take advantage of this feature when necessary to assure only the release of trustworthy data.

REFERENCES

1. U.S. Environmental Protection Agency, National Exposure Research Laboratory, *Environmental Technology Verification (ETV) Report: Field Portable Gas Chromatograph/Mass Spectrometer, Inficon, Inc., HAPSITE*. EPA/600/R-98/142. November 1998. Report available on-line at: *http://www.epa.gov/etv/02/inf_vr.pdf*

2. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Method 8260B: Volatile Organic Compounds by Gas Chromatography/Mass Spectrometry (GC/MS). Available on-line at: *http://www.epa.gov/SW-846/8260b.pdf*

3. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Method 5021: Volatile Organic Compounds in Soils and Other Solid Matrices Using Equilibrium Headspace Analysis. Available on-line at: *http://www.epa.gov/SW-846/5021.pdf*

REFERENCES (continued)

4. Cantrell, Patricia. U.S. Army Corps of Engineers. Letter to Harry B. McCarty of SAIC. Dated 12 April 2000.

5. See the Cleanup Information (CLU-IN) website for EPA documents discussing sampling variability: *http://www.cluin.org/char1_edu.cfm#stat_samp*

6. U.S. Army Corps of Engineers, Environmental Design Section, Sacramento District. Field Sampling Plan: Trichloroethene Ground water Investigation, Monterey Peninsula Airport, California. March 1999.

7. U.S. Army Corps of Engineers, Environmental Design Section, Sacramento District. *Monterey Peninsula Airport Trichloroethene Groundwater Investigation Final Report.* September 1999.

8. Himebaugh, Grant. California Regional Water Quality Control Board. Personal Communication, April 30, 2001.

9. Crume, Craig. Field-Portable Analytical, Inc. Cameron Park, CA. Personal communication.

10. Field-Portable Analytical, Inc. Standard Operating Procedure for GC/MS Analysis of Water by Equilibrium Headspace. May 1999.

11. Sadowski, Chuck. INFICON, Inc., Two Technology Place, East Syracuse, NY 13057. Personal communication.

12. U.S. Environmental Protection Agency. *A Rationale for the Assessment of Errors in the Sampling of Soils*. Office of Research and Development. EPA 600/4-90/013. May 1990. Available on-line at: *http://cluin.org/download/stats/rationale.pdf*

13. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Chapter Two: Choosing the Correct Procedure. Available on-line at: *http://www.epa.gov/SW-846/chap2.pdf*

14. U.S. Environmental Protection Agency. *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods* (SW-846). Method 5035: Closed-System Purge-and-Trap and Extraction for Volatile Organics in Soil and Waste Samples. Available on-line at: *http://www.epa.gov/SW-846/5035.pdf*

15. See the Cleanup Information (CLU-IN) website for EPA documents discussing dynamic work plans: *http://cluin.org/char1_edu.cfm#dyna_work*

16. Crume, C. *The Business of Making a Lab Field-Portable: Getting the Big Picture on an Emerging Market.* Environmental Testing & Analysis. November/December 2000. pp. 28-37. Available on-line at: *http://cluin.org/char1_edu.cfm#usin_fiel*