EPA/600/R-98/144
November 1998

Environmental Technology Verification Report

Field-Portable Gas Chromatograph

Perkin-Elmer Photovac, Voyager

by

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IAG DW89936700-01-0

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Notice

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded and managed, under Interagency Agreement No. DW89936700-01-0 with the U.S. Department of Energy's Sandia National Laboratory, the verification effort described in this document. This report has received both technical peer and administrative policy reviews and has been approved for publication as an EPA document. Mention of corporate names, trade names, or commercial products does not constitute endorsement or recommendation for use.

UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Development
Washington, D.C. 20460

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE: **FIELD-PORTABLE GAS CHROMATOGRAPH**

APPLICATION: **MEASUREMENT OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN WATER**

TECHNOLOGY NAME: **Voyager**

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PROGRAM DESCRIPTION

The U.S. Environmental Protection Agency (EPA) created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative environmental technologies through verification of performance and dissemination of information. The goal of the ETV program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. The ETV program is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies.

Under this program, in partnership with recognized testing organizations, and with the full participation of the technology developer, the EPA evaluates the performance of innovative technologies by developing demonstration plans, conducting field tests, collecting and analyzing the demonstration results, and preparing reports. The testing is conducted in accordance with rigorous quality assurance protocols to ensure that data of known and adequate quality are generated and that the results are defensible. The EPA National Exposure Research Laboratory, in cooperation with Sandia National Laboratories, the testing organization, evaluated field-portable systems for monitoring chlorinated volatile organic compounds (VOCs) in water. This verification statement provides a summary of the demonstration and results for the Perkin-Elmer Photovac, Voyager field-portable gas chromatograph (GC).

DEMONSTRATION DESCRIPTION

The field demonstration of the Voyager portable GC was held in September 1997. The demonstration was designed to assess the instrument's ability to detect and measure chlorinated VOCs in groundwater at two contaminated sites: the Department of Energy's Savannah River Site, near Aiken, South Carolina, and the McClellan Air Force Base, near Sacramento, California. Groundwater 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

The accompanying notice is an integral part of this verification statement trichloroethene, tetrachloroethene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, and *trans*-1,3-dichloropropene. These sites were chosen because they contain varied concentrations of chlorinated VOCs and exhibit different climatic and geological conditions. The conditions at these sites are typical, but not inclusive, of those under which this technology would be expected to operate. A complete description of the demonstration, including a data summary and discussion of results, may be found in the report entitled *Environmental Technology Verification Report, Field-Portable Gas Chromatograph, Perkin-Elmer Photovac, Voyager*. (EPA/600/R-98/144).

TECHNOLOGY DESCRIPTION

Gas chromatography with electron capture detection is a proven analytical technology that has been used in environmental laboratories for many years. The gas chromatographic column separates the sample into individual components. The electron capture detector measures a change in electron current from a sealed radioactive source as compounds exit the chromatographic column, move through the detector, and capture electrons. The electron capture detector is particularly sensitive to chlorinated compounds. Compounds are identified by matching the column retention time of sample components, run under controlled temperature conditions, to those of standard mixtures run under similar conditions. Quantitation is achieved by comparing the detector response intensity of the sample component and the standard. A GC offers some potential for identification of unknown components in a mixture; however, a confirmational analysis by an alternative method is often advisable. Portable GC is a versatile technique that can be used to provide rapid screening data or routine monitoring of groundwater samples. In many GC systems, the instrument configuration can also be quickly changed to accommodate different sample matrices such as soil, soil gas, water, or air. As with all field analytical studies, it may be necessary to send a portion of the samples to an independent laboratory for confirmatory analyses.

The Voyager includes an on-board processor and is encapsulated in a weather-resistant case. The GC unit weighs about 15 pounds and the accessories for water analysis weigh about 33 pounds. Both units can be easily transported and operated in the rear compartment of a minivan. The instrument utilizes an equilibrium headspace technique for the analysis of VOCs in water. Instrument detection limits for many chlorinated VOCs in water are in the range of 5 to 10 μg/L. Sample processing and analysis can be accomplished by a chemical technician with 1 day of training; however, instrument method development and initial calibration may require additional experience and training. At the time of the demonstration, the baseline cost of the Voyager and headspace sampling accessories was $24,000. Operational costs, which take into account consumable supplies, are on the order of $25 per 8-hour day.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the Voyager were observed:

Sample Throughput: Throughput was one to three samples per hour. This rate includes the periodic analysis of blanks and calibration check samples. The sample throughput rate is influenced by the complexity of the sample, with less complex samples yielding higher throughput rates.

Completeness: The Voyager reported results for all 166 PE evaluation and groundwater samples provided for analysis at the two demonstration sites.

Analytical Versatility: The Voyager was calibrated for and detected 75% (24 of 32) of the PE sample VOCs provided for analysis at the demonstration. Three pairs of coeluting compounds were encountered in the GC methods used during this demonstration. For the groundwater contaminant compounds for which it was calibrated, the Voyager detected 39 of the 44 compounds reported by the reference laboratory at concentration levels in excess of 1 μg/L. A total of 68 compounds were detected by the reference laboratory in all groundwater 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 in terms of relative standard deviations (RSD). The RSDs compiled for all reported compounds from both sites had a median value of 20% and a 95th percentile value of 69%. By comparison, the compiled RSDs from the reference laboratory had a median value of 7% and a 95th percentile value of 25%. The range of Voyager RSD values for specific target compounds was as follows: trichloroethene, 7 to 71%; tetrachloroethene, <30% (limited data—-only one value was available); 1,2-dichloroethane and 1,2-dichloropropane (coeluting pair), 4 to 44%; 1,1,2-trichloroethane, 11 to 103%; and *trans*-1,3-dichloropropene, 8 to 46%.

Accuracy: Instrument accuracy was evaluated by comparing Voyager results with the known concentrations of chlorinated organic compounds in PE mixtures. Absolute percent difference (APD) values from both sites were calculated for all reported compounds in the PE mixtures. The APDs from both sites had a median value of 41% and a 95th percentile value of 170%. By comparison, the compiled APDs from the reference laboratory had a median value of 7% and a 95th percentile value of 24%. The range of Voyager APD values for target compounds was as follows: trichloroethene, 8 to 244%; tetrachloroethene, 24 to 99%; 1,2-dichloroethane and 1,2-dichloropropane (coeluting pair), 14 to 70%; 1,1,2-trichloroethane, 16 to 50%; and *trans*-1,3-dichloropropene, 3 to 62%.

Comparability: A comparison of Voyager and reference laboratory data was based on 33 groundwater samples analyzed at each site. The correlation coefficient (*r*) for all compounds detected by both the Voyager and the laboratory at or below the 100 µg/L concentration level was 0.890 at Savannah River and 0.660 at McClellan. The *r* values for compounds detected at concentration levels in excess of 100 µg/L were 0.830 for Savannah River and 0.999 for McClellan. These correlation coefficients reveal a moderately linear relationship between Voyager and laboratory data. The median absolute percent difference between groundwater compounds mutually detected by the Voyager and reference laboratory was 74%, with a 95th percentile value of 453%.

Deployment: The system was ready to analyze samples within 60 minutes of arrival at the site. At both sites, the instrument was transported in and operated from the rear luggage compartment of a minivan. The instrument was powered by self-contained batteries or from a small dc-to-ac inverter connected to the vehicle's battery.

The results of the demonstration revealed that sample handling methodologies may have adversely affected the observed precision and accuracy of the instrument. Perkin-Elmer Photovac has developed an improved field method for sample preparation and handling that includes the use of an internal standard. The new method is expected to result in improved instrument precision and accuracy. The Voyager may be suitable for both field screening and routine analysis applications. In the selection of a technology for use at a particular site, the user must determine what is appropriate through consideration of instrument performance and the project's data quality objectives.

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NOTICE: EPA verifications are based on an evaluation of technology performance under specific, predetermined criteria and the appropriate quality assurance procedures. EPA makes no expressed or implied warranties as to the performance of the technology and does not certify that a technology will always, under circumstances other than those tested, operate at the levels verified. The end user is solely responsible for complying with any and all applicable federal, state and local requirements.

Foreword

The U.S. Environmental Protection Agency (EPA) is charged by Congress with protecting the nation's natural resources. The National Exposure Research Laboratory (NERL) is the EPA center for the investigation of technical and management approaches for identifying and quantifying risks to human health and the environment. The NERL research goals are to (1) develop and evaluate technologies for the characterization and monitoring of air, soil, and water; (2) support regulatory and policy decisions; and (3) provide the science support needed to ensure effective implementation of environmental regulations and strategies.

The EPA created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative technologies through verification of performance and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. It is intended to assist and inform those involved in the design, distribution, permitting, and purchase of environmental technologies.

Candidate technologies for this program originate from the private sector and must be market ready. Through the ETV Program, developers are given the opportunity to conduct rigorous demonstrations of their technologies under realistic field conditions. By completing the evaluation and distributing the results, the EPA establishes a baseline for acceptance and use of these technologies.

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Executive Summary

The U.S. Environmental Protection Agency, through the Environmental Technology Verification Program, is working to accelerate the acceptance and use of innovative technologies that improve the way the United States manages its environmental problems. As part of this program, the Consortium for Site Characterization Technology was established as a pilot program to test and verify field monitoring and site characterization technologies. The Consortium is a partnership involving the U.S. Environmental Protection Agency, the Department of Defense, and the Department of Energy. In 1997 the Consortium conducted a demonstration of five systems designed for the analysis of chlorinated volatile organic compounds in groundwater. The developers participating in this demonstration were Electronic Sensor Technology, Perkin-Elmer Photovac, and Sentex Systems, Inc. (field-portable gas chromatographs); Inficon, Inc. (field-portable gas chromatograph/mass spectrometer, GC/MS); and Innova AirTech Instruments (photoacoustic infrared analyzer). This report documents demonstration activities, presents demonstration data, and verifies the performance of the Perkin-Elmer Photovac Voyager field-portable gas chromatograph. Reports documenting the performance of the other technologies have been published separately.

The demonstration was conducted at two geologically and climatologically different sites: the U.S. Department of Energy's Savannah River Site, near Aiken, South Carolina, and McClellan Air Force Base, near Sacramento, California. Both sites have groundwater resources that are significantly contaminated with a variety of chlorinated volatile organic compounds. The demonstrations designed to evaluate the capabilities of each field-transportable system were conducted in September 1997 and were coordinated by Sandia National Laboratories.

The demonstration provided adequate analytical and operational data with which to evaluate the performance of the Voyager gas chromatograph. Instrument precision and accuracy were determined from analyses of replicate samples from 16 multicomponent standard mixtures of known composition. The relative standard deviations obtained from analysis of 4 replicate samples from each of the 16 standard mixtures were used as measures of precision. The distribution of relative standard deviations from all compounds had a median value of 20% and a 95th percentile value of 69%. Accuracy was expressed as the absolute percent difference between the Voyager measured value and the true value of the component in the standard mixtures. The distribution of absolute percent difference values for all compounds in all standard mixtures had a median value of 41% and a 95th percentile value of 170%. A comparison of Voyager and reference laboratory results from 33 groundwater samples at each site resulted in a median absolute percent difference of 74%, with a 95th percentile value of 453%. A correlation analysis between Voyager and laboratory groundwater yields correlation coefficients (*r*) greater than 0.66 at low (≤100 µg/L) contaminant concentrations and greater than 0.83 at high (>100 µg/L) concentrations. The sample throughput rate of the Voyager was determined to be between 1 and 3 samples per hour.

The results of this study suggest that the sample handling methodology used in this demonstration may have adversely affected instrument precision and accuracy. A refinement of sample handling methods may improve overall instrument performance. Under appropriate applications, the Voyager gas chromatograph can provide useful, cost-effective data for environmental site characterization and routine monitoring. As with any technology selection, the user must determine what is appropriate by taking into account instrument performance and the project's data quality objectives.

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Acronyms and Abbreviations

ac	alternating current
APD	absolute percent difference
BNZN	benzene
BTEX	xylene
°C	degrees centigrade
CCC	calibration check compounds
CCL4	carbon tetrachloride
CLFRM	chloroform
dc	direct current
11DCA	1,1-dichloroethane
12DCA	1,2-dichloroethane
DCE	dichloroethene
11DCE	1,1-dichloroethene
c12DCE	*cis*-1,2-dichloroethene
t12DCE	*trans*-1,2-dichloroethene
DCL	DataChem Laboratories
DOE	Department of Energy
ECD	electron capture detector
EPA	Environmental Protection Agency
ETV	Environmental Technology Verification Program
eV	electron-volt
GC	gas chromatograph
GW	groundwater
GC/MS	gas chromatograph/mass spectrometer
Hz	hertz, cycles per second
L	liter
m	meter
mg	milligram
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
MAFB	McClellan Air Force Base
MCL	maximum concentration level
MDL	method detection limit
MS	mass spectroscopy
NA	not analyzed

ND	not detected
NERL	National Exposure Research Laboratory
ng/L	nanograms per liter
NR	not reported
PC	personal computer
PCE	tetrachloroethene (perchloroethene)
PE	performance evaluation
PID	photoionization detector
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
PQL	practical quantitation limit
PVC	poly (vinyl chloride)
QA	quality assurance
QC	quality control
r	correlation coefficient
RPD	relative percent difference
RSD	relative standard deviation
SPCC	system performance check compounds
SRS	Savannah River Site
TCE	trichloroethene
V	volts
V ac	volts alternating current
VOA	volatile organics analysis
VOC	volatile organic compound
µg	microgram
µg/L	micrograms per liter
µL	microliter
µm	micrometer

Acknowledgments

The author wishes to acknowledge the support of all those who helped to plan and conduct the demonstrations, analyze the data, and prepare this report. In particular, the technical expertise of Gary Brown, Robert Helgesen, Michael Hightower, and Dr. Brian Rutherford of Sandia National Laboratories in the planning and conduct of the study are recognized. The assistance of Dr. Timothy Jarosch and Joseph Rossabi of Westinghouse Savannah River Co. in planning the demonstration and field activities at both Savannah River and McClellan is also recognized. The willingness of Phillip Mook and Timothy Chapman of the Environmental Directorate at McClellan Air Force Base to host the McClellan phase of the study is also greatly appreciated. The availability of funding from the Department of Defense's Strategic Environmental Research and Development Program helped to make the McClellan phase of the study possible. The guidance and contributions of project technical leaders Dr. Stephen Billets and Eric Koglin of the EPA National Exposure Research Laboratory, Environmental Sciences Division, in Las Vegas, Nevada, during all phases of the project are also recognized.

The participation of personnel from Perkin-Elmer Photovac in this technology demonstration is also acknowledged. Susan Johnke and Suzanne Moller operated the instrument during the demonstrations.

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Chapter 1
Introduction

Site Characterization Technology Challenge

The U.S. Environmental Protection Agency (EPA) created the Environmental Technology Verification (ETV) Program to facilitate the deployment of innovative environmental technologies through verification of performance and dissemination of information. The goal of the ETV Program is to further environmental protection by substantially accelerating the acceptance and use of improved and cost-effective technologies. It is intended to assist and inform those involved in the design, distribution, permitting, purchase, and use of environmental technologies. The ETV Program capitalizes on and applies the lessons that were learned in the implementation of the Superfund Innovative Technology Evaluation Program to twelve pilot programs: Drinking Water Systems, Pollution Prevention for Waste Treatment, Pollution Prevention for Innovative Coatings and Coatings Equipment, Indoor Air Products, Advanced Monitoring Systems, EvTEC (an independent, private-sector approach), Wet Weather Flows Technologies, Pollution Prevention for Metal Finishing, Source Water Protection Technologies, Site Characterization and Monitoring Technology, Climate Change Technologies, and Air Pollution Control.

For each pilot, the EPA utilizes the expertise of partner "verification organizations" to design efficient procedures for performance tests of the technologies. The EPA selects its partners from both public and private sectors, including federal laboratories, states, and private sector entities. Verification organizations oversee and report activities based on testing and quality assurance protocols developed with input from all major stakeholder and customer groups associated with the technology area. The U.S. Department of Energy's (DOE's) Sandia National Laboratories in Albuquerque, New Mexico, served as the verification organization for the demonstration described in this report.

The performance verification reported here is based on data collected during a demonstration of technologies for the characterization and monitoring of chlorinated volatile organic compounds (VOCs) in groundwater. Rapid, reliable, and cost-effective field screening and analysis technologies are needed to assist in the complex task of characterizing and monitoring hazardous and chemical waste sites. Environmental regulators and site managers are often reluctant to use new technologies that have not been validated in an objective EPA-sanctioned testing program or other similar process. Until the field performance of a technology can be verified through objective evaluations, users will remain skeptical of innovative technologies, despite the promise of better, less expensive, and faster environmental analyses. This demonstration was administered by the Site Characterization and Monitoring Technology Pilot Program, which is also known as the Consortium for Site Characterization Technology. The mission of the Consortium is to identify, demonstrate, and verify the performance of innovative site characterization and monitoring technologies. The Consortium also disseminates information about technology performance to developers, environmental remediation site managers, consulting engineers, and regulators.

Technology Verification Process

The technology verification process consists of the four key steps shown here and discussed in more detail in the following paragraphs:

1. identification of needs and selection of technology;
2. planning and implementation of demonstration;
3. preparation of report; and
4. distribution of information.

Identification of Needs and Selection of Technology

The first aspect of the verification process is to determine the technology needs of the EPA and the regulated community. The EPA, the U.S. Department of Energy, the U.S. Department of Defense, industry, and state agencies are asked to identify technology needs for site characterization and monitoring. Once a need is recognized, a search is conducted to identify suitable technologies that will address this need. This search and identification process consists of reviewing responses to *Commerce Business Daily* announcements, searching industry and trade publications, attending related conferences, and following up on suggestions from technology developers and experts in the field. Candidate characterization and monitoring technologies are evaluated against the following criteria:

- may be used in the field or in a mobile laboratory;
- has a regulatory application;
- is applicable to a variety of environmentally affected sites;
- has a high potential for resolving problems for which current methods are unsatisfactory;
- has costs that are competitive with current methods;
- has performance as good or better than current methods in areas such as data quality, sample preparation, and/or analytical turnaround time;
- uses techniques that are easier and safer than current methods; and
- is a commercially available, field-ready technology.

Planning and Implementation of Demonstration

After a technology has been selected, the EPA, the verification organization, and the developer(s) agree on a strategy for conducting the demonstration and evaluating the technology. A conceptual plan for designing a demonstration for a site characterization technology has been published by the Site Characterization and Monitoring Technology Pilot Program (EPA, 1996a). During the planning process, the following steps are carried out:

- identification of at least two demonstration sites that will provide the appropriate physical or chemical attributes in the desired environmental media;
- identification and definition of the roles of demonstration participants, observers, and reviewers;
- determination of logistical and support requirements (for example, field equipment, power and water sources, mobile laboratory, communications network);
- arranging for field sampling and reference analytical laboratory support; and

- preparation and implementation of a demonstration plan that addresses the experimental design, sampling design, quality assurance and quality control (QA/QC), health and safety considerations, scheduling of field and laboratory operations, data analysis procedures, and reporting requirements.

Preparation of Report

Each of the innovative technologies is evaluated independently and, when possible, against a reference technology. The technologies are operated in the field by the developers in the presence of independent observers who are provided by the EPA or the verification organization. Demonstration data are used to evaluate the capabilities, limitations, and field applications of each technology. Following the demonstration, all raw and reduced data used to evaluate each technology are compiled in a technology evaluation report, which is a record of the demonstration. A data summary and detailed evaluation of each technology are published in an environmental technology verification report. The report includes a verification statement, which is a concise summary of the instrument's performance during the demonstration.

Distribution of Information

The goal of the information distribution strategy is to ensure that environmental technology verification reports and accompanying verification statements are readily available to interested parties through traditional data distribution pathways, such as printed documents. Related documents and updates are also available on the World Wide Web through the ETV Web site (*http://www.epa.gov/etv*) and through a Web site supported by the EPA Office of Solid Waste and Emergency Response Technology Innovation Office *(http://clu-in.com)*. Additional information at the ETV Web site includes a summary of the demonstration plan, test protocols (where applicable), demonstration schedule and participants, and in some cases a brief narrative and pictorial summary of the demonstrations.

The Wellhead VOC Monitoring Demonstration

In August 1996, the selection of a technology for monitoring chlorinated VOCs in water was initiated by publication in the *Commerce Business Daily* of a solicitation and notice of intent to conduct such a technology demonstration. Potential participants were also solicited through manufacturer and technical literature references. The original demonstration scope was limited to market-ready *in situ* technologies; however, only a limited response was obtained, so the demonstration scope was expanded to include technologies that could be used to measure groundwater at or near the wellhead. The final selection of technologies was based on the readiness of the technologies for field demonstration and their applicability to the measurement of chlorinated VOCs in groundwater at environmentally affected sites.

For this demonstration, five instrument systems were selected. Three of them were field-portable gas chromatographs with various detection systems: one with a surface acoustic wave detector from Electronic Sensor Technology, one with dual electron capture and photoionization detectors from Perkin-Elmer Photovac, and one with an argon ion/electron capture detector from Sentex Systems. The fourth instrument was a field-portable gas chromatograph/mass spectrometer (GC/MS) from Inficon, and the fifth was a photoacoustic infrared spectrometer from Innova AirTech Instruments. This report documents demonstration activities, presents demonstration data, and verifies the performance of the Perkin-Elmer Photovac Voyager gas chromatograph. Reports documenting the performance of the other four technologies have been published separately.

The demonstration was conducted in September 1997 at the DOE Savannah River Site (SRS) near Aiken, Georgia, and at McClellan Air Force Base (MAFB), near Sacramento, California. Both sites have subsurface plumes of chlorinated VOCs and extensive networks of groundwater monitoring wells. The demonstrations were coordinated by Sandia National Laboratories with the assistance of personnel from the Savannah River Site.

The primary objective of this demonstration was to evaluate and verify the performance of field-portable characterization and monitoring technologies for analysis of chlorinated VOCs in groundwater. Specific demonstration objectives were to:

- verify instrument performance characteristics that can be directly quantified (such factors include response to blank samples, measurement accuracy and precision, sample throughput, and data completeness);
- verify instrument characteristics and performance in various qualitative categories such as ease of operation, required logistical support, operator training requirements, transportability, versatility, and other related characteristics; and
- compare instrument performance with results from standard laboratory analytical techniques currently used to analyze groundwater for chlorinated VOCs.

The goal of this and other ETV demonstrations is to verify the performance of each instrument as a separate entity. Technologies are not compared with each other in this program. The demonstration results are summarized for each technology independent of other participating technologies. In this demonstration, the capabilities of the five instruments varied and in many cases were not directly comparable. Some of the instruments are best suited for routine monitoring where compounds of concern are known and there is a maximum contaminant concentration requirement for routine monitoring to determine regulatory compliance. Other instruments are best suited for characterization or field-screening activities where groundwater samples of unknown composition can be analyzed in the field to develop an improved understanding of the type of contamination at a particular site. This field demonstration was designed so that both monitoring and characterization technologies could be verified.

Chapter 2
Technology Description

This chapter was provided by the developer and was edited for format and relevance. The data presented include performance claims that may not have been verified as part of the demonstration. Chapters 5 and 6 report instrument features and performance observed in this demonstration. Publication of this material does not represent the EPA's approval or endorsement.

Technology Overview

The Voyager is a field-portable, computer-controlled, gas chromatograph that incorporates three columns and dual detectors to achieve broadened analytical capabilities. The instrument's triple column and dual detector configuration is shown schematically in Figure 2-1.

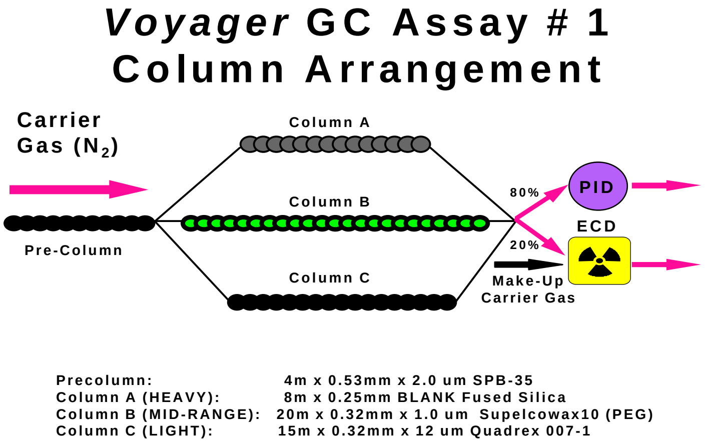

Figure 2-1. A schematic diagram of the Voyager GC.

The Voyager has dimensions of 15.4 inches × 10.6 inches × 5.4 inches and weighs 15 pounds. It incorporates a high-sensitivity photoionization detector (PID) and a miniature electron capture detector (ECD). The instrument is the fourth generation in the evolutionary design of field-portable GCs from the Photovac division of the Perkin-Elmer Corporation. The Voyager was developed with consideration of ergonomic and analytical performance demands in field environments. Previous generations of Perkin-Elmer Photovac field-portable GCs, such as the 10S50 and 10S70 GC, have been utilized by the EPA Emergency Response Team based in Edison, New Jersey. This team has generated standard operating procedures for using these instruments to analyze water, soil, ambient air, and soil gas.

A unique internal analytical engine includes a specially designed miniature stainless steel valve array to provide fast sample delivery and minimize sample carryover (and contamination) caused by high VOC concentrations. The instrument also incorporates a unique triple-column arrangement, with precolumn and backflush, and a syringe injection port for headspace sampling of aqueous and soil extract media. The two detectors are configured in parallel. Gas flow from the three internal columns is split to the detectors, with 80% going to the PID and 20% going to the ECD. Columns A, B, and C, whose configurations are shown in Figure 2-1, are for heavy (C_7 to C_{12}), midrange (C_4 to C_7), and light (C_1 to C_3) hydrocarbon compounds, respectively. The internal sampling train, sample loop, GC columns, valves, and injection port are heated isothermally at temperatures from 55 to 80 °C. The Voyager is also unique in that it is the only GC of its kind in the world that is classified as intrinsically safe (Class 1, Division I, Groups A, B, C, and D), rendering it useful in hazardous locations.

The instrument is powered by field-rechargeable and replaceable batteries that allow up to 9 hours of field use with a 5-hour charge time. Alternatively, the Voyager can be operated from an external 10 to 18-V dc power supply such as a vehicle battery using a cigarette lighter receptacle. The instrument can also be operated on ac power.

The Voyager can be effectively used to monitor many of the volatile organic compounds listed in EPA Method 8240A (EPA, 1996b), including chlorinated and aromatic hydrocarbons. Sample matrices of applicability include soil, soil gas, water, and ambient air. Method detection limits (MDLs) for VOCs range from parts per trillion (ppt) in water (ng/L) to about 500 parts per million (ppm) in ambient air, depending upon the type of compound and detector used.

Analytical results are displayed on the built-in liquid crystal display and include a list of compounds detected, with concentrations as well as chromatograms. Built-in data logging allows storage of up to 40 10-minute chromatograms or 400 analyses obtained during operation in a total-VOC screening mode.

Analytical Methods

The Voyager GC can be configured with one analytical method (assay) at a time. The assay includes the compound library, column temperature, carrier gas pressure (flow rate), and sampling method (internal variable volume loop or syringe injection). The preferred method of setting up a new analytical method is by using a PC interface and downloading files. A laptop computer is required for on-site operation if various types of samples are to be analyzed that require the installation of different methods. The PC does not have to be connected continuously to the instrument; however, for accurate quantification of trace concentrations of target compounds, it is recommended that correct integration of chromatogram peak areas be visually verified on the computer screen.

Advantages

The instrument is lightweight and small. The triple-column configuration and dual PID and ECD give this instrument sensitivity and selectivity (through confirmational analysis) for a wide cross-section of VOCs on site. Furthermore, the ability to use the internal pump to draw air samples or to perform syringe injections from headspace samples of soil and groundwater adds further analytical flexibility for different monitoring tasks. The Voyager has the added advantage of multiple columns and dual detector systems, which can aid in identifying unknown compounds.

Limitations

The instrument contains radioactive components in the electron capture detector and normally requires state-specific licensing and periodic inventory. As a gas chromatograph, the instrument is also somewhat limited in its ability to identify unknown compounds. Column retention time is used as an indicator; however, as with most GC systems, an additional data dimension such as mass spectra, provided by GC/MS systems, is not available.

The Voyager utilizes an equilibrium headspace method to determine VOCs in water. Thus it is only able to analyze those compounds with solubilities and vapor pressures that promote the formation of a detectable equilibrium headspace concentration.

Applications

The Voyager GC will detect chlorinated solvents such as trichloroethene (TCE) and tetrachloroethene (sometimes identified as perchloroethene, PCE) at sub-parts-per-billion (ppb or µg/L) levels in aqueous media using the PID and ECD. Benzene, toluene, ethyl benzene, and xylene isomers are also detected at these trace levels using the PID.

Operator Training

One full day of operator training is adequate. The training covers instrument operation, calibration, automatic (pump) sampling, headspace syringe injection, data storage and retrieval, and method customization and development, as well as routine maintenance and troubleshooting.

Performance Characteristics

Method Detection Limits and Practical Quantitation Limit

Voyager, in the Assay No. 1 configuration, which includes a PID and ECD and uses a 500-µL headspace injection, will give the method detection limits for the chlorinated hydrocarbons shown in Table 2-1 with 95% confidence. Assay No. 1 covers 40 of the compounds listed in EPA Methods 8260A (EPA, 1996b) and TO-14 (EPA, 1988). Method detection limits are estimated by determining the Voyager's average sensitivity for a particular compound (e.g., parts per billion per millivolt × seconds) in its working range, and then multiplying this sensitivity factor by the minimum detectable peak area (also in units of millivolts × seconds). The Voyager with the Assay No. 1 column-PID/ECD configuration will give a practical quantitation limit (PQL) at a level 5 to 10 times the standard deviation of the instrument noise signal. Table 2-1 gives the MDLs, PQLs, and upper ranges for various chlorinated hydrocarbons, including TCE and PCE.

Accuracy

Voyager will provide an accuracy within ±20% for each target compound, over its working range, 95% of the time through the use of a three-point calibration.

Table 2-1. Voyager Specifications for MDL, PQL, and Upper Range for Selected Chlorinated Hydrocarbons

Compounds	**MDL (µg/L)**		**PQL (µg/L)**		**Upper Range (µg/L) PQL × 500**	
	PID	**ECD**	**PID**	**ECD**	**PID**	**ECD**
Column A (C_7 – C_{12})						
Bromoform	20.00	10.00	60.00	30	30,000	15,000
1,1,2,2-Tetrachloroethane	180.00	30.00	540.00	90	270,000	45,000
1,3-Dichlorobenzene	0.80		2.40		1200	
1,4-Dichlorobenzene	0.60		1.80		900	
1,2-Dichlorobenzene	1.60		4.80		2400	
Column B (C_4 – C_7)						
Trichloroethene	0.08		0.24		120	
1,2-Dichloropropane	6.00		18.00		9000	
Tetrachloroethene	0.06	0.03	0.18	0.10	90	48
2-Chloroethyl vinyl ether	10.00		30		15,000	
cis-1,3-Dichloropropene	0.60		1.80		900	
Bromodichloromethane	32.00	0.10	96.00	0.30	48,000	150
trans-1,3-Dichloropropene	1.40	1200	4.20	3600	2100	
Chlorobenzene	0.12		0.36		180	
1,1,2-Trichloroethane	280.00		840		420,000	
Dibromochloromethane	6.00		18.00		9000	
Column C (C_1 – C_3)						
Bromomethane	0.12		0.36		180	
1,1-Dichloroethene	0.08	0.06	0.24	0.18	120	90
Methylene chloride	1.80		5.40		2700	
trans-1,2-Dichloroethene	0.04		0.12		60	
Vinyl acetate	10.00		30		15,000	
cis-1,2-Dichloroethene	0.60		1.80		900	
Chloroform		1.20		3.60		1800
1,2-Dichloroethane	40.00	80.00	120	240	60,000	120,000
1,1,1-Trichloroethane	12.00	0.18	36.00	0.54	18,000	270
Carbon tetrachloride		0.40		1.20		600

Note: Blank cells indicate no determination.

Precision

The precision of the Voyager, as represented by the relative standard deviation (RSD)[1] on six replicate measurements, will be ≤ 20% over the working range of the instrument for each compound.

Comparison with Reference Laboratory Analyses

To date, comparison checks that follow EPA protocols have not been carried out on the Voyager against reference analytical methods for chlorinated species in water.

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[1] The relative standard deviation is the sample standard deviation divided by the mean value and multiplied by 100.

Data Completeness

A complete analysis for TCE; PCE; and benzene, toluene, ethyl benzene, and xylene (BTEX) may take up to 20 minutes. Under these conditions, throughput will be approximately 20 samples and 1 calibration in an 8-hour day. If there are only 2 analytes (e.g., TCE and PCE), the analysis time will be greatly reduced and sample throughput will be significantly increased.

Specificity

Specificity is defined in this performance statement as the degree of separation in a mixture of analytes as indicated by the chromatographic resolution (R).[2] The Voyager's resolution is provided in Table 2-2 and is within 20% reproducibility 95% of the time. Compounds with $R < 1$ coelute with those immediately above or immediately below them in the table.

Other Field Performance Characteristics

Instrument Setup and Disassembly Time

The daily operational procedure consists of the following steps:

1. Fill the built-in carrier gas cylinder with nitrogen (assuming portable field operation).
2. Turn the instrument on.
3. Allow stabilization for 60 minutes.
4. Download desired method (assuming a different method is to be used than in the previous day's work).
5. Prepare standards and calibrate for the target compounds at a specified concentration.
6. Analyze samples.

If the carrier gas pressure drops below 200 pounds per square inch, as indicated on the Voyager's internal cylinder gauge, the cylinder can be recharged from an external supply cylinder. If the "battery voltage low" message is displayed on the instrument's display panel, the Voyager can be switched off and the battery replaced with a fully charged one (assuming field operation). After the battery is replaced, the Voyager should be recalibrated in order to meet specifications. If the Voyager was not connected to a computer before being switched off on the previous day, the instrument should be connected to a PC running the Windows-based SiteChart software so that any logged data files may be downloaded. Shutdown time for the Voyager is less than 5 minutes.

Instrument Calibration Frequency During Field Use

Multipoint calibration curves can be prepared for target compounds prior to field deployment. Accuracy specifications assume that such curves have been established for each compound under headspace conditions. This will increase sample throughput rather than utilizing a "generic environmental assay." The Voyager requires daily calibration checks with target analytes.

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[2] Chromatographic resolution, R, is defined as the time between the maximum values of two adjacent peaks divided by 4 times the standard deviation of the peak. The standard deviation of the peak is half the peak width at its inflection point.

Table 2-2. Voyager Retention Times and Resolution Factors

Compound	Retention Time (seconds)	Chromatographic Resolution (R)
Column A		
ortho-Xylene	472.8	0.73
Styrene	506	2.55
Bromoform	638.6	1.27
1,1,2,2-Tetrachloroethane	715.3	5.86
1,3-Dichlorobenzene	1199.5	1.07
1,4-Dichlorobenzene	1313.5	2.55
1,2-Dichlorobenzene	1629	
Column B		
Benzene	267.5	1.38
Trichloroethene	329.6	3.15
Methyl isobutyl ketone	381.3	1.84
1,2-Dichloropropane	413.7	2.94
Toluene	468.8	0.79
Tetrachloroethene	484.4	4.14
2-Hexanone	571.7	2.61
2-Chloroethyl vinyl ether	632	1.50
cis-1,3-Dichloropropene	668.6	1.57
Bromodichloromethane	708.7	4.53
Ethyl benzene	833.9	1.30
meta-Xylene	872.8	0
para-Xylene	872.8	4.25
trans-1,3-Dichloropropene	1010	3.73
ortho-Xylene	1144	0.47
Chlorobenzene	1162	5.00
1,1,2-Trichloroethane	1367	6.39
Dibromochloromethane	1673	
Column C		
Chloromethane	105.7	1.02
Vinyl chloride	118.4	2.08
Bromomethane	147.2	0.62
Chloroethane	156.6	2.03
Acetone	190.2	2.63
1,1-Dichloroethene	241.1	0.54
Dichloromethane	252.8	1.35
Carbon disulfide	283.7	1.31
trans-1,2-Dichloroethene	316.3	0.84
Vinyl acetate	339	1.09
Methyl ethyl ketone	370.3	1.49
cis-1,2-Dichloroethene	416.8	3.63
1,2-Dichloroethene	552.1	0.49
1,1,1-Trichloroethane	573.3	1.57
Benzene	645.2	0.62
Carbon tetrachloride	675.8	

Note: Blank cells indicate no determination.

Ancillary Equipment Requirements

If the Voyager is used in a stationary (indoor) location, ac or dc power will be required for on-going analyses. Sample handling accessories include such items as 40-mL volatile organics analysis (VOA) vials, gas-tight syringes for headspace sampling, spare septa for the syringe injection port, and a small water bath for sample equilibration. A cylinder of zero-grade nitrogen should be available with a two-stage regulator to run the Voyager in a stationary location or to refill the internal carrier gas cylinder during field use.

Field Maintenance Requirements

Periodic refilling of the internal carrier gas cylinder is required. The Voyager's on-board battery pack can be replaced in the field as required. The 10.6-eV light source in the PID can also be cleaned or replaced in the field if necessary.

Sample Throughput Rate

Depending upon the number and molecular weights of the analytes to be monitored, a typical GC column run for TCE, PCE, and BTEX may take about 20 minutes in a complex sample background. Additional time is required for sample preparation and headspace equilibration. For an 8-hour workday and a daily calibration (not including blanks), the sample throughput would be about 20 per day. If only TCE and PCE are being monitored, the daily sample throughput will be significantly higher.

Ease of Operation

Once the analytical method has been installed in the Voyager, the instrument can be disconnected from the PC for field use and the start/stop key can be used to begin and end analyses as required. All Voyager data, including chromatograms, are logged on an internal data logger and are automatically downloaded when a PC connection is made.

The Voyager's mode of operation in the field can also be set to a "user only" mode. In this mode, the field operator can only access the method parameters by entering a password established during method development. In this manner, the Voyager is used as a simple "point-and-press" instrument with no access to method parameters in the field.

Chapter 3
Demonstration Design and Description

Introduction

This chapter summarizes the demonstration objectives and describes related field activities. The material is condensed from the Demonstration Plan for Wellhead Monitoring Technology Demonstration (Sandia, 1997), which was reviewed and approved by all participants prior to the field demonstration.

Overview of Demonstration Design

The primary objective was to test and verify the performance of field-portable characterization and monitoring technologies for the analysis of chlorinated VOCs in groundwater. Specific demonstration objectives are listed below:

- verify instrument performance characteristics that can be directly quantified; such factors include response to blank samples, measurement accuracy and precision, data completeness, sample throughput, etc.;
- verify instrument characteristics and performance in various qualitative categories such as ease of operation, required logistical support, operator training requirements, transportability, versatility, and other considerations; and
- compare instrument results with data from standard laboratory analytical methods currently used to analyze groundwater for chlorinated VOCs.

The experimental design included a consideration of both quantitative and qualitative performance factors for each participating technology.

Quantitative Factors

The primary quantitative performance factors that were verified included such instrument parameters as precision and accuracy, blank sample response, instrument performance at sample concentrations near its limit of detection, sample throughput, and comparability with reference methods. An overview of the procedures used to determine quantitative evaluation factors is given below.

Precision

Measurement uncertainty was assessed over the instrument's working range by the use of blind replicate samples from a number of performance evaluation (PE) mixtures. Eight PE mixtures containing chlorinated VOCs at concentrations ranging from 50 µg/L to over 1000 µg/L were prepared and distributed at each site. The mixtures were prepared from certified standard mixes with accompanying documentation giving mixture content and purity. The relative standard deviation was computed for each compound contained in each set of replicate PE samples and was used as a measure of instrument precision.

Accuracy

Instrument accuracy was also evaluated by using results from the PE samples. A mean recovery was computed for each reported compound in each PE mixture. The average instrument result for each compound, based on four blind replicate sample analyses, was compared against the known concentration in the PE mixture and reported as the average percent recovery and the absolute percent difference.

Blank Sample Response

At least two blank groundwater samples were analyzed with each instrument system per demonstration day. These were distributed as blind samples in the daily set of samples provided to each instrument operator. The results from these samples were used to assess the degree to which instrument contamination and sample-to-sample carryover resulted in a false positive.

Low-Level Sample Response

The scope of this demonstration did not include an exhaustive determination of instrument detection limits. However, 10 replicate spiked samples at concentrations near typical regulatory action limits were provided for analysis at each site to validate the instrument performance at these low concentration levels. The results from these analyses were compiled as detects and nondetects and were used to calculate the percentage of correct determinations and false negatives.

Sample Throughput

Sample throughput takes into account all aspects of sample processing, including sample preparation, instrument calibration, sample analysis, and data reduction. The multiday demonstration design permitted the determination of sample throughput rates over an extended period. Thus the throughput rates are representative of those likely to be observed in routine field use of the instrument.

Laboratory–Field Comparability

The degree to which the field measurements agree with reference laboratory measurements is a useful parameter in instrument evaluation. In this demonstration, comparisons were made on groundwater samples by computing the absolute percent difference between laboratory and field technology results for all groundwater contaminants detected. Linear regression of the two data sets was also carried out to determine the strength of the linear correlation between the two data sets.

Qualitative Factors

Key qualitative instrument performance factors observed during the demonstration were instrument portability, logistical support requirements, operator training requirements, and ease of operation. Logistical requirements include the technology’s power requirements, setup time, routine maintenance, and the need for other equipment or supplies, such as a computers, reagent solutions, or gas mixtures. Qualitative factors were assessed during the demonstration by review of vendor information and on-site audits. Vendors provided information concerning these factors during preparation of the demonstration plan. Vendor claims regarding these specifications and requirements are included in Chapter 2. During the field demonstration phase, auditors from the verification organization observed instrument operation and documented the degree of compliance with the instrument specifications and methodology. Audit results are included in Chapter 6.

Site Selection and Description

Two sites—the DOE Savannah River Site near Aiken, South Carolina, and McClellan Air Force Base near Sacramento, California—were chosen for this demonstration. This section provides a brief history of each site, a discussion of important geological features, and an outline of the nature and extent of contamination at each site. The sites chosen met the following selection criteria:

- presence of chlorinated VOCs in groundwater;
- multiple wells at the site with a variety of contaminants and depths;
- documented well-sampling history with characterization and monitoring data;
- convenient access; and,
- support facilities and services at the site.

Savannah River Site

The Savannah River Site is operated under contract by the Westinghouse Savannah River Company. The complex covers 310 square miles in western South Carolina, adjacent to the Savannah River, as shown in Figure 3-1. The SRS was constructed during the early 1950s to produce the basic materials used in the fabrication of nuclear weapons, primarily tritium and plutonium-239. Production of weapons material at the SRS also produced unusable byproducts such as intensely radioactive waste. In addition to these high-level wastes, other wastes at the site include low-level solid and liquid radioactive wastes, transuranic waste, hazardous chemical waste, and mixed waste.

Figure 3-1. The general location of the Savannah River Site in the southeast United States.

Geological Characteristics

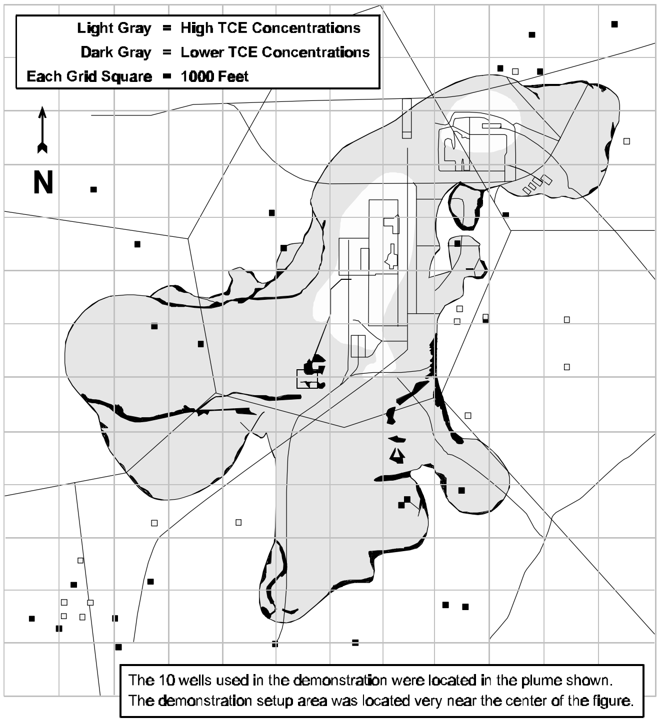
The SRS is located on the upper Atlantic Coastal Plain. The site is underlain by a thick wedge (approximately 1000 feet) of unconsolidated Tertiary and Cretaceous sediments that overlie Precambrian and Paleozoic metamorphic rocks and consolidated Triassic sediments (siltstone and sandstone). The younger sedimentary section consists predominantly of sand and sandy clay. The depth to the water table from the surface ranges from 50 to 170 feet for the wells used in this demonstration.

Groundwater and Monitoring Wells

The wells selected for sampling in this demonstration were in the A/M area, located in the northwest section of the site. This area encompasses an abandoned process transfer line that, beginning in 1958, carried wastewater for 27 years from M-area processing facilities to a settling basin. Site characterization data indicate that several leaks occurred in the transfer line, which is buried about 20 feet below the surface, producing localized contamination. Past industrial operations resulted in the release of chlorinated solvents, primarily trichloroethene (TCE), tetrachloroethene (PCE), and 1,1,1-trichloroethane, to the subsurface.

The A/M area monitoring-well network, shown in Figure 3-2, consists of approximately 400 wells. The dark squares in the figure indicate soil borings and the light squares indicate monitoring wells. The largest group of wells, comprising approximately 70% of the total, are associated with the plume originating from the process transfer lines and the settling basin. The majority of these wells are constructed of 4-inch poly(vinyl chloride) (PVC) casing with wire-wrapped screens varying in length from 5 to 30 feet. The wells are screened either in the water-table aquifer (M-area aquifer, well depths ranging from 30 to 170 feet), the underlying tertiary aquifer (Lost Lake aquifer, well depths ranging from 170 feet to 205 feet), or a narrow permeable zone within the confining unit above the cretaceous aquifer (Crouch Branch Middle Sand, well depths ranging from 215 to 260 feet). The wells are all completed with approximately 2.5 feet of standpipe above ground and a protective housing. Most wells are equipped with a dedicated single-speed centrifugal pump (1/2 hp Grundfos Model 10S05-9) that can be operated with a control box and generator. Wellhead pump connections also contain a flow meter and totalizer for monitoring pumped volumes.

All the wells are measured quarterly for water levels. On a semiannual basis, all point-of-compliance wells (41), plume definition wells (236), and background wells (6) are sampled to assess compliance with groundwater protection standards. Other water quality parameters such as conductivity, turbidity, temperature, and pH are



The 10 wells used in the demonstration were located in the plume shown. The demonstration setup area was located very near the center of the figure.

Figure 3-2. A map of the A/M area at the Savannah River Site showing the subsurface TCE plume.

also measured. As a part of the monitoring program, VOCs are measured using EPA Method 8260A at an off-site contract laboratory. The most recent (winter of 1996) quarterly water analysis results for the 10 wells used in this demonstration are shown in Table 3-1. Well cluster numbers shown in the table include a letter designation (A through D) that indicates the relative screening depth and aquifer zone. The A wells are the deepest of a cluster, while the D wells mark the shallowest.

Table 3-1. Quarterly Monitoring Results for SRS Wells Sampled in the Demonstration

Sample Description	Well Number	Compound	Qtrly. Results[a] (μg/L)
Very low 1	MSB 33B	Trichloroethene Tetrachloroethene	10 5
Very low 2	MSB 33C	Trichloroethene Tetrachloroethene	5 12
Low 1	MSB 18B	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	12 12 3
Low 2	MSB 37B	Trichloroethene Tetrachloroethene Carbon tetrachloride	28 2 2
Mid 1	MSB 4D	Trichloroethene Tetrachloroethene	219 178
Mid 2	MSB 64C	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	51 337 13
Very high 1	MSB 4B	Trichloroethene Tetrachloroethene	830 43
Very high 2	MSB 70C	Trichloroethene Tetrachloroethene 1,1-Dichloroethane 1,1,1-Trichloroethane	1290 413 61 17
Very high 1	MSB 14A	Trichloroethene Tetrachloroethene	3240 2440
Very high 2	MSB 8C	Trichloroethene Tetrachloroethene	3620 2890

[a] Winter 1996.

McClellan Air Force Base

McClellan Air Force Base is located 7 miles northeast of downtown Sacramento, California, as shown in Figure 3-3. The installation consists of about 3000 acres bounded by the city of Sacramento on the west and southwest, the city of Antelope on the north, the unincorporated areas of Rio Linda on the northwest, and North Highlands on the east.

McClellan has been an active industrial facility since its dedication in 1936, when it was called the Sacramento Air Depot. Operations have changed from maintenance of bombers during World War II and the Korean War, to maintenance of jet aircraft in the 1960s, and now include the maintenance and repair of communications equipment and electronics. McClellan currently operates as an installation of the Air Force Materiel Command and employs approximately 13,400 military and civilian personnel.

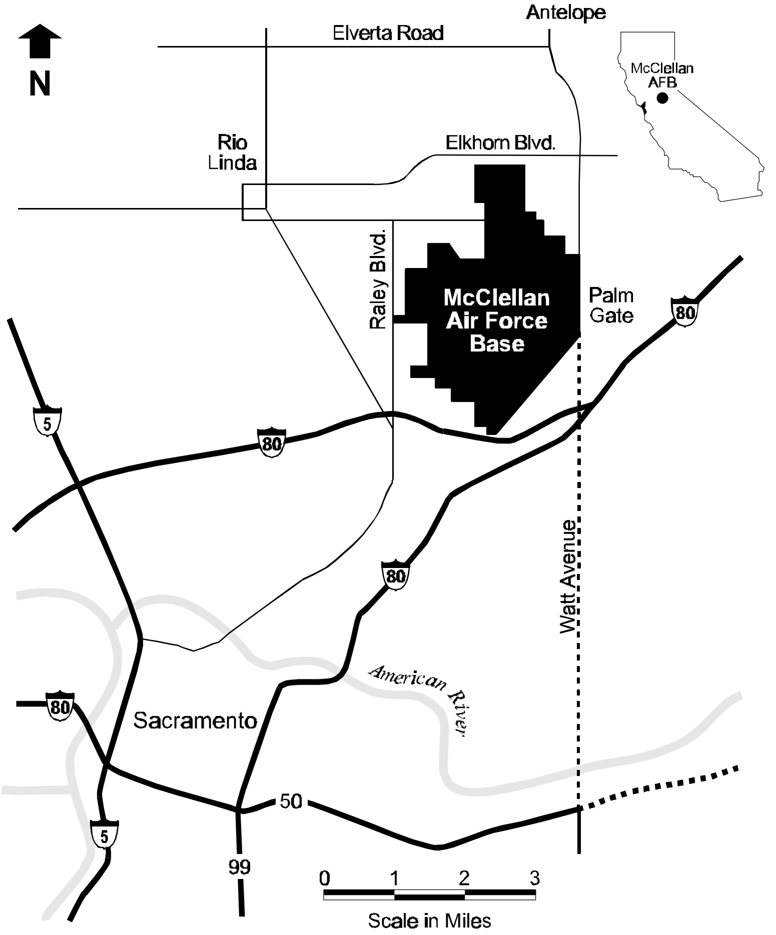


Figure 3-3. A map of Sacramento and vicinity showing the location of McClellan Air Force Base.

Currently, most of the industrial facilities are located in the southeastern portion of the base. The southwestern portion has both industrial and storage areas. In the far western part are vernal pools and wetland areas. Between these wetlands and the engine test cells along the taxiways is an open area that was used for disposal pits.

McClellan Air Force Base is listed on the EPA Superfund National Priorities List of hazardous waste sites. The most important environmental problem at MAFB is groundwater contamination caused by the disposal of hazardous wastes, such as solvents and oils, into unlined pits. Approximately 990 acres beneath McClellan are contaminated with volatile organic compounds. Remediation activities at MAFB include an extensive groundwater pump-and-treat network, as well as soil-vapor extraction systems.

McClellan has been designated a Chlorinated Hydrocarbons Remedial Demonstration Site as part of the National Environmental Technology Test Sites program. The Strategic Environmental Research and Development Program is the parent organization that provides support staff for the environmental technologies undergoing development and testing at MAFB.

Geological Characteristics

Surface features at MAFB include open grassland, creeks and drainages, and vernal pools, as well as industrial, residential, and runway areas. The land surface is a relatively flat plain that slopes gently to the west. Surface elevations range from about 75 feet above mean sea level on the eastern side of the base to about 50 feet above mean sea level on the western side.

Surface soils at MAFB are variable, but are generally sediments that have formed from stream erosion of granite rocks in the Sierra Nevada. Soil in the vadose zone—the unsaturated region between the surface and the groundwater table—is composed of interbedded layers of sands, silts, and clays. The vadose zone ranges from 90 to 105 feet. Clays and hardpan layers in this zone slow, but do not halt, infiltration of liquids into the underlying aquifer.

The groundwater beneath MAFB behaves as one hydrogeologic unit. This single aquifer has been divided into five groundwater monitoring zones, designated A, B, C, D, and E, from shallowest to deepest.

Groundwater and Monitoring Wells

An estimated 14 billion gallons of contaminated water underlie MAFB. Trichloroethene is the most frequently detected contaminant in the subsurface groundwater. Over 90% of the contaminant mass is located in the A zone, the shallowest portion of the aquifer. An estimated surface area of approximately 664 acres is underlain by a plume in the A zone that exceeds the 5-µg/L maximum contaminant level for TCE, as shown in Figure 3-4. Groundwater contaminants consistently detected above federal maximum concentration limits (MCLs) are shown in Table 3-2.

Other detected compounds that are either below regulatory levels or are not currently regulated are also shown in the table.

Monitoring wells at McClellan range from 2 to 8 inches in diameter. Well casings are Schedule 5 stainless steel (304) and the well screen is Johnson stainless steel (304) with a 0.01- or 0.02-inch screen slot size. The screen is surrounded by either 16 × 40 or 8 × 20 mesh gravel pack to a level about 3 feet above the screen. An approximately 3-foot sand bridge and 3-foot bentonite seal are placed above the gravel pack. A concrete sanitary seal containing about 3% bentonite powder is used to seal the well casing between the bentonite seal and the ground surface.

For this demonstration, monitoring wells that penetrate both A and B aquifer zones in operational units A and B were selected for sample collection. Quarterly monitoring data exist for 354 wells at the A and B zone aquifer levels in these operational units. Monitoring results for TCE were used to select ten wells. Groundwater TCE concentrations in the selected wells ranged from very low (~10 µg/L) to very high (>5000 µg/L) levels.

Wells that had multiple contaminants or nonchlorinated contaminants were given selection preference over those with only a few chlorinated hydrocarbons. The most recent (winter of 1996) monitoring results for the wells chosen for this demonstration are shown in Table 3-3.

Sample Set Descriptions

The experimental design of the demonstration specified the preparation and collection of an approximately equal number of PE samples and groundwater samples for distribution to the participants and reference laboratory. Descriptions of the PE and groundwater samples and their preparation are given below.

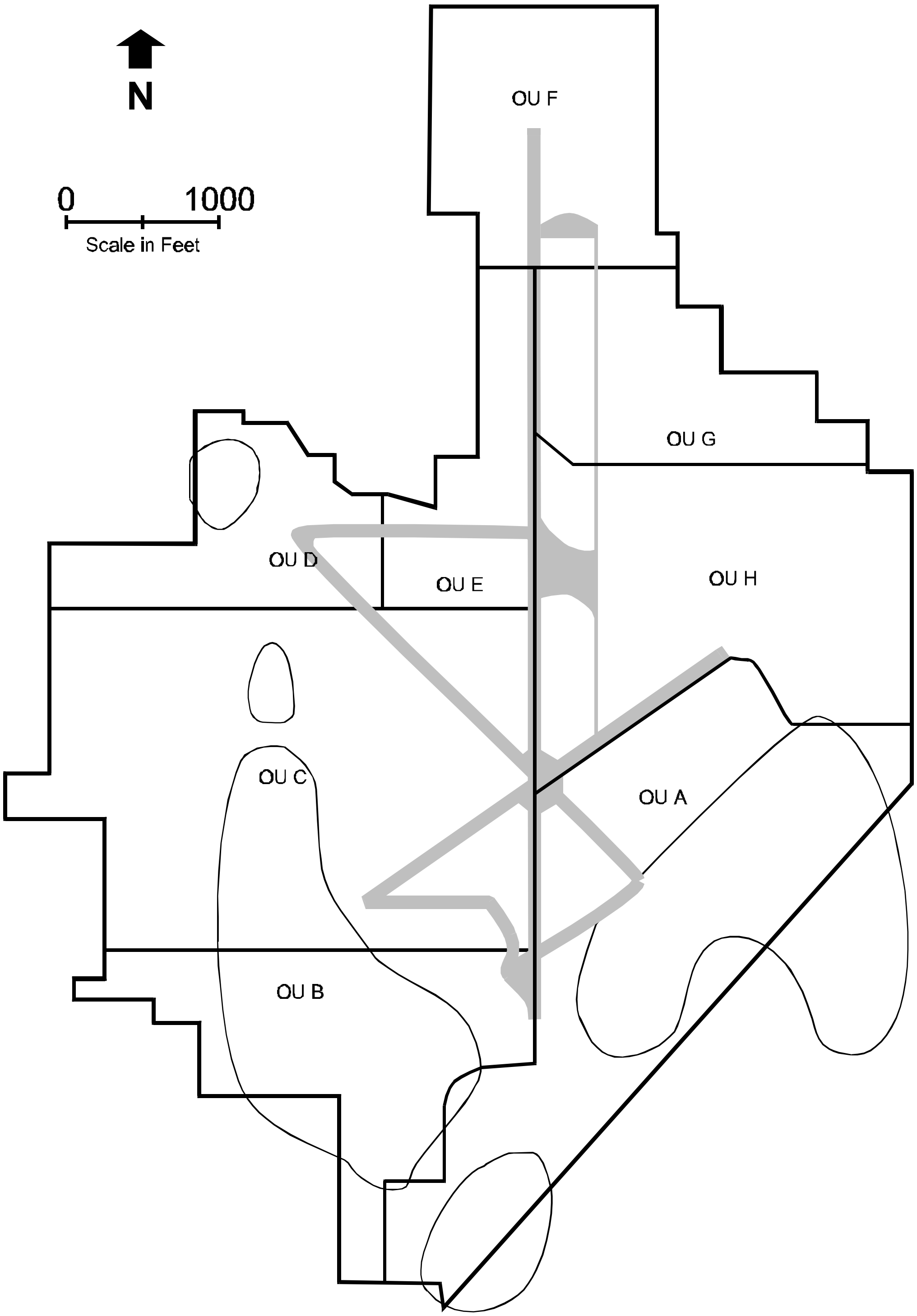


Figure 3-4. Subsurface TCE plumes at McClellan Air Force Base in the shallowest (A) aquifer layer. The circular lines enclose plume concentrations in excess of 5 µg/L TCE. OU refers to operational units. Monitoring wells used in the demonstration were primarily in OUs A and B. The demonstration setup area was very near OU D (upper left in the figure).

Table 3-2. Groundwater Contaminants at MAFB

Detected above MCL[a]	Detected below MCL	Detected – Not Regulated
Benzene	Bromodichloromethane	Acetone
Carbon tetrachloride	Trichlorofluoromethane	2-Butanone
Chloroform		1,1-Dichloroethane
1,2-Dichlorobenzene		4-Methyl-2-pentanone
1,2-Dichloroethane		Toluene
1,1-Dichloroethene		
1,2-Dichloroethene (cis and trans)		
Tetrachloroethene		
1,1,1-Trichloroethane		
Trichloroethene		
Vinyl chloride		

[a] MCL = maximum concentration limit.

Table 3-3. Quarterly Monitoring Results for MAFB Wells Sampled in the Demonstration

Sample Description	Well Number	Compound	Qtrly. Results[a] (µg/L)
Very low 1	EW-86	Trichloroethene	8
		1,1-Dichloroethene	13
Very low 2	MW-349	Trichloroethene	9
		Tetrachloroethene	5
		Chloroform	8
		Acetone	9
Low 1	MW-331	1,1-Dichloroethane	16
		Carbon tetrachloride	5
		Chloroform	7
		Trichloroethene	19
		cis-1,2-Dichloroethene	41
Low 2	MW-352	1,1-Dichloroethane	6
		Tetrachloroethene	5
		Freon11	115
Mid 1	EW-87	1,1,1-Trichloroethane	17
		1,1-Dichloroethene	334
		Trichloroethene	220
		cis-1,2-Dichloroethene	5
Mid 2	MW-341	Trichloroethene	350
		cis-1,2-Dichloroethene	18
High 1	MW-209	Chloroform	53
		Trichloroethene	586
		cis-1,2-Dichloroethene	80
		trans-1,2-Dichloroethene	13
High 2	MW-330	Chloroform	44
		Trichloroethene	437
		cis-1,2-Dichloroethene	64
		trans-1,2-Dichloroethene	9

Table 3-3. Quarterly Monitoring Results for MAFB Wells Sampled in the Demonstration (Continued)

Sample Description	Well Number	Compound	Qtrly. Results[a] (μg/L)
Very high 1	MW-334	1,1-Dichloroethene	1000
		Benzene	705
		Carbon tetrachloride	728
		Chloroform	654
		Dichloromethane	139
		Trichloroethene	20,500
		cis-1,2-Dichloroethene	328
		Xylene	59
Very high 2	MW-369	1,2-Dichloroethane	13
		Carbon tetrachloride	91
		Chloroform	84
		Tetrachloroethene	6
		Trichloroethene	10,200
		cis-1,2-Dichloroethene	246

[a] Winter 1996.

PE Samples and Preparation Methods

Three different commercially available (Supelco, Bellefonte, Pennsylvania) standard solutions of chlorinated VOCs in methanol were used to prepare the PE mixtures. The standard solutions were supplied with quality control documentation giving the purity and weight of the compounds in the mixture. The contents of the three mixtures, termed mix 1, mix 2, and mix 3, are given in Table 3-4. VOC concentration levels in these standard solutions were either 200 μg/L or 2000 μg/L. The PE mixtures were prepared by dilution of these standard solutions.

The number of replicate samples and the compound concentrations from each of the nine PE mixtures prepared at each site are given in Table 3-5 for the SRS and Table 3-6 for MAFB. Ten replicates of the mixture with the lowest concentration level were prepared so technology performance statistics near typical regulatory action levels could be determined. Four replicates were prepared for each technology and the reference laboratory from the other eight PE mixtures. The highest-level PE mixture, denoted “spike/low” in the tables, consisted of high-level (>1000 μg/L) concentrations of TCE and PCE (and other compounds at MAFB as noted in the table) in the presence of a low-level (50 or 100 μg/L) PE mixture background. Eight blank samples were also provided to each technology at each site. The blank samples were prepared from the same batch of deionized, carbon-filtered water used to prepare the PE mixtures.

Performance evaluation mixtures were prepared in either 8-L or 10-L glass carboys equipped with bottom spigots. Stock PE solutions were dispensed with microsyringes into a known volume of deionized, carbon-filtered water in the carboy. The mixture was gently stirred for 5 minutes with a Teflon-coated stir bar prior to dispensing samples from the bottom of the carboy. A twofold excess volume of PE mixture was prepared in order to ensure a sample volume well in excess of the required volume. The mixture was not stirred during sample dispensing to minimize headspace losses in the lower half of the carboy. Headspace losses that did occur during dispensing were limited to the top portion of the mixture, which was discarded after the samples were dispensed. Samples were dispensed into

Table 3-4. Composition of PE Source Materials

PE Mix 1 - Purgeable A Supelco Cat. No. 4-8059 Lot LA68271	PE Mix 2 - VOC 3 Supelco Cat. No. 4-8779 Lot LA64701	PE Mix 3 - Purgeable B Supelco Cat. No. 4-8058 Lot LA 63978
Trichlorofluoromethane	1,1-Dichloropropene	1,2-Dichloroethane
1,1-Dichloroethane	1,2-Dichloroethane	1,1,2,2-Tetrachloroethane
Dichloromethane	Trichloroethene	*cis*-1,3-Dichloropropene
1,1-Dichloroethene	1,2-Dichloropropane	*trans*-1,3-Dichloropropene
Chloroform	1,1,2-Trichloroethane	*trans*-1,2-Dichloroethene
Carbon tetrachloride	1,3-Dichloropropane	1,1,1-Trichloroethane
Trichloroethene	1,2-Dibromoethane	Benzene
1,2-Dichloropropane	1,1,1,2-Tetrachloroethane	Bromodichloromethane
1,1,2-Trichloroethane	1,1,2,2-Tetrachloroethane	Toluene
Tetrachloroethene	1,2,3-Trichloropropane	Ethyl benzene
Dibromochloromethane	1,2-Dibromo-3-chloropropane	Bromoform
Chlorobenzene	*cis*-1,3-Dichloropropene	
1,2-Dichlorobenzene	*trans*-1,3-Dichloropropene	
2-Chloroethyl vinyl ether	Hexachlorobutadiene	

Table 3-5. PE Sample Composition and Count for SRS Demonstration

Sample Concentration Level	PE Mixture - Mixture Concentration[a]	No. of Replicates
Very low level	VOC Mix 1 - 10 µg/L	10
Low level	VOC Mix 1 - 50 µg/L	4
	VOC Mix 2 - 100 µg/L	4
Mid level	VOC Mix 1 - 200 µg/L	4
	VOC Mix 2 - 200 µg/L	4
High level	VOC Mix 1 - 600 µg/L	4
	VOC Mix 2 - 800 µg/L	4
Spike / low	1.02 mg/L TCE spike + 50 µg/L mix 1	4
	1.28 mg/L TCE and 1.23 mg/L PCE spike + 100 µg/L mix 2	4
Total number of samples		42

[a] TCE = trichloroethene; PCE = tetrachloroethene.

bottles specified by participants (40 mL, 250 mL, and 1 L) with zero headspace. The samples for field analysis were not preserved with chemical additives since sterile, nutrient-free water was used in their preparation.

Reference laboratory samples were preserved by acidification as specified in Method 8260A. Following preparation, all samples were kept under refrigeration until they were distributed to participants. All PE mixtures were prepared and dispensed on the weekend before the demonstration week.

Table 3-6. PE Sample Composition and Count for MAFB Demonstration

Sample Concentration Level	PE Mixture - Mixture Concentration[a]	No. of Replicates
Very low level	VOC Mix 3 - 10 µg/L	10
Low level	VOC Mix 3 - 50 µg/L	4
	VOC Mix 2 - 100 µg/L	4
Mid level	VOC Mix 3 - 200 µg/L	4
	VOC Mix 2 - 300 µg/L	4
High level	VOC Mix 1 - 600 µg/L	4
	VOC Mix 2 - 800 µg/L	4
Spike / low	1.22 mg/L TCE, 1.00 mg/L PCE, 0.50 mg/L 11DCA, and 0.50 mg/L BNZN spike + 100 µg/L mix 3	4
	1.04 mg/L 11DCA, 0.86 mg/L BNZN, 0.57 mg/L TCE, and 0.51 mg/L PCE spike + 50 µg/L mix 2	4
Total number of samples		42

[a] TCE = trichloroethene; PCE = tetrachloroethene; 11DCA = 1,1-dichloroethane; BNZN = benzene.

Groundwater Samples and Collection Methods

A total of 33 groundwater samples were provided to each participant and reference laboratory at each demonstration site. These samples were collected from 10 wells selected to cover TCE concentrations ranging from 10 µg/L to >1000 µg/L. The presence of other groundwater contaminants was also considered in well selection, as noted previously. Samples from each well were prepared in either triplicate or quadruplicate to allow statistical evaluation of instrument precision and accuracy relative to the reference laboratory results.

Groundwater at both sites was sampled by the same contract personnel who conduct sampling for quarterly well monitoring. Site-specific standard operational procedures, published in the demonstration plan, were followed at both sites. The sampling procedure is briefly summarized in the next paragraph.

The wells were purged with three well volumes using a submersible pump. During the purge, pH, temperature, and conductivity were monitored. Following well purge, pump flow was reduced and the purge line was used to fill a 10-L glass carboy. This initial carboy volume of groundwater was discarded. The carboy was filled to between 9 and 10 L a second time at a fill rate of 2 to 3 L/minute with the water stream directed down the side of the carboy for minimal agitation. The filled carboy was gently mixed with a Teflon stir bar for 5 minutes. Zero-headspace samples were immediately dispensed from the carboy while it was at the wellhead in the same manner as PE samples. Either three or four replicate samples were prepared for each technology and the reference laboratory. Following dispensing, the sample bottles were placed in a cooler and held under refrigeration until they were distributed to the participants. Groundwater sampling was completed during the first 2 days of each demonstration. Lists of the sampled wells and quarterly monitoring results are given in Tables 3-1 and 3-3 for the SRS and MAFB, respectively.

Sample Handling and Distribution

The distribution and status of all samples were tracked with chain-of-custody forms. Samples were dispensed to participants in small coolers containing a supply of blue ice. Normally, two sets of either 10 or 11 samples were distributed to participants each day during the 4 days of the demonstration, for a total of 83 samples, including blanks, at each site.

Some of the participants required information concerning the content of the samples prior to carrying out an analysis. This information was noted on the chain-of-custody form for each PE and groundwater sample, and was made available to the participants. Recorded information included:

- number of contaminants in the sample;
- list of contaminants in the sample;
- boiling point range of sample constituents; and
- approximate concentration range of contaminants in sample (low, mid, high).

The type of information provided during this demonstration would be required by the technology as a part of its normal operational procedure and did not compromise the results of the test. The information provided to each of the participants is documented in Chapter 5.

Field Demonstration Schedule and Operations

The following schedule was followed at both sites. The field team arrived on the Thursday prior to the demonstration week. Performance evaluation samples were prepared on Friday, Saturday, and Sunday. Technology participants arrived at the site on Monday morning and immediately began instrument setup. The first set of PE samples was normally distributed to all participants by midday Monday. The groundwater sampling crew, consisting of at least two on-site contractors and at least one ETV field-team member, carried out sampling of the 10 wells on Monday and Tuesday. The first groundwater samples were distributed on Wednesday. Thursday was reserved as a visitor day during which local and regional regulatory personnel and other potential instrument users were invited to hear presentations about instrument capabilities as well as to view the instruments in operation. Sample analysis was also performed on Thursday. On Friday, the final day of the demonstration, participants finished sample analysis, packed up, and departed by midafternoon.

Site Operations and Environmental Conditions

Instruments were deployed in parking lots or open fields adjacent to the well networks sampled during each demonstration. All participants came to the site self-equipped with power and shelter. Some came with field-portable generators and staged under tent canopies; others operated their instruments inside vehicles and used dc-to-ac power inverters connected to the vehicle's battery. Tables were provided for those participants who required a work space. Each team provided its own instrument operators. Specifics regarding instrument setup and the qualifications, training, and experience of the instrument operators are given in Chapter 6.

The SRS demonstration took place on September 8 through 12, 1997, and the MAFB demonstration on September 22 through 26, 1997. The verification organization team staged its operations out of a tent at the SRS and out of a mobile laboratory at MAFB. The PE mixtures at the SRS were prepared at a nearby SRS laboratory facility and in the mobile laboratory at MAFB. Refrigerators at on-site facilities of the groundwater sampling contractors were used to store the samples at both sites prior to their distribution.

Environmental conditions at both sites are summarized in Table 3-7. Conditions at SRS were generally hot and humid. Sporadic rain showers were encountered on one of the test days, but did not impede demonstration activities. Conditions at MAFB were initially hot and progressed to unseasonably hot. Moderately high winds were also encountered during the last 2 days at MAFB.

Table 3-7. Weather Summary for SRS and MAFB During Demonstration Periods

Site/Parameters	Mon	Tue	Wed	Thu	Fri
SRS					
Temperature range (°C)	20 – 34	21 – 33	21 – 28	18 – 30	19 – 33
Relative humidity range (%)	25 – 68	28 – 67	51 – 71	40 – 70	26 – 70
MAFB					
Temperature range (°C)	17 – 33	18 – 36	18 – 37	24 – 35	24 – 35
Relative humidity range (%)	17 – 72	25 – 47	15 – 59	17 – 67	31 – 83
Wind speed range (knots)	0 – 7	3 – 6	1 – 6	4 – 13	2 – 11

Note: Ranges are given for the 7 a.m. to 7 p.m. time interval.

Field Audits

Field auditors were used to observe and record specific features of technology operations. The demonstration goal was to have at least two auditors observe each technology over the course of the two field demonstrations. Audit results are documented in Chapter 6. The following checklist was used by the audit team as a guideline for gathering information during the audit:

- description of equipment used;
- logistical considerations, including size and weight, shipping and power requirements, other required accessories;
- historical uses and applications of the technology;
- estimated cost of the equipment and its field operation;
- number of operators required;
- required operator qualifications;
- description of data produced;
- compounds that the equipment can detect;
- approximate detection limits for each compound, if available;
- initial calibration criteria;
- calibration check criteria;
- corrective actions for unacceptable calibrations;
- specific QC procedures followed;
- QC samples used;
- corrective action for QC samples;
- sample throughput rate;
- time requirements for data analysis and interpretation;
- data output format and description;
- specific problems or breakdowns occurring during the demonstration;
- possible sample matrix interference; and
- other auditor comments and observations.

Data Collection and Analysis

The analytical results were collected in hardcopy format at the end of each day. These results were used to document sample completion and throughput. The participants also provided a compilation of their results on computer disks at the conclusion of each demonstration week. No feedback on analytical results or performance was given to the participants during the course of either demonstration week. Following the SRS demonstration, and only after all results were submitted, was qualitative verbal feedback given to each participant concerning their accuracy and precision on SRS PE sample results. This was reasonable since a well-defined monitoring plan would use preliminary samples to determine control limits and to make system modifications or refinements prior to advancing to the next phase of sampling and analysis. Three weeks following the MAFB demonstration, copies of all submitted data were entered into spreadsheets by the verification organization and transmitted to participants for final review. This gave each participant the opportunity to detect and change calculation or transcription errors. If other more substantive changes were proposed, they were submitted to the verification organization, along with documentation outlining the rationale for the change. Following this final data review opportunity, no other data changes were permitted. The extent and nature of any changes are discussed in Chapter 6.

Demonstration Plan Deviations

The following deviations from the written demonstration plan were recorded during the field demonstration. The impact of each deviation on the overall verification effort, if any, is also included.

- Five blank samples were submitted to the reference laboratory from the SRS demonstration instead of the 8 samples specified in the demonstration plan. The impact on the verification effort was minimal since a total of 13 blanks (8% of the total field sample count) were analyzed by the reference laboratory.
- During groundwater sampling of SRS well MSB 14A, two 250-mL sample bottles were not filled. Omission of this sample resulted in a double replicate sample set instead of a triple replicate for Electronic Sensor Technology and Sentex. The impact on the study was insignificant since this omission accounted for only 1 sample out of a total groundwater sample count of 33.
- The demonstration plan specified that only two VOC mixtures would be used at each demonstration site. In fact, three mixtures were used at the MAFB demonstration (Table 3-6) to add complexity to the sampling. This change caused some minor confusion with one of the developers, who was not expecting this particular set of compounds at MAFB. The most significant impact of this change was a loss of time for the affected developer as a result of extended data review of the unanticipated mixture. The misunderstanding was verbally clarified and no further problems were encountered. The results from the high-level VOC mix 1 were not used in the statistical analyses.

Chapter 4
Laboratory Data Results and Evaluation

Introduction

A reference laboratory was used to verify PE sample concentrations and to generate analytical results for all groundwater samples using EPA Method 8260A. This chapter includes a brief description of the reference laboratory and its data quality control program; the methodology and accompanying quality control procedures employed during sample analysis; and laboratory results and associated measures of data quality for both demonstration sites.

Reference Laboratory

DataChem Laboratories (DCL) in Salt Lake City, Utah, was chosen as the reference laboratory for both phases of this demonstration. This is a full-service analytical laboratory with locations in Salt Lake City and Cincinnati, Ohio. It provides analytical services in support of environmental, radiological, mixed-waste, and industrial hygiene programs. DataChem's qualifications include U.S. EPA Contract Laboratory Program participation in both inorganic and organic analysis and American Industrial Hygiene Association accreditation, as well as U.S. Army Environmental Center and U.S. Army Corps of Engineers (Missouri River Division) certification. State-specific certifications for environmental analytical services include Utah, California, Washington, New Jersey, New York, Florida, and others.

Laboratory Selection Criteria

Selection criteria for the reference laboratory included the following: relevant laboratory analytical experience, adequacy of QC documentation, turnaround time for results, preselection audit results, and cost. Early discussions with DCL revealed that the laboratory conducts a high number of water analyses using Method 8260A. Prior to laboratory selection, a copy of the DataChem Quality Assurance Program Plan (DataChem, 1997) was carefully reviewed. This document outlines the overall quality assurance program for the laboratory and provides specific quality control measures for all the standard analytical methods used by the laboratory. Laboratory analysis and reporting time for sample analysis was 21 days, with a per-sample cost of $95.

In June 1997, Sandia sent several PE water samples to DCL for evaluation. Laboratory performance on these samples was reviewed during an audit in June 1997. The laboratory detected all compounds contained in the PE mixtures. Reported concentration levels for all compounds in the mixtures were within acceptable error margins. The audit also indicated that the laboratory conducted its operations in accordance with its QA plan. The results of this preliminary investigation justified the selection of DCL as the reference laboratory and provided ample evidence of the laboratory's ability to correctly use Method 8260A for the analysis of demonstration samples.

Summary of Analytical Work by DataChem Laboratories

In addition to the preselection audit samples noted above, DCL also analyzed predemonstration groundwater samples collected at SRS in August 1997. During the demonstration phase, DCL was sent split samples of all PE and groundwater samples given to the demonstration participants from both the Savannah River and McClellan sites. A total of 90 and 91 samples from the SRS and MAFB demonstrations, respectively, were received and analyzed by the laboratory. Over the course of 1 month, demonstration samples were run in 9 batches of approximately 20 samples per batch. The results were provided in both hardcopy and electronic format. The hard copy included all paperwork associated with the analysis, including the mass spectral information for each compound detected and complete quality control documentation. The electronic copy was provided in spreadsheet format and included only the computed result for each target compound in each sample.

Preselection evaluation of DCL established their competence in the use of Method 8260A. In light of these findings and in an effort to expedite laboratory analysis of demonstration samples, an estimate of the concentration levels of target compounds in both PE and groundwater samples was provided to the laboratory with each batch of samples. With a knowledge of the approximate concentration range of the target compounds, the analyst was able to dilute the sample appropriately, thereby eliminating the need to do multiple dilutions in order to obtain a suitable result within the calibrated range of the instrument.

Summary of Method 8260A

Method 8260A, which is included in the EPA SW-846 compendium of methods, is used to measure volatile organic compounds in a variety of solid waste matrices, including groundwater (EPA, 1996b). The method can be used to quantify most volatile organic compounds with boiling points below 200 °C that are either insoluble or only slightly soluble in water. The method employs a chromatography/mass spectrometric procedure with purge-and-trap sample introduction. An inert gas is bubbled through a vessel containing the water sample. The volatile organic compounds partition into the gas phase and are carried to a sorbent trap, where they are adsorbed. Following the purge cycle, the sorbent trap is heated and the volatile compounds are swept into the GC column, where they are separated according to their boiling points. The gas chromatograph is interfaced directly to a mass spectrometer that bombards the compounds with electrons as they sequentially exit the GC column. The resulting fragments, which possess charge and mass characteristics that are unique for each compound, are detected by the spectrometer's mass detector. The signal from the mass detector is used to build a compound mass spectrum that is used to identify the compound. The detector signal intensities for selected ions unique to each target compound are used to quantify the amount of the compound in the sample.

Method 8260A Quality Control Requirements

Method 8260A specifies a number of quality control activities to be carried out in conjunction with routine sample analysis. These activities are incorporated into DCL QA documentation and are summarized in Table 4-1 (DataChem, 1997). Corrective actions are specified in the event of failure to meet QC criteria; however, for the sake of brevity they are not given in the table. In most cases the first corrective action is a calculation check. Other corrective actions include system recalibration, sample rerun, batch rerun, or flag data.

Summary of Laboratory QC Performance

The following sections summarize the QC activities and results that accompanied the analysis of each sample batch.

Table 4-1. Method 8260A Quality Control Summary

Activity	Frequency	Data Acceptance Criteria
Spectrometer tune check	Bromofluorobenzene standard every 12 hours	Relative abundance; range of characteristic mass fragments meets specifications.
System performance check	SPCC[a] sample every 12 hours	Compound relative response factors must exceed required minimums.
System calibration check	CCC[b] sample every 12 hours	Response factor of CCC varies by no more than ±25% from initial calibration. Internal standard retention time within 30 seconds of last check. Internal standard area response within –50 to 100% of last check.
Lab method blank	One or more per batch (approx. 20 samples)	≤ 3× Detection limit.
Field blank	One or more per batch	≤ 3× Detection limit.
Laboratory control standard	One or more per batch	Compound recovery within established limits.[c]
Matrix spike	One or more per batch	Spike recovery within established limits. [c]
Matrix spike duplicate	One or more per batch	Relative percent difference of check compounds ≤50%.
Surrogate standards	Included in every sample	Recovery within established limits. [c]
Internal standards	Included in every sample	Recovery within established limits. [c]

[a] SPCC = system performance check compounds.

[b] CCC = calibration check compounds.

[c] The laboratory generates control limits that are based on 100 or more analyses of designated compounds. The upper and lower acceptable recovery limits are based on a 3-standard-deviation-interval about the mean recovery from the multiple analyses. The result from a single analysis must fall within these control limits in order to be considered valid.

Target Compound List and Method Detection Limits

The method detection limits and practical quantitation limits for the 34 target compounds used in this demonstration are given in Table 4-2. The PQL marks the lower end of the calibrated working range of the instrument and indicates the point at which detection and reported results carry a 99% certainty. Detects reported between the MDL and PQL carry less certainty and are flagged accordingly in the tabulated results.

Sample Holding Conditions and Times

Method 8260A specifies a maximum 14-day holding time for refrigerated water samples. All samples prepared in the field were kept under refrigeration before and during shipment to the laboratory. Upon receipt at the laboratory, they were held under refrigeration until analysis. All samples were analyzed within the 14-day time period following their preparation or collection.

System Calibration

Method 8260A stipulates that a five-point calibration be carried out using standard solutions for all target compounds across the working range of the instrument. Each mix of compounds is run five times at each of the five points in the instrument range. For an acceptable calibration, precision from these multiple analyses, as

Table 4-2. Reference Laboratory Method Detection Limits for Target Compounds

Target Compound	Method Detection Limit (µg/L)	Practical Quantitation Limit (µg/L)
Trichlorofluoromethane	0.15	1
1,1-Dichloroethane	0.08	1
Methylene chloride	0.10	1
1,1-Dichloroethene	0.08	1
Chloroform	0.07	1
Carbon tetrachloride	0.10	1
1,1-Dichloropropene	0.10	1
1,2-Dichloroethane	0.04	1
Trichloroethene	0.14	1
1,2-Dichloropropane	0.04	1
1,1,2-Trichloroethane	0.09	1
Tetrachloroethene	0.10	1
1,3-Dichloropropane	0.06	1
Dibromochloromethane	0.08	1
1,2-Dibromoethane	0.09	1
Chlorobenzene	0.06	1
1,1,1,2-Tetrachloroethane	0.05	1
1,1,2,2-Tetrachloroethane	0.07	1
1,2,3-Trichloropropane	0.50	1
1,2-Dibromo-3-chloropropane	0.62	1
Hexachlorobutadiene	0.10	1
cis-1,3-Dichloropropene	0.17	1
trans-1,3-Dichloropropene	0.08	1
1,2-Dichlorobenzene	0.17	1
trans-1,2-Dichloroethene	0.17	1
1,1,1-Trichloroethane	0.26	1
Benzene	0.12	1
Bromodichloromethane	0.11	1
Toluene	0.15	1
Ethyl benzene	0.14	1
Bromoform	0.10	1
cis-1,2-Dichloroethene	0.14	1
ortho-Xylene	0.11	1
Acetone	2.9	5

Notes: Detection limits are given for an undiluted 5-mL sample volume. Detection limits are determined annually using the method outlined in 40 CFR Part 136 Appendix B (seven replicates of deionized water spiked at 1 µg/L concentration level). Dilutions of the original sample raise the MDL and PQL values accordingly. Surrogate standards used in the analyses were 1,2-dichloroethane-d_4, toluene-d_8, and 4-bromofluorobenzene. Internal standards were fluorobenzene, chlorobenzene-d_5, and 1,4-dichlorobenzene-d_4.

given by the relative standard deviation, must be 30% or less. A minimum instrument response factor[1] is also prescribed by the method for a designated subset of compounds termed system performance check compounds (SPCC). The five-point calibration curve from the most recent instrument calibration met the specified precision criteria. The system performance check compound response factors also met method criteria.

Daily Instrument Performance Checks

Daily mass spectrometer tune checks as well as other system performance and calibration checks noted in Table 4-1 were carried out for each of the nine sample batches and met Method 8260A on quality control criteria.

Batch-Specific Instrument QC Checks

Method Blanks

All method blank analyses met established criteria (Table 4-1), with one exception. Hexachlorobutadiene, one of the demonstration target compounds, was detected in two of the method blanks at levels in excess of 3 times the MDL. This compound was a component in one of the standard mixes used in preparing the PE samples because reference laboratory data for this compound were not used in the study. Only one of the participating technologies was calibrated to detect this particular compound. Occasional detection of this compound as a minor instrument contaminant does not adversely affect the analytical results for other target compounds.

Laboratory Control Standard

At least one laboratory control standard was run with each of the nine batches of samples. Recovery values for each component in the mixture are given in Figure 4-1 for SRS analyses and Figure 4-2 for MAFB analyses. Recovery values were all within the laboratory-specific control criteria.

Matrix Spike and Matrix Spike Duplicate

The compounds in the matrix spike were the same as those in the laboratory control standard. Computed matrix spike and matrix spike duplicate recoveries were all within the recovery ranges noted in Table 4-1. The relative percent differences (RPDs)[2] calculated for the matrix spike and matrix spike duplicate samples also met the laboratory criteria of ≤50%. All RPD values from matrix spike analyses were less than 10% for the SRS samples and less than 13% for MAFB samples.

Sample-Specific QC Checks

Internal Standard

All samples met internal standard acceptance criteria except one. All three internal standards in sample SP31 failed to meet area response criteria and results from that sample were not included in the reference data set.

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[1] The response factor is the ratio of instrument response for a particular target compound to the instrument response for an internal standard.

[2] The relative percent difference between two samples is the absolute value of their difference divided by their mean and multiplied by 100.

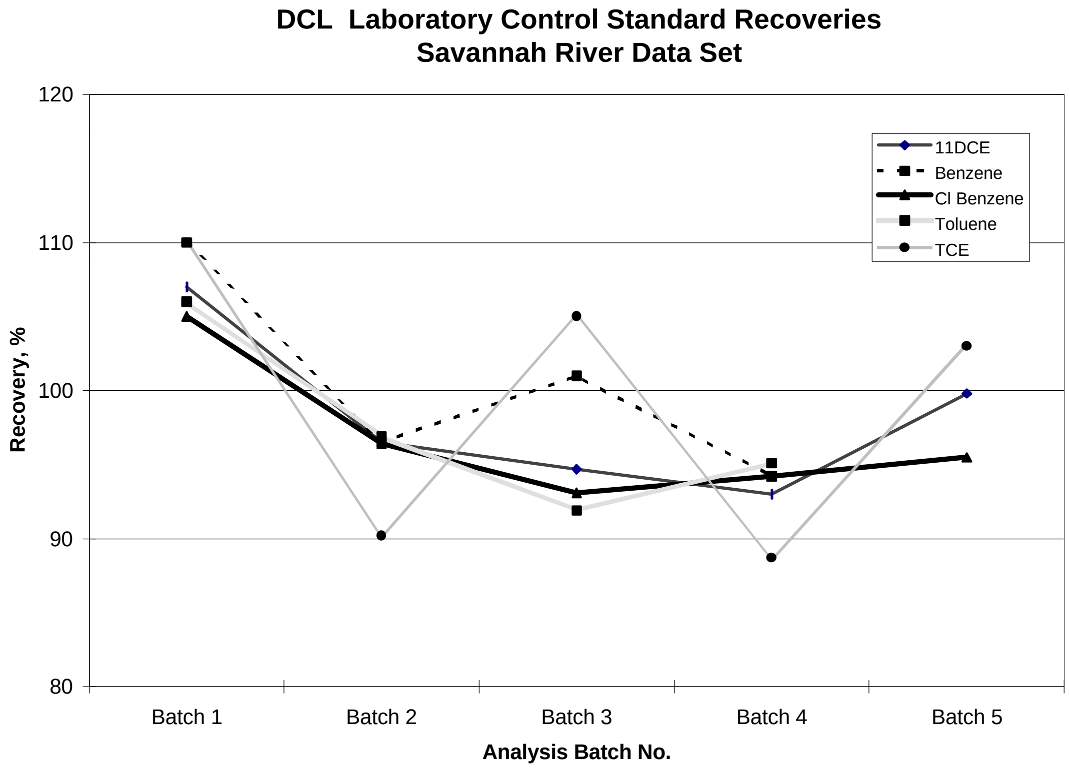

Figure 4-1. Laboratory control standard recovery values for SRS analyses.

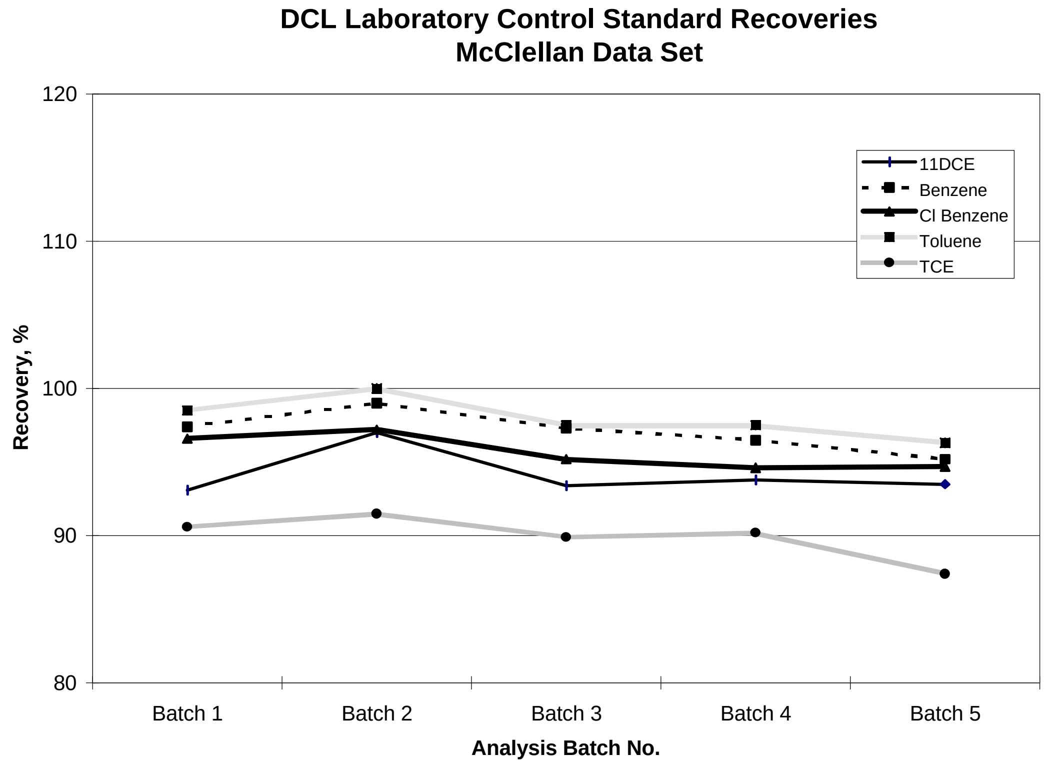

Figure 4-2. Laboratory control standard recovery values for MAFB analyses.

Surrogate Standard

With the following exceptions, surrogate standard recoveries met the criteria established by the laboratory, as noted in Table 4-1. Six samples (SP12, SP16, SP26, SP29, SP33, and SP65) failed surrogate recovery criteria for 1,2-dichloroethane-d_4 and passed recovery criteria for 4-bromofluorobenzene and toluene-d_8. The actions taken are noted in Table 4-3.

Summary of Analytical and QC Deviations

A summary of QC deviations as well as other analytical errors or omissions is given in Table 4-3. The actions taken with regard to the affected data and the reference data set are also tabulated, along with a brief rationale.

Table 4-3. Summary of Reference Laboratory Quality Control and Analytical Deviations

Deviation or QC Criteria Failure	Action
Required dilution not made on two samples (SP20 and SP21). Some compounds were present above instrument linear range.	Data Included: Data values for affected samples fall in the range of the other three replicate samples.
Three field blanks were not sent to DCL from SRS demonstration.	No Action: Five field blanks and 10 method blanks were run, yielding an adequate data set.
Calculation error in original DCL report. Dilution factors applied incorrectly in two samples (SP55 and SP57).	Data Corrected and Included: The correct dilution factors were applied following a teleconference with the DCL analyst.
Sample SP31 failed internal standard recovery limits.	Data Not Included.
The following samples failed one or more surrogate standard recovery limits: SP12, SP16, SP26, SP29, SP33, and SP65.	Data Not Included: SP12; results clearly fall outside of the range of other three replicate samples. Data Included: All others; nearly all target compounds fall within the range of concentration reported for the other three replicate samples.
Hexachlorobutadiene detected as a contaminant in selected blanks and samples.	No Action: This compound was not a target compound for any of the technologies. Its presence as a low-level contaminant does not affect the results of other target compounds.
Chloroethyl vinyl ether was not detected in PE samples known to contain this compound.	No Action: The GC/MS was not calibrated for this compound. None of the technologies included this compound in their target compound lists.
Three sample results (MG20, MG51, and MG59) are from a second withdrawal from the original zero-headspace sample vial.	Data Included: The original volume withdrawn from the vial was 0.05 mL, resulting in an insignificant headspace volume and no expected impact on the composition of the second sample.

Other Data Quality Indicators

The demonstration design incorporated nine PE mixtures of various target compounds at each site that were prepared in the field and submitted in quadruplicate to each technology as well as to the laboratory. Laboratory accuracy and precision checks on these samples were assessed. Precision on replicate analysis of groundwater samples was also evaluated. The results of these assessments are summarized in the following sections.

PE Sample Precision

The relative standard deviation from quadruplicate laboratory analyses of each PE mixture prepared in the field was computed for each target compound in the mixture. As noted in Chapter 3, care was taken to ensure the preparation and distribution of homogeneous samples from each PE mixture. The RSD values represent an overall estimate of precision that takes into account field handling, shipping, storage, and analysis of samples.

The precision data are shown in Figures 4-3 and 4-4 for SRS and Figures 4-5 and 4-6 for MAFB. (See Tables 3-5 and 3-6 for the composition and concentration level of each PE mixture.) The compiled RSDs for all PE sample results had a median value of 7% and a 95th percentile value of 25%. In selected instances, precision in excess of Method 8260A specifications (≤30% RSD) is observed for tetrachloroethene, trichloroethene, *cis*-1,3-dichloropropene, 1,2,3-trichloropropane, and 1,1,2,2-tetrachloroethane. Precision well in excess of method specifications is observed for 1,2-dibromo-3-chloropropane, *trans*-1,3-dichloropropene, and 1,1-dichloropropene. The implications of these results with respect to evaluation of the technology performance are discussed, when applicable, in Chapters 5 or 7.

PE Sample Accuracy

An error propagation analysis was carried out to estimate the degree of uncertainty in the stated "true" concentration level of the PE samples prepared in the field. The sources of uncertainty and their magnitude encountered during PE sample preparation are listed in Table 4-4. These errors are combined using the methodology described by Bevington (1969) to arrive at a combined uncertainty in the PE sample value of ±5%. Thus, for a 100-µg/L PE mix, the true value is known with 99% certainty to be within the range of 95 to 105 µg/L.

Table 4-4. Sources of Uncertainty in PE Sample Preparation

Type of Uncertainty	Magnitude	Source of Estimate
Weight of component in PE mix ampule.	0.5 mg in 1200 mg	Gravimetric balance uncertainty included in PE mix certification documents
Volume of methanol solvent used to dilute neat compounds.	0.2 mL in 600 mL	Published tolerances for volumetric flasks (Fisher Catalog)
Volume of PE solution (from ampule) used in final PE solution.	±5% of microsyringe volume; e.g., 25 µL for a 500-µL syringe	Published tolerances in certificates shipped with microsyringes
Volume of water diluent in final PE solution.	5 ml in 10 L	Published tolerances for volumetric flasks (Fisher Catalog)

The laboratory results for PE samples are compared with the "true" value of the mixture to provide an additional measure of laboratory performance. A mean recovery[3] was computed for each PE compound in each of the four sample splits analyzed from each mixture. The SRS recovery values are shown in Figures 4-7 and 4-8, and MAFB recoveries are shown in Figures 4-9 and 4-10. Acceptable mean percent recovery values, specified in Method 8260A, fall within the range of 70 to 130% with exceptions for a few compounds that pose analytical difficulties. With the following exceptions, all PE compounds at all concentration ranges met the Method 8260A recovery criteria. The exceptions are 1,2,3-trichloropropane, 1,1-dichloropropene, 1,2-dibromo-3-chloropropane,

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[3] Recovery is the ratio of the mean concentration level from analysis of the four sample splits to the reference or "true" concentration levels of the target compounds in each PE mix.

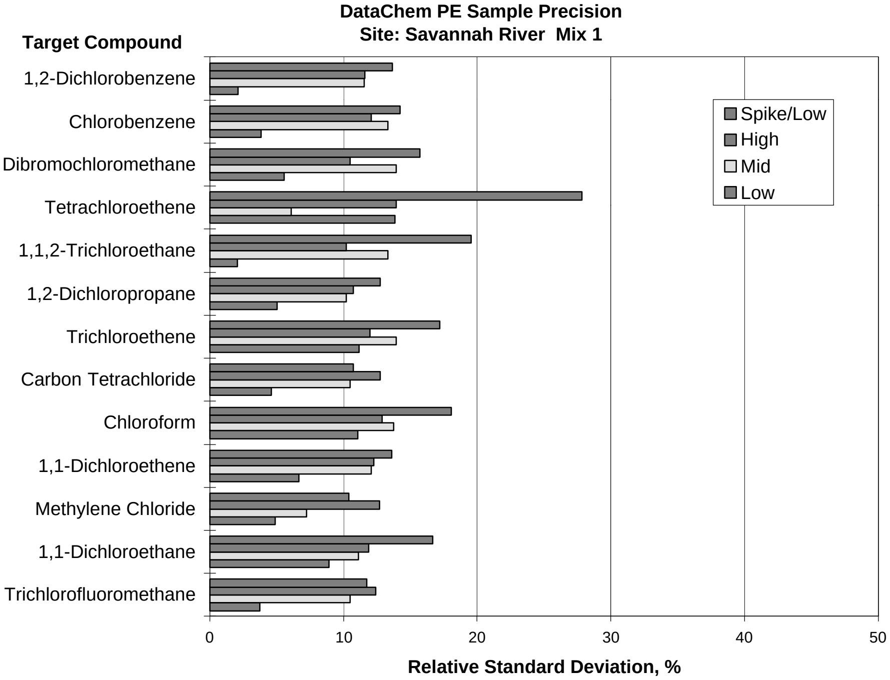

Figure 4-3. Laboratory precision on SRS PE samples containing mix 1. Trichloroethene was spiked into the spike/low samples.

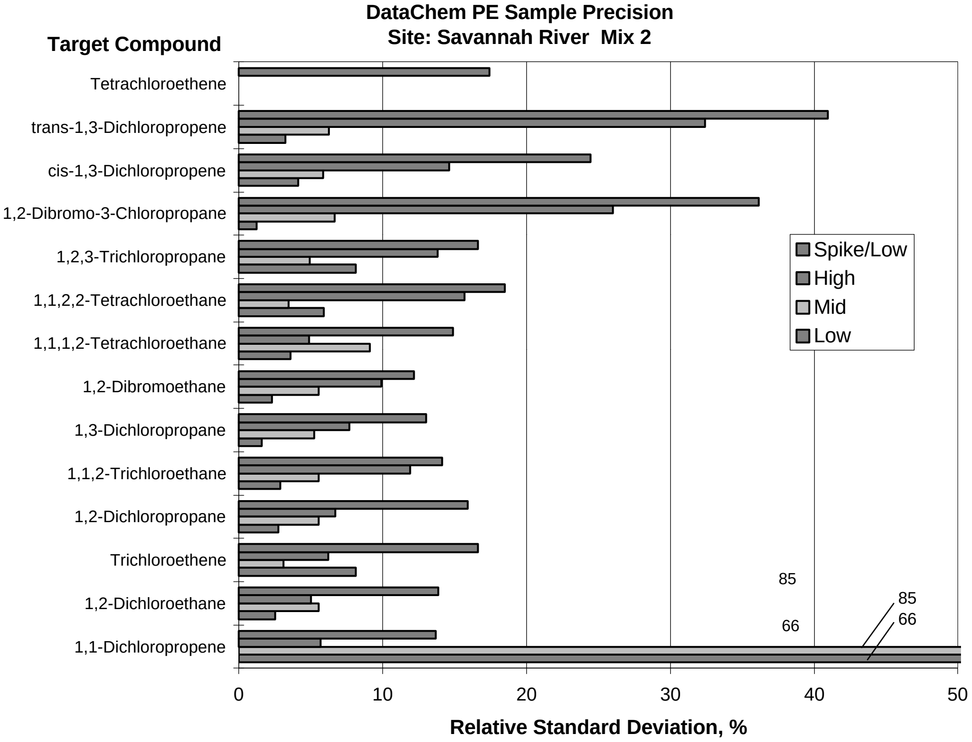

Figure 4-4. Laboratory precision on SRS PE samples containing mix 2. Tetrachloroethene was spiked into the mix 2 samples. Trichloroethene and tetrachloroethene were spiked into the spike/low samples.

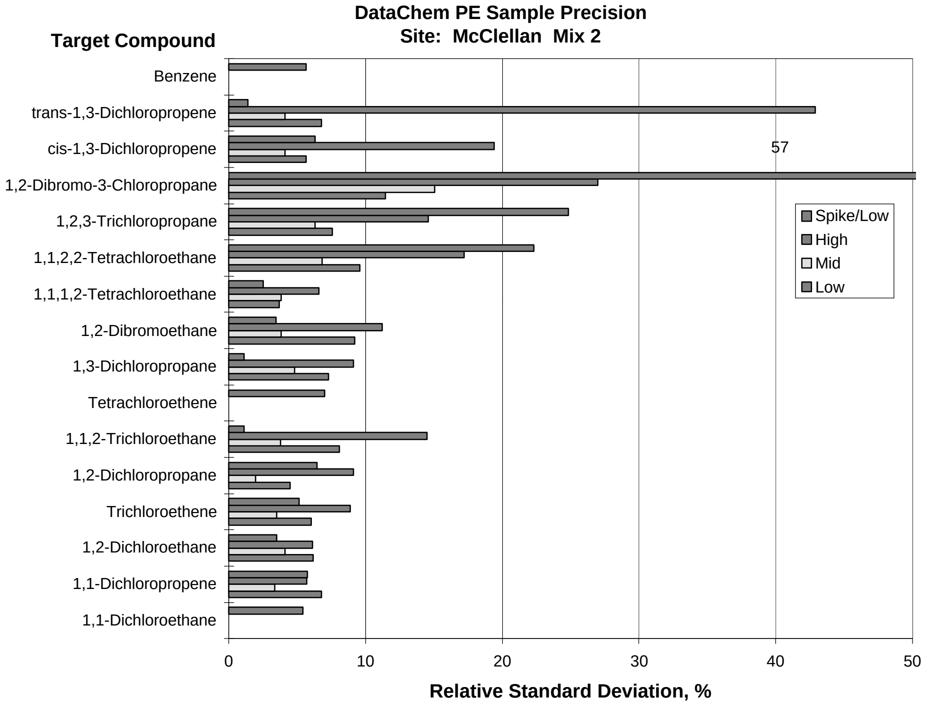

Figure 4-5. Laboratory precision on MAFB PE samples containing mix 2. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

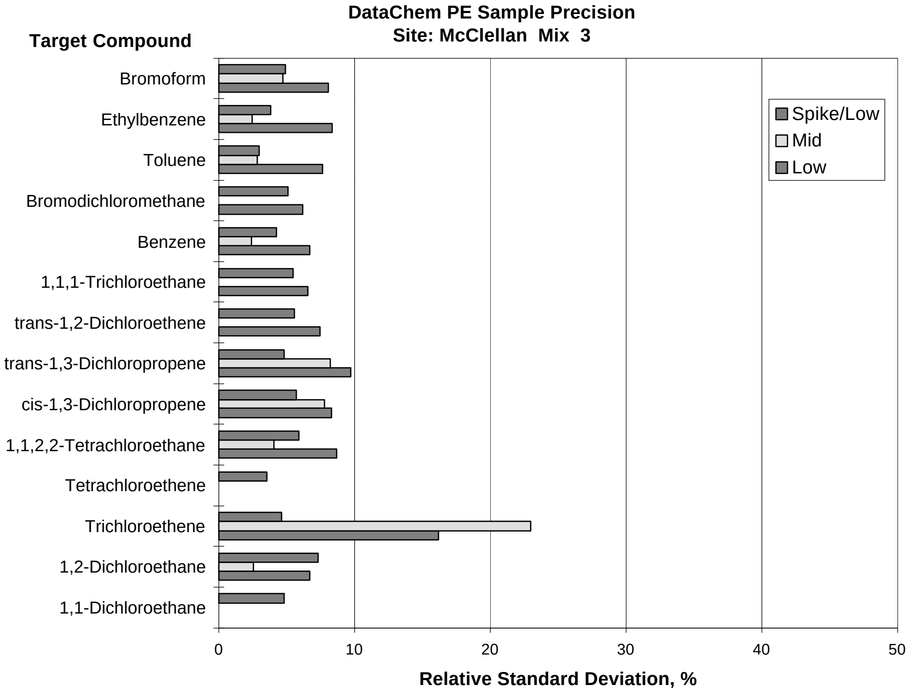

Figure 4-6. Laboratory precision on MAFB PE samples containing mix 3. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

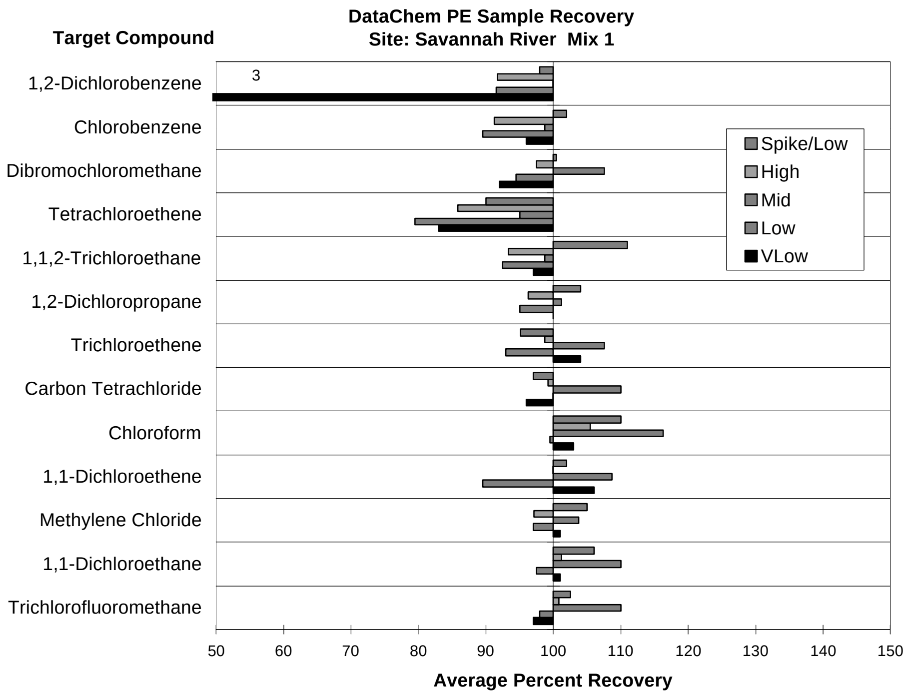

Figure 4-7. Laboratory mean recoveries for SRS PE samples containing mix 1. Trichloroethane was spiked into the spike/low samples.

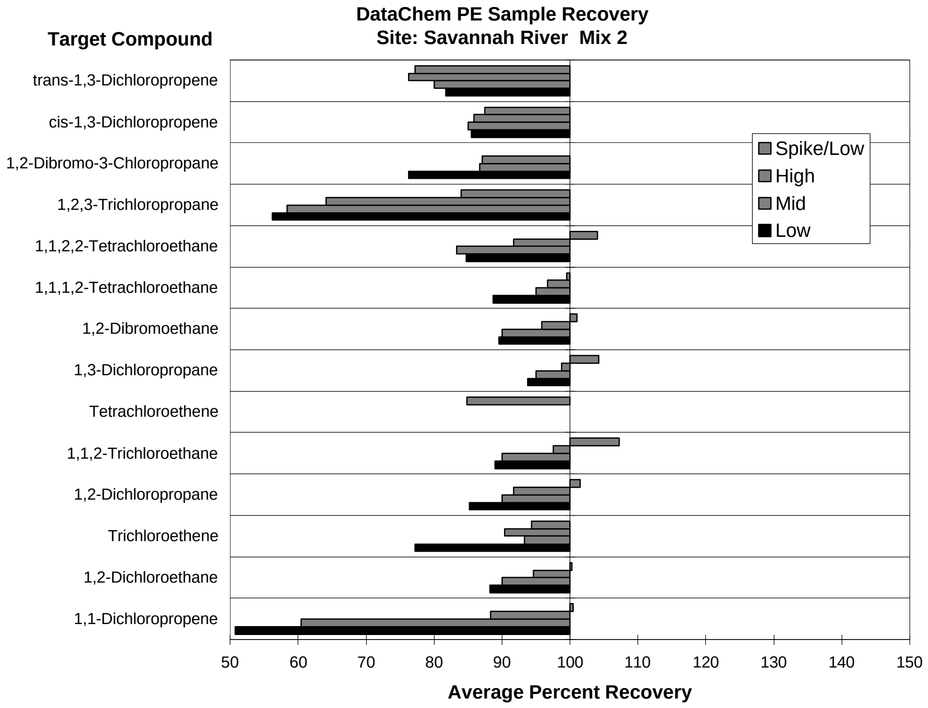

Figure 4-8. Laboratory mean recoveries for SRS PE samples containing mix 2. Trichloroethane and tetrachloroethene were spiked into the spike/low samples.

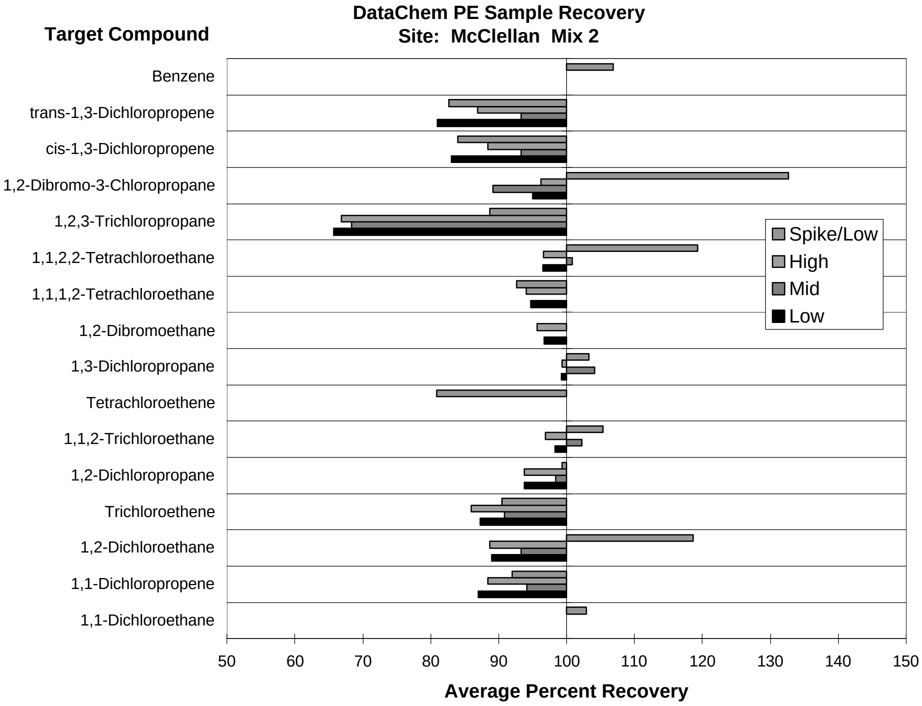

Figure 4-9. Laboratory mean recoveries for MAFB PE samples containing mix 2. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

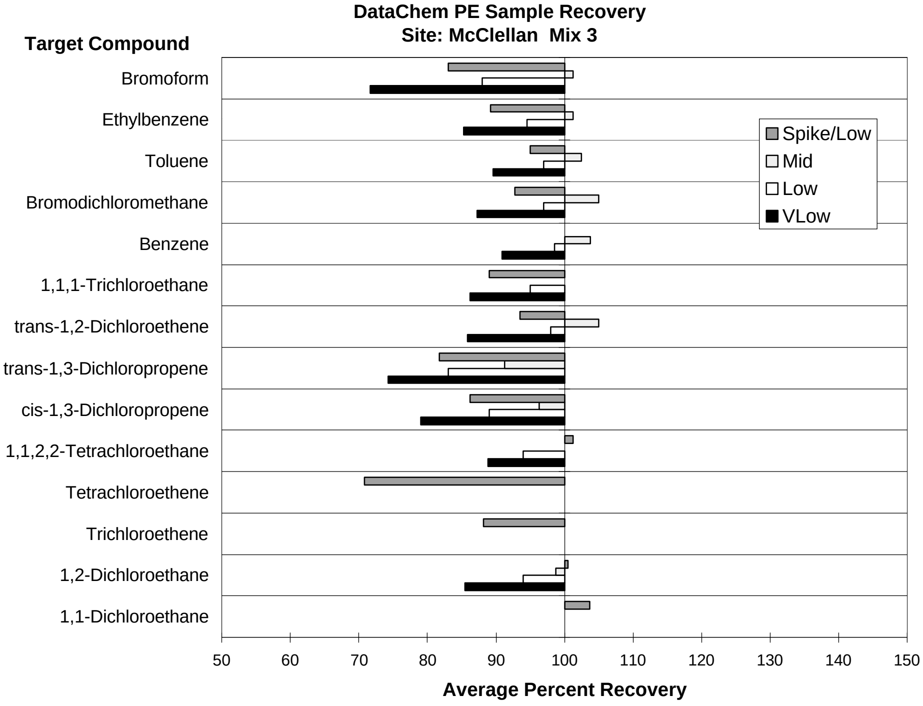

Figure 4-10. Laboratory mean recoveries for MAFB PE samples containing mix 3. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

and 1,2-dichlorobenzene at selected concentration levels. The implications of these exceptions for the technology evaluation are further discussed, if applicable, in Chapter 5. The compiled absolute percent differences (APDs)[4] for all PE sample results had a median value of 7% and a 95th percentile value of 25%.

Groundwater Sample Precision

Relative standard deviations are given in Table 4-5 for compound concentrations in excess of 1 µg/L in groundwater samples from the SRS demonstration. Trichloroethene and tetrachloroethene were the only contaminants detected in SRS groundwater samples. A similar compilation of RSD values from the MAFB groundwater samples is included in Table 4-6. These values are based on analytical results from either three or four replicate samples. With three exceptions, all tabulated values are less than 20%.

Table 4-5. Summary of SRS Groundwater Analysis Precision

Sample Description	Relative Standard Deviation (%)	
	TCE	PCE
Very low 1	10.6	14.3
Very low 2	34.4	12.4
Low 1	5.4	5.7
Low 2	7.1	8.7
Mid 1	9.4	11.6
Mid 2	7.3	4.2
High 1	0.8	1.8
High 2	11.8	7.9
Very high 1	8.4	5.7
Very high 2	6.2	6.3

Table 4-6. Summary of MAFB Groundwater Analysis Precision

Sample Description	Relative Standard Deviation (%)								
	11DCE	TCE	CLFRM	CCL4	PCE	11DCA	c12DCE	t12DCE	BNZN
Very low 1	9.1	5.0							
Very low 2	2.6	<0.1	1.3	4.2	5.7				
Low 1	6.8	3.7	2.0	1.9		<0.1			
Low 2	11.5	5.2		4.0	22.3	4.1	3.8		
Mid 1	12.0	10.5			13.9	9.4	12.6		
Mid 2		3.6	4.9				3.8		
High 1		2.4	20.9				4.1		
High 2		5.3	5.3				5.1	3.8	
Very high 1	2.5	5.4	5.2				6.5		4.9
Very high 2		8.0	6.4	4.9			10.1		

Notes: 11DCE = 1,1-dichloroethene; TCE = trichloroethene; CLFRM = chloroform; CCL4 = carbon tetrachloride; PCE = tetrachloroethene; 11DCA = 1,1-dichloroethane; c12DCE = *cis*-1,2-dichloroethene; t12DCE = *trans*-1,2-dichloroethene; BNZN = benzene.
Blank cells indicate that the compound was not present.

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[4] The absolute percent difference is the absolute value of the percent difference between a measured value and a true value.

Summary of Reference Laboratory Data Quality

With the exceptions noted below, a review of DCL analytical data showed that all Method 8260A QC criteria were met. Internal standard recovery limits were not met for one sample. The results for this sample were markedly different from the other three samples in the replicate set and the sample was omitted from the data set. Six samples failed one or more surrogate standard recovery criteria. These sample results were compared with replicate sample results. Five of the six samples were comparable and were included in the reference data set.

The data for the remaining sample were not comparable and were omitted from the reference data set. Other quality control deviations, which are summarized in Table 4-3, did not significantly affect the quality of the laboratory data.

A review of DCL precision and accuracy on field-prepared PE mixtures corroborates laboratory internal QC results. A similar precision evaluation on groundwater samples from both sites further supports these observations. Overall, the internal and external QC data reveal appropriate application and use of Method 8260A by DataChem Laboratories. The laboratory results for groundwater samples from both sites are considered suitable for use as a reference data set.

Chapter 5
Demonstration Results

Voyager Calibrated and Reported Compounds

Prior to the field demonstration, the participants were given a list of all compounds that were to be used in the PE mixtures to facilitate preparations for predemonstration instrument calibration. The Voyager system was calibrated for 24 compounds at the SRS and 17 compounds at the MAFB site (Table 5-1). The number of target analytes was reduced at MAFB in order to increase sample throughput. A total of 32 chlorinated and nonchlorinated hydrocarbon compounds were included in the PE mixtures noted in Table 3-4. The Voyager was also calibrated at both sites for *cis*-1,2-dichloroethene, which was not a PE compound. Three pairs of compounds were reported as coeluting pairs, as also noted in Table 5-1. The Voyager was not calibrated for the following nine PE compounds at either site: trichlorofluoromethane, 1,1-dichloroethane, 1,2-dichlorobenzene, 2-chloroethyl vinyl ether, 1,1,2,2-tetrachloroethane, 1,2,3-trichloropropane, 1,2-dibromo-3-chloropropane, hexachlorobutadiene, and bromoform.

Table 5-1. Voyager Calibrated and Reported Compounds

Calibrated Compounds at Both Sites	
1,3-Dichloropropane	1,1,2-Trichloroethane$^{(c)}$
1,2-Dichloroethane$^{(a)}$	1,2-Dibromoethane$^{(c)}$
1,2-Dichloropropane$^{(a)}$	Toluene
1,1-Dichloropropene	Dibromochloromethane
Benzene	Tetrachloroethene
Bromodichloromethane	1,1,1,2-Tetrachloroethane
Trichloroethene	Chlorobenzene
cis-1,3-Dichloropropene	Ethyl benzene
cis-1,2-Dichloroethene	
Additional Calibrated Compounds at SRS	
1,1-Dichloroethene$^{(b)}$	Carbon tetrachloride
Methylene chloride$^{(b)}$	*trans*-1,2-Dichloroethene
Chloroform	1,1,1-Trichloroethane
trans-1,3-Dichloropropene	

Note: Superscripts denote coeluting compound pairs.

Preanalysis Sample Information

Samples were provided to the Voyager team without additional information on the number of compounds in the sample or compound concentration levels.

Sample Completion

All 166 PE and groundwater samples submitted for analysis to the Voyager team were completed at both demonstration sites. All Voyager PE and groundwater results are included in Appendix B.

Blank Sample Results

Eight blank samples were provided for analysis at each demonstration site. False positive detects were counted only for compounds reported at concentration levels greater than 1 µg/L. A list of false positive detects is given for both sites in Table 5-2.

Table 5-2. False Positive Rates from Blank Sample Analysis

SRS Blank Samples		MAFB Blank Samples	
Compound	**False Positive**	**Compound**	**False Positive**
Trichloroethene	2 of 8 (25%)	1,1-Dichloropropene	1 of 8 (13%)
cis-1,3-Dichloropropene	1 of 8 (13%)	Trichloroethene	1 of 8 (13%)
Chlorobenzene	1 0f 8 (13%)	Tetrachloroethene	1 of 8 (13%)
		trans-1,3-Dichloropropene	1 of 8 (13%)

Performance at Instrument Detection Limit

Ten replicate samples of a PE mixture at a concentration level of 10 µg/L were provided for analysis at each site. Reported nondetects were compiled and are given as percent false negatives in Table 5-3. Vendor-provided compound detection limits, where available, are also shown in the table for comparison.

Table 5-3. False Negative Rates from Very Low-Level PE Sample Analysis

SRS PE Mix 1 (10 µg/L)		MAFB PE Mix 3 (10 µg/L)	
Compound	**False Negative**	**Compound**	**False Negative**
1,1-Dichloroethene (0.06)	0 of 10	*trans*-1,2-Dichloroethene (1)	10 of 10 (100%)
Dichloromethane (NA)	0 of 10	1,2-Dichloroethane (80)	10 of 10
Chloroform (11)	10 of 10 (100%)	Benzene (1)	0 of 10
Carbon tetrachloride (1)	0 of 10	Bromodichloromethane (1)	5 of 10 (50%)
1,2-Dichloropropane (NA)	8 of 10 (80%)	*cis*-1,3-Dichloropropene (1)	0 of 10
Trichloroethene (1)	0 of 10	*trans*-1,3-Dichloropropene (3)	0 of 10
1,1,2-Trichloroethane (NA)	10 of 10 (100%)	Toluene (1)	1 of 10 (10%)
Dibromochloromethane (1)	9 of 10 (90%)	Ethyl benzene (1)	6 of 10 (60%)
Tetrachloroethene (3)	0 of 10	Bromoform	No calibration
Chlorobenzene (3)	0 of 10	1,1,2,2-Tetrachloroethane	No calibration
2-Chloroethyl vinyl ether	No calibration	1,1,1-Trichloroethane	No calibration
Trichlorofluoromethane	No calibration		
1,1-Dichloroethane	No calibration		
1,2-Dichlorobenzene	No calibration		

Notes: Vendor-provided detection limits (in µg/L) are shown in parentheses after each compound.
NA = not available; the vendor provided no MDL for these compounds.

PE Sample Precision

Precision results from each of the four replicate sample sets provided to the participant from eight PE mixtures at the SRS and seven mixtures at MAFB are shown in Figures 5-1 and 5-2 for the SRS and Figures 5-3 and 5-4 for MAFB. In instances where no data are reported, no compound names or graph bars are shown. The figures show the relative standard deviation for each compound in the PE mixtures at the four concentration levels used in the study.[1] (The compositions and concentrations of each of these mixtures were given in Table 3-5 for the SRS and Table 3-6 for MAFB. Note that precision and accuracy were not determined for the "very low" concentration level.) Relative standard deviations for coeluting compound pairs are also shown in the figures. Instrument precision data for six target compounds which are all regulated under the Safe Drinking Water Act are shown in Table 5-4. The relative standard deviations are given for each target compound at each of the four concentration levels used in the study. The RSD range for each target compound is also given in the last column of the table.

Table 5-4. Target Compound Precision at Both Sites

Target Compound	Site	Relative Standard Deviation (%)				
		Low	Mid	High	Spike/Low	Range
Trichloroethene	SRS	32	15	7	15	7 – 71
	MAFB	7	71	14	3	
1,2-Dichloroethane[(a)]	SRS	37	19	25	4	4 – 44
	MAFB	31	21	44	ND	
1,2-Dichloropropane[(a)]	SRS	37	19	25	4	4 – 44
	MAFB	31	21	44	ND	
1,1,2-Trichloroethane	SRS	ND	ND	ND	ND	11 – 103
	MAFB	19	30	11	103	
Tetrachloroethene	SRS	ND	ND	ND	29	≤ 29
	MAFB	ND	ND	ND	ND	
trans-1,3-Dichloropropene	SRS	14	8	33	23	8 – 46
	MAFB	46	30	37	18	

Notes: 1,2-Dichloroethane and 1,2-dichloropropane are reported as a coeluting compound pair (a); the same results are reported for each compound of the pair.
ND = not detected.

A summary of overall instrument precision is given in Table 5-5 for the PE mixtures used at both sites. For this summary, RSD values from all PE sample analyses for all compounds at each site were pooled, and the median and 95th percentile values of the distribution were computed.

PE Sample Accuracy

The Voyager accuracy for PE sample analyses was determined by comparing the average value from each of the four-sample replicate sets with the known concentration of the PE mixture (Tables 3-5 and 3-6 for the SRS and MAFB, respectively). These comparisons are shown as percent recoveries[2] in Figures 5-5 and 5-6 for the SRS

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[1] Precision data for the PE mix 1 sample set at MAFB are not shown in a figure. Precision results from this mixture were comparable to those obtained from the same mixture at SRS.

[2] Percent recovery is the Voyager value divided by the true value, multiplied by 100.

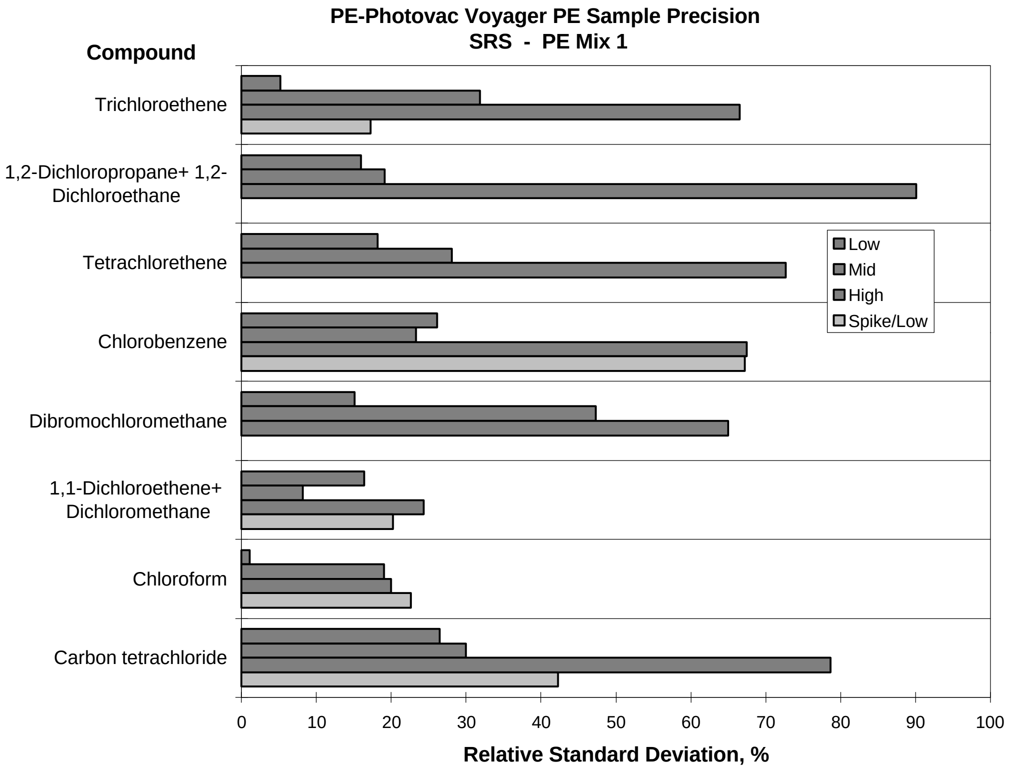

Figure 5-1. Voyager precision on PE mix 1 at the SRS.

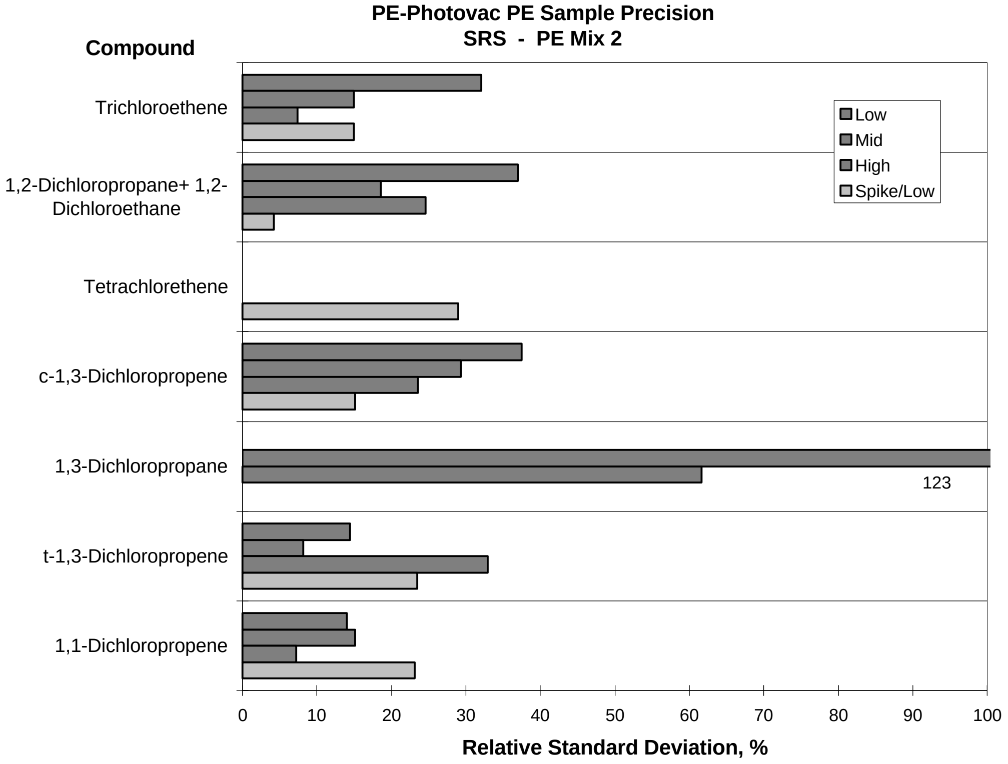

Figure 5-2. Voyager precision on PE mix 2 at the SRS.

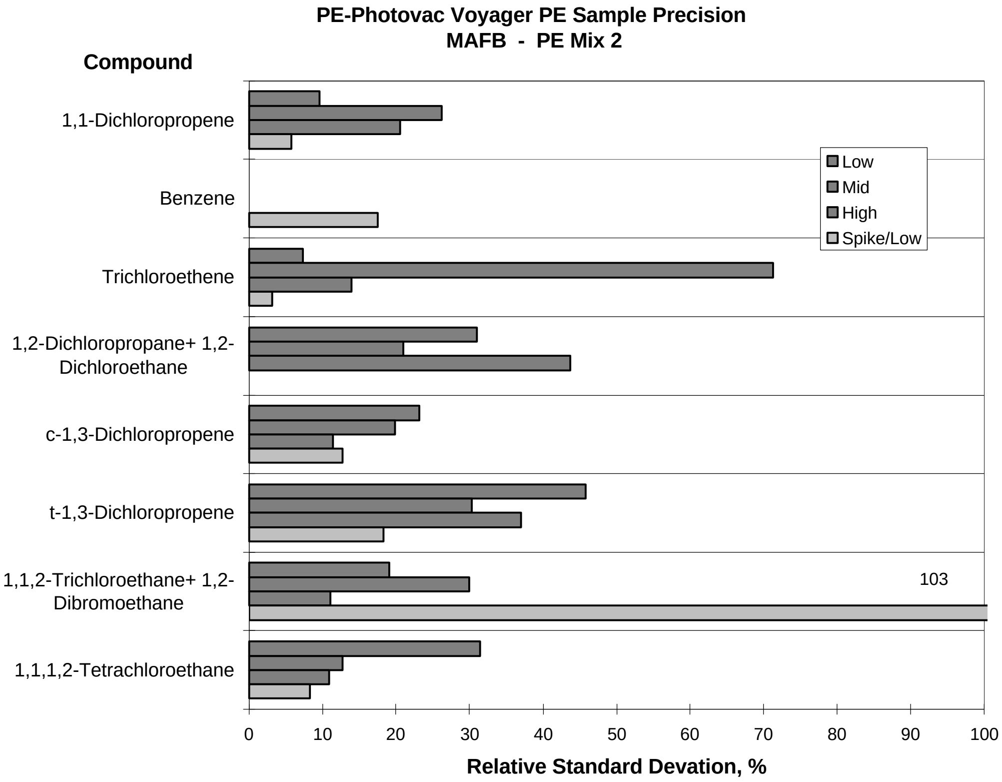

Figure 5-3. Voyager precision on PE mix 2 at MAFB.

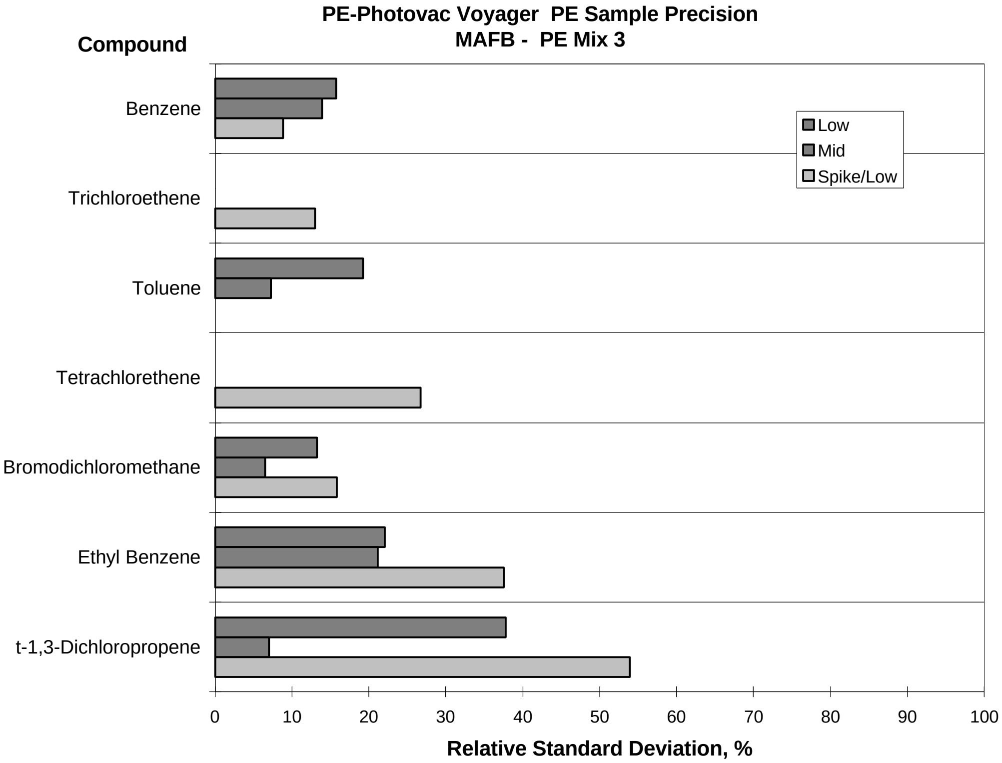

Figure 5-4. Voyager precision on PE mix 3 at MAFB.

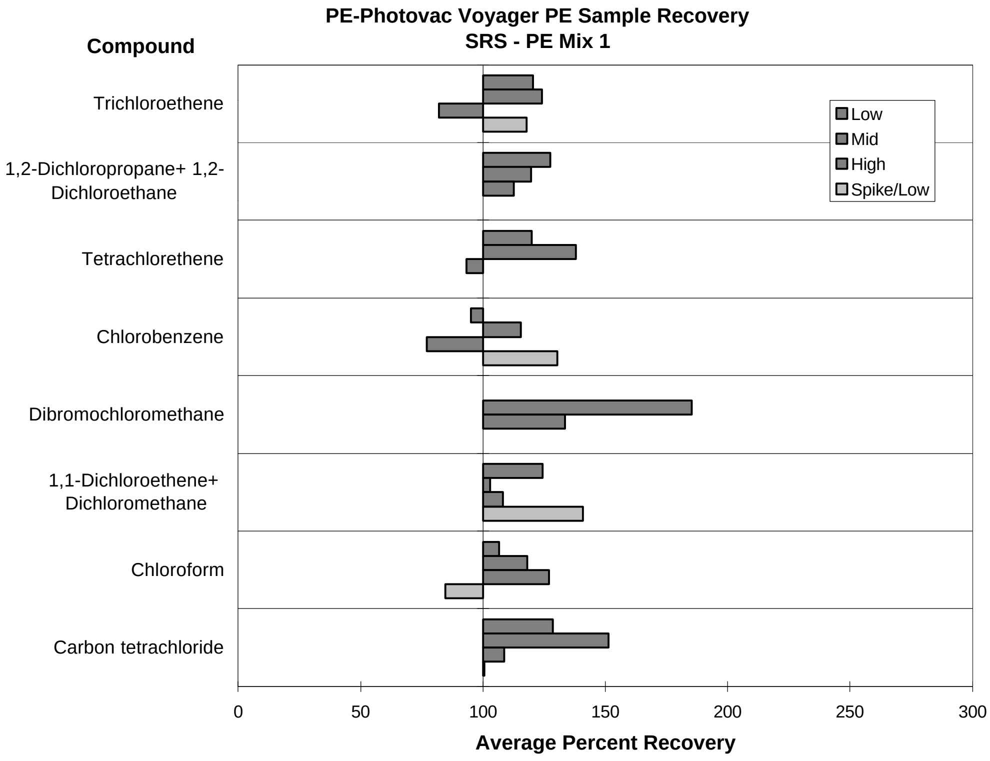

Figure 5-5. Voyager recovery on PE mix 1 at the SRS.

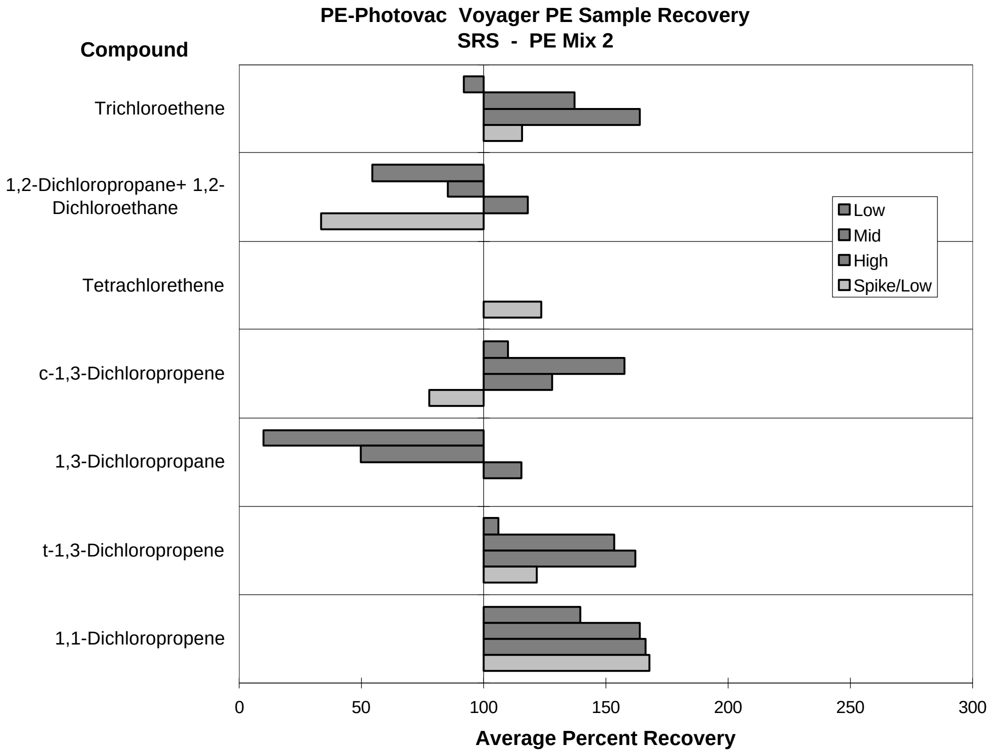

Figure 5-6. Voyager recovery on PE mix 2 at the SRS.

and Figures 5-7 and 5-8 for MAFB.[3] In instances where no data were reported, no compound names or graph bars are shown. To assist in assessing the sign of the difference, the percent recovery data are plotted as either a positive or negative deviation from the 100% recovery line. Instrument recovery performance for the six target compounds (in PE mix 2 at both sites) is shown in Table 5-6, which contains the average percent recoveries and associated ranges for each compound.

A summary of overall Voyager recovery differences relative to PE mixture true values is given for both sites, alongside the precision summary in Table 5-5. For this summary, percent recoveries were expressed as percent difference (e.g., a 90% recovery is equivalent to a –10% difference; a 120% recovery is equivalent to a +20% difference), and all data from PE mixtures were pooled. The median and 95th percentiles of the absolute values of these pooled values were computed and are reported under the absolute percent difference (APD) category in Table 5-5.[4]

Table 5-5. Summary of PE Sample Precision and Percent Difference Statistics for the SRS and MAFB

Parameter	Percentile	SRS		MAFB		Combined Sites
		PE Mix 1	PE Mix 2	PE Mix 2	PE Mix 3	Combined Mixes
RSD, %	50th	24	20	19	19	20
	95th	77	59	61	56	69
	Number in pool	29	28	29	25	111
Absolute percent difference	50th	20	48	50	77	41
	95th	47	156	219	170	170
	Number in pool	29	28	29	25	111

Table 5-6. Target Compound Recovery for PE Mix 2 at Both Sites

Target Compound	Site	Average Recovery (%)				
		Low	Mid	High	Spike/Low	Range
Trichloroethene	SRS	92	137	164	116	92 – 344
	MAFB	231	246	333	344	
1,2-Dichloroethane[(a)]	SRS	55	86	85	34	34 – 170
	MAFB	82	133	170	ND	
1,2-Dichloropropane[(a)]	SRS	55	86	85	34	34 – 170
	MAFB	82	133	170	ND	
1,1,2-Trichloroethane	SRS	ND	ND	ND	ND	50 – 116
	MAFB	116	54	50	116	
Tetrachloroethene	SRS	ND	ND	1	124	1 – 124
	MAFB	ND	ND	ND	ND	
trans-1,3-Dichloropropene	SRS	106	154	162	122	72 – 162
	MAFB	95	97	143	72	

Notes: 1,2-Dichloroethane and 1,2-dichloropropane are reported as a coeluting compound pair (a); the same results are reported for each compound of the pair.
ND = not detected.

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[3] Percent recovery data for the single PE mix 1 sample set at MAFB are not shown in a figure. Recovery results from this mixture were comparable to those obtained from the same mixture at the SRS.

[4] The absolute percent difference is the absolute value of the percent difference between a field and reference (in this case the reference laboratory) measurement. As an example, the percent difference between a field measurement of 85 and a laboratory measurement of 110 is –22.7% and the absolute percent difference is 22.7%.

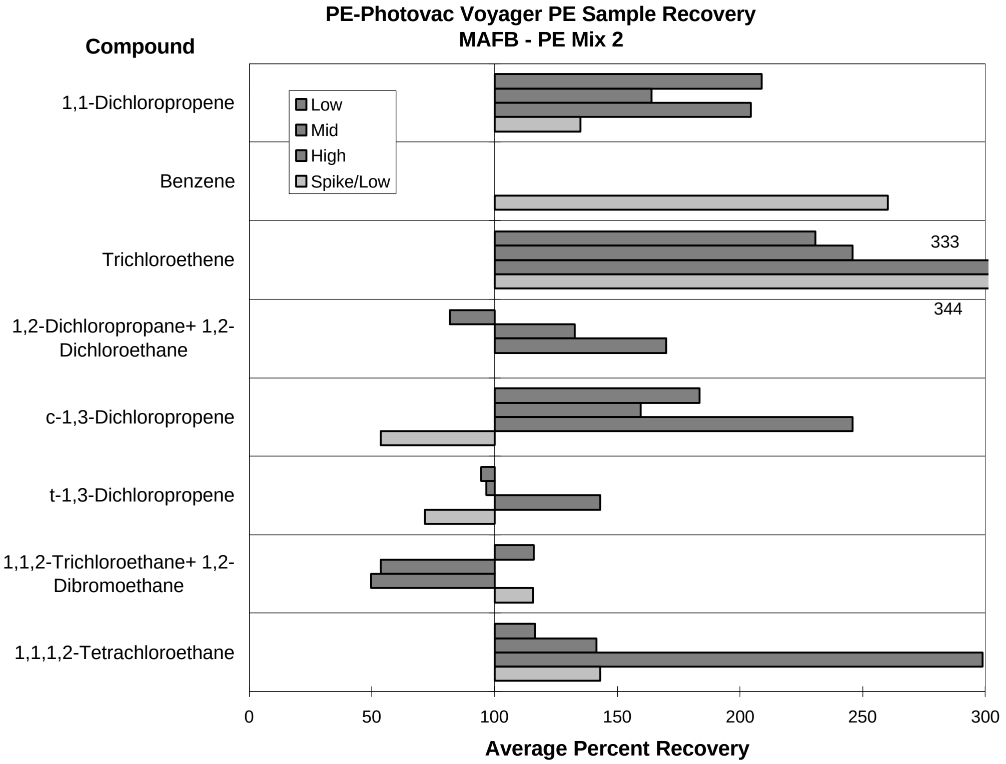

Figure 5-7. Voyager recovery on PE mix 2 at MAFB.

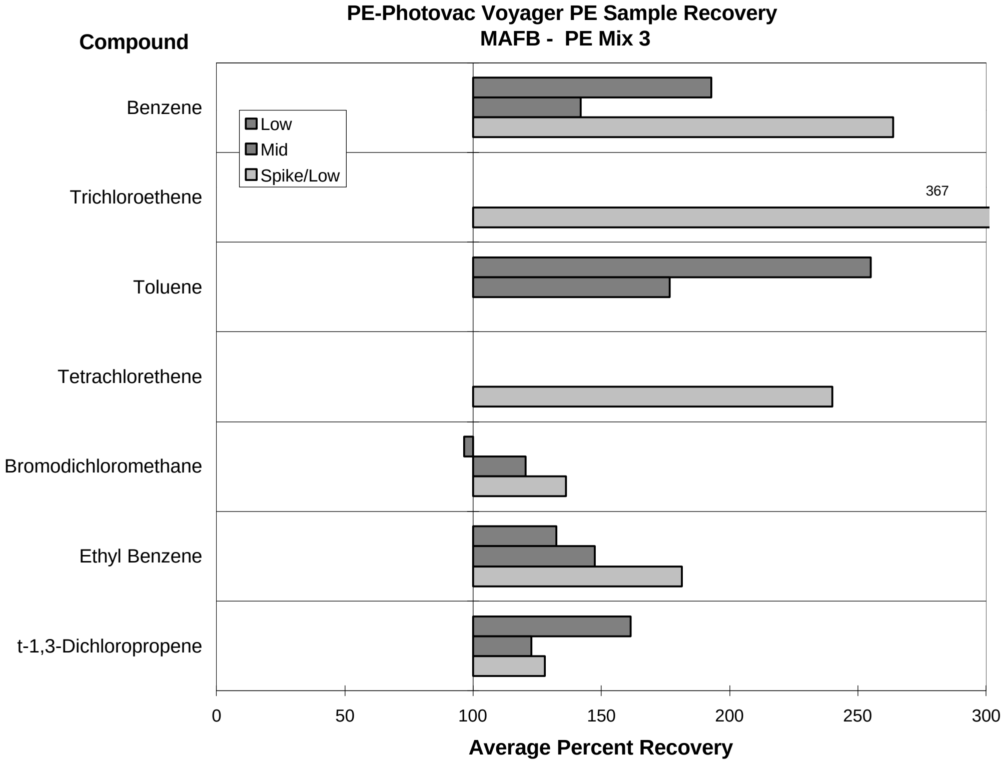

Figure 5-8. Voyager recovery on PE mix 3 at MAFB.

Comparison with Laboratory Results

At each demonstration site, a total of 33 samples collected from 10 wells were provided to the participants and to the reference laboratory. Replicate sample sets were composed of either 3 or 4 samples from each well. Average laboratory results from each replicate set were used as the reference values for comparison with technology results. A side-by-side comparison of laboratory and Voyager results for all groundwater samples is given in Table 5-7 for the SRS and Table 5-8 for MAFB. The RSD values and their statistical summaries are included in the table. Well designation (very low, low, mid, high, and very high) is based on TCE concentration levels; however, other compounds were present in the groundwater samples at concentration levels noted in the tables. The precision of the Voyager on replicate groundwater samples is also shown in the last column of the table.

The average percent difference between average Voyager and laboratory results for the compounds detected in each set of groundwater samples is shown in Figures 5-9 and 5-10 for the SRS and MAFB, respectively. Average laboratory results for groundwater contaminants reported at levels less than 1 μg/L are not included in the comparison. The SRS groundwater comparison in Figure 5-9 includes only TCE and PCE. Two well samples were also contaminated with 1,1-dichloroethene (11DCE) and one well contained chloroform (CLFRM) and carbon tetrachloride (CCL4), as noted in Table 5-7. The groundwater samples at MAFB were by choice more complex, as indicated by the additional compounds shown in Table 5-8 and Figure 5-10.

The median and 95th percentiles of the distribution of absolute percent differences between Voyager and laboratory results for all groundwater samples are given in Table 5-9.

To assess the degree of linear correlation between the Voyager and laboratory groundwater data pairs shown in Tables 5-7 and 5-8, correlation coefficients (*r*) were computed. The data pairs were divided into two subsets for each site to reduce the likelihood of spuriously high *r* values caused by large differences in the data (e.g., concentrations ranging from 1 μg/L to those in excess of 1000 μg/L) (Havlicek and Crain, 1988). One subset contained all data pairs with laboratory results less than or equal to 100 μg/L and the other subset included all data pairs with laboratory values greater than 100 μg/L. The computed correlation coefficients are shown in Table 5-10.

Sample Throughput

Voyager throughput rates ranged from one to three samples per hour. Throughput rates were assessed by using the time lapsed between sample checkout in the morning and delivery of hardcopy results in the afternoon and the number of samples completed. Voyager GC run times were influenced to some extent by sample complexity. Groundwater samples with fewer and known components could be run relatively quickly, whereas multicomponent PE mixtures required longer run times.

Performance Summary

Table 5-11 contains a summary of Voyager performance characteristics, including important instrument performance parameters and operational features verified in this demonstration. For groundwater samples, the results from the reference laboratory are given alongside Voyager performance results to facilitate comparison of the two methodologies.

Table 5-7. Voyager and Reference Laboratory Results for SRS Groundwater Samples

Sample Description	Well Number	Compound	Replicates	Lab. Avg. (μg/L)	Lab. RSD (%)	Voyager[a] Avg. (μg/L)	Voyager[a] RSD (%)
Very low 1	MSB 33B	Trichloroethene	3	9.0	11	18	22
		Tetrachloroethene		3.5	14	18	28
Very low 2	MSB 33C	Trichloroethene	3	2.4	34	7.0	100
		Tetrachloroethene		0.7	12	5.3	93
Low 1	MSB 18B	Trichloroethene	3	11	5	71	79
		Tetrachloroethene		27	6	148	120
Low 2	MSB 37B	Trichloroethene	4	27	7	46	5
		Tetrachloroethene		22	9	40	6
		Chloroform		1.3	0	NR	NR
		Carbon tetrachloride		1.0	15	NR	NR
Mid 1	MSB 4D	Trichloroethene	4	150	9	242	9
		Tetrachloroethene		87	12	261	75
Mid 2	MSB 64C	Trichloroethene	3	35	7	55	19
		Tetrachloroethene		240	4	427	15
		1,1-Dichloroethene		12	8	NR	NR
High 1	MSB 4B	Trichloroethene	3	747	1	968	29
		Tetrachloroethene		33	2	67	88
High 2	MSB 70C	Trichloroethene	4	1875	12	1321	13
		Tetrachloroethene		520	8	1016	22
		1,1-Dichloroethene		32	8	NR	NR
Very high 1	MSB 14A	Trichloroethene	3	1367	8	1378	27
		Tetrachloroethene		800	6	1585	6
Very high 2	MSB 8C	Trichloroethene	3	4933	6	2231	13
		Tetrachloroethene		3668	6	3356	10
Range					0 – 34		5 – 120
Median					8		22
95th Percentile					15		101

[a] NR = Not reported.

Table 5-8. Voyager and Reference Laboratory Results for MAFB Groundwater Samples

Sample Description	Well Number	Replicates	Compound	Lab. Avg. (µg/L)	Lab. RSD (%)	Voyager[a] Avg. (µg/L)	Voyager[a] RSD (%)
Very low 1	EW-86	3	Trichloroethene	4.6	5	3.3	17
			1,1-Dichloroethene	7.7	9	NR	NR
Very low 2	MW-349	3	Trichloroethene	13	0	16	9
			Tetrachloroethene	2.0	6	6	0
			Chloroform	9.0	1	NR	NR
			1,1-Dichloroethene	3.8	3	NR	NR
			Carbon tetrachloride	137	4	NR	NR
Low 1	MW-331	4	1,1-Dichloroethene	2.5	7	NR	NR
			1,1-Dichloroethane	15	0	NR	NR
			cis-1,2,dichloroethene	NR	NR	45	3
			Carbon tetrachloride	7.5	2	NR	NR
			Chloroform	4.8	2	NR	NR
			Trichloroethene	16	4	25	4
Low 2	MW-352	3	Freon11	20	6	NR	NR
			1,1-Dichloroethene	1.5	12	NR	NR
			1,1-Dichloroethane	5.1	4	NR	NR
			cis-1,2-Dichloroethene	1.5	4	1.3	43
			Carbon tetrachloride	1.4	4	NR	NR
			Trichloroethene	22	5	43	15
Mid 1	EW-87	4	1,1-Dichloroethene	180	12	NR	NR
			1,1-Dichloroethane	3.0	9	NR	NR
			cis-1,2-Dichloroethene	3.3	13	2.8	18
			1,1,1-Trichloroethane	6.8	12	NR	NR
			Trichloroethene	114	11	214	4
			Tetrachloroethene	1.2	14	5.0	0
Mid 2	MW-341	3	*cis*-1,2-Dichloroethene	15	4	16	16
			Chloroform	3.5	5	NR	NR
			Trichloroethene	280	4	463	59
High 1	MW-209	3	*cis*-1,2-Dichloroethene	38	4	46	1
			Chloroform	6.9	21	NR	NR
			Trichloroethene	238	2	497	26
High 2	MW-330	4	*trans*-1,2-Dichloroethene	7.7	4	NR	NR
			cis-1,2-dichloroethene	66	5	86	5
			Chloroform	42	5	NR	NR
			1,2-Dibromochloropropane	6.1	6	NR	NR
			Trichloroethene	380	5	946	5
Very high 1	MW-334	3	1,1-Dichloroethene	690	3	NR	NR
			cis-1,2-dichloroethene	237	7	404	4
			Chloroform	397	5	NR	NR
			Benzene	283	5	468	9
			Trichloroethene	10,667	5	27,300	0
			Carbon tetrachloride	350	5	NR	NR
Very high 2	MW-369	3	*cis*-1,2-Dichloroethene	207	10	261	15
			Chloroform	63	6	NR	NR
			Carbon tetrachloride	51	5	NR	NR
			Trichloroethene	6167	8	17,433	7
Range					0 – 21		0 – 59
Median					5		7
95th Percentile					13		43

[a] NR = not reported.

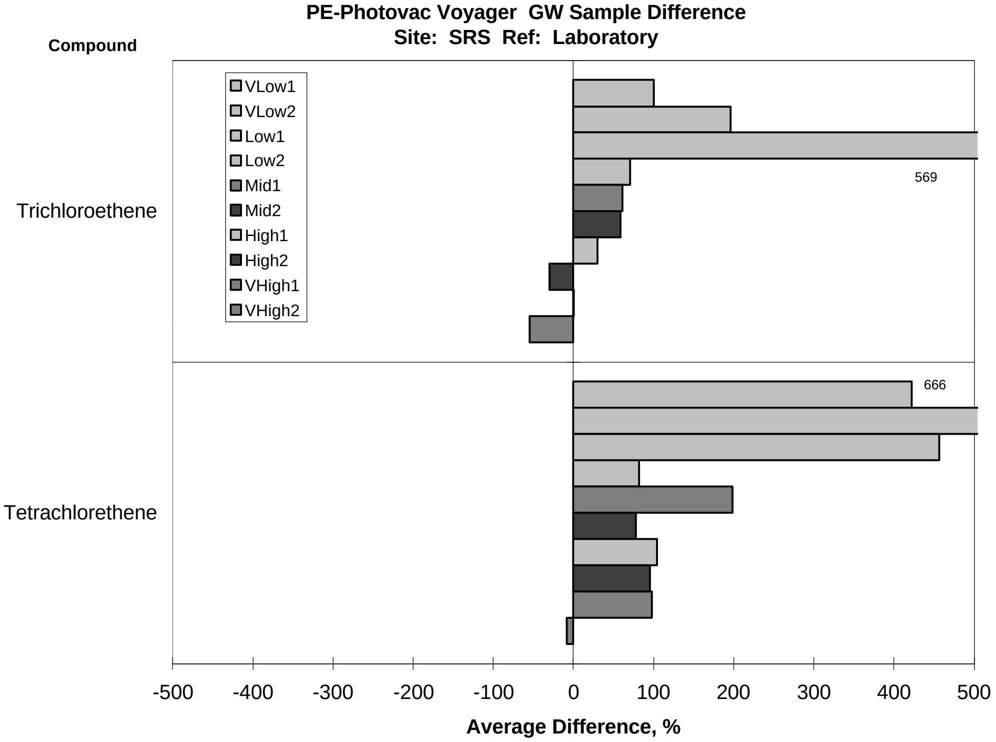

Figure 5-9. Voyager groundwater results at the SRS relative to laboratory results.

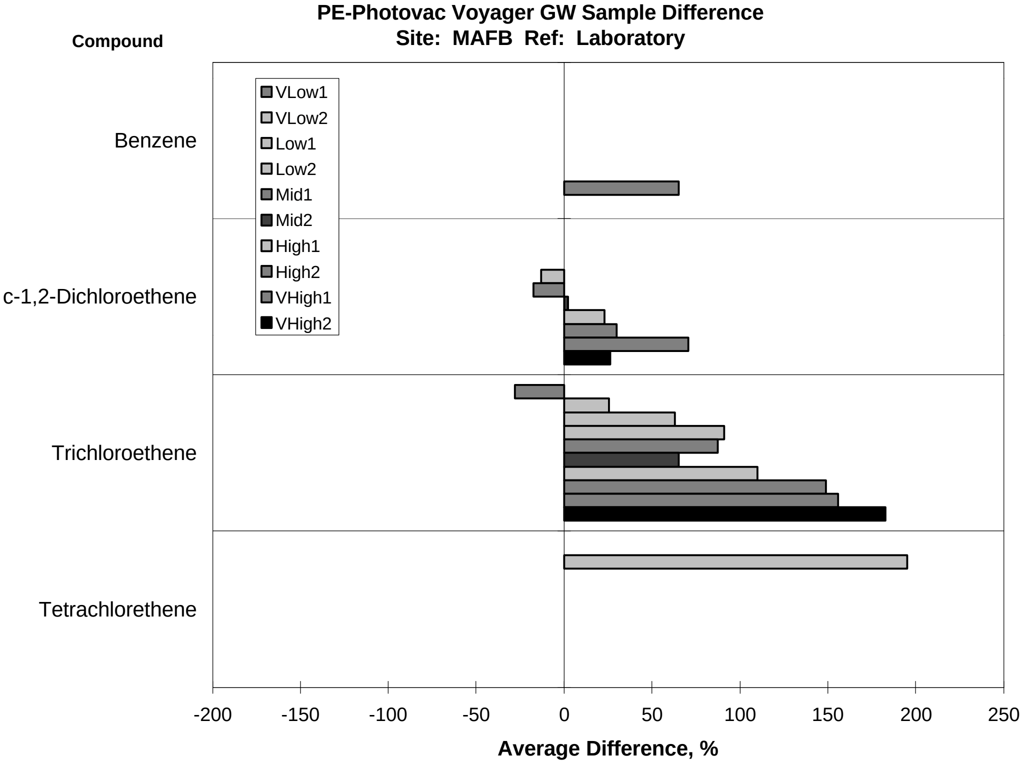

Figure 5-10. Voyager groundwater results at MAFB relative to laboratory results.

Table 5-9. Voyager Absolute Percent Difference Summary for Pooled Groundwater Results

Percentile	SRS	MAFB	Combined Sites
50thθ	89	65	74
95th	551	206	453
Number of samples in pool	20	20	40

Table 5-10. Correlation Coefficients for Laboratory and Voyager Groundwater Analyses

Data Set	Correlation Coefficient	Number of Data Pairs
SRS Laboratory (1 through 100 µg/L)	0.890	10
SRS Laboratory (> 100 µg/L)	0.830	9
MAFB Laboratory (1 through 100 µg/L)	0.660	15
MAFB Laboratory (> 100 µg/L)	0.999	9

Table 5-11. Summary of Voyager Performance

Instrument Feature/Parameter	Performance Summary
Blank sample	False positives detected at low (13 to 25%) rates for 6 of 24 reported compounds.
Detection limit sample	False negatives reported at rates between 10 and 100% for 8 of 18 compounds at concentration levels of 10 µg/L.
PE sample precision	Target compounds, RSD range: 4 to 103% All compounds, Voyager median RSD: 20%; 95th percentile RSD: 69% All compounds, laboratory median RSD: 7%; 95th percentile RSD: 25% (Target compounds: TCE, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, PCE, and *trans*-1,3-dichloropropene)
PE sample accuracy	Target compounds: absolute percent difference range: 8 to 244% All compounds, Voyager median APD: 41%; 95th percentile APD: 170% All compounds, laboratory median APD: 7%; 95th percentile APD: 24%; (Target compounds same as those for sample precision)
Voyager comparison with laboratory results for groundwater samples	Voyager median RSD: 15% Laboratory median RSD: 6% Voyager 95th percentile RSD: 93% Laboratory 95th percentile RSD: 14% Voyager: laboratory median APD: 74%; 95th percentile APD: 453% Voyager: laboratory correlation: SRS low conc. (≤ 100 µg/L) *r* = 0.890 SRS high conc. (> 100 µg/L) *r* = 0.830 MAFB low conc. (≤ 100 µg/L) *r* = 0.660 MAFB high conc. (> 100 µg/L) *r* = 0.999

Table 5-11. Summary of Voyager Performance (Continued)

Instrument Feature/Parameter	Performance Summary
Analytical versatility	PE samples: calibrated for 24 of 32 PE compounds (75%) Three pairs of coeluting compounds were reported. GW samples: For the compounds for which it was calibrated, Voyager reported 39 of 44 compounds detected by the laboratory in all GW samples at or above the 1 µg/L concentration level. A total of 68 compounds were detected by the laboratory in all groundwater samples.
Sample throughput	1 to 3 samples per hour
Support requirements	Water bath Radioactive detector permit/license
Operator requirements	Sample processing: field technician with 1-day training Data processing and review: B. S. chemist or equivalent
Total system weight	48 pounds
Portability	GC is field-portable; accessories (water bath) are transportable
Total system cost	$24,000 (with notebook computer and printer)
Shipping requirements	Air freight, hand carry, luggage check (no compressed gas via commercial flight) Recharge carrier gas cylinder requires drop shipment

Chapter 6
Field Observations and Cost Summary

Introduction

The following subsections summarize the audit findings obtained while observing instrument operation at both field sites. The purpose of the audits was to observe the instrument in operation as well as to verify that analytical procedures used during the demonstration were consistent with written procedures submitted to the verification organization prior to the field demonstration. An instrument cost summary and an applications assessment are provided.

Method Summary

The Voyager uses a static equilibrium headspace method with temperature control. The headspace vapors from a temperature-equilibrated sample are manually withdrawn with a gas-tight syringe and injected into the Voyager. The instrument is a three-column GC with dual (photoionization and electron capture) detectors. Compounds are identified by retention time and quantified by integrating the peak area of the compound and comparing it with that of calibration standards. Internal and surrogate standards are not used. (See Chapter 7 for discussion of a revised method that incorporates internal standards.)

Equipment

The Voyager dimensions are 15 inches × 11 inches × 5 inches and it weighs 15 pounds. A notebook computer (8 pounds) and field-portable printer (10 pounds) were also used during the demonstration for data download, review, and printing. Equipment weights include batteries and self-contained carrier gas. A small, ac-powered water bath (15 pounds) was used for temperature equilibration of the sample vials. The system was deployed on the folded-down middle seat of a minivan. The Voyager is field-portable and could be easily carried to a wellhead (Figure 6-1); however, the accessory water bath requires ac power. The entire system is best regarded as transportable in a vehicle to a site. A small cylinder of compressed nitrogen was used for periodic recharge of the internal carrier gas cylinder. Battery lifetime is normally about 9 hours; however, for this demonstration, the instrument and computer were powered by a dc-to-ac inverter that was connected to the vehicle's battery.

Additional equipment used at the demonstration included 40-mL, screw-cap sample vials with septa; chemical standards; 20-mL syringes and vent needles for sample transfer; and 500-µL gas-tight syringes for sample injection into the GC.

Sample Preparation and Handling

For sample handling at the SRS, a zero-headspace, 40-mL sample vial was inverted and placed in a 30 °C water bath. Following a 15-minute equilibration, the vial was uncapped and a 20-mL quantity poured into a second 40-mL vial and capped. The second vial was vigorously shaken for 2 minutes and then returned to the water bath

Figure 6-1. The Voyager GC.

and held for 5 minutes. The vial was removed from the bath and a 500-µL, gas-tight syringe was used to withdraw a headspace sample from the vial through the cap septum. This syringe sample was then manually injected into the Voyager.

The sampling procedures at MAFB were modified as follows: The zero-headspace, 40-mL sample vial was inverted and placed into a 30 °C water bath. Following a 15-minute equilibration, the vial was removed from the bath for withdrawal of a portion of the sample. The needle of a 20-mL syringe was inserted, along with a second vent needle, through the septum and a 20-mL portion of the water sample was withdrawn. The withdrawn portion was discarded and the original vial was returned to the water bath for an additional 5 minutes. A headspace vapor sample was then withdrawn with a gas-tight syringe and injected into the Voyager, in the same manner as carried out at the SRS.

Consumables

An internal gas bottle contains nitrogen carrier gas. An external cylinder is used to periodically refill the internal cylinder.

Historical Use

This is the first demonstration of the Voyager GC for VOC analysis in water. The instrument and its predecessors have been used extensively for air and soil gas analysis.

Equipment Cost

The Voyager, as equipped at the demonstration, has a purchase price of $20,000. This includes the proprietary SiteChart software but does not include a notebook computer for data processing and instrument control. Ancillary equipment costs are about $4000. Instrument costs are summarized in Table 6-1. Laboratory costs were $95 per sample plus overnight Express Mail costs, which were about $30 per batch of 12 samples. Voyager sample throughput is in the range of 1 to 3 samples per hour.

Table 6-1. Voyager GC Cost Summary

Instrument/Accessory	Cost
Instrument (Voyager three-column GC and dual PID, ECD; SiteChart software)	$20,000
Instrument accessories (notebook computer, field-portable printer)	$3000 (notebook computer) $500 (printer)
Shipping case (option)	
Thermally insulated soft case (option)	
Water bath	$200
Sample handling accessories (carrier gas, syringes, vials, standards)	$500 per 100 samples
Maintenance costs: periodic PID window cleaning, column replacement, etc.	One-year parts and labor warranty Service maintenance agreement ~$2000 per year

Operators and Training

The Voyager was operated by two sales and application technicians at the demonstration. Both of them had bachelors'-level training in chemistry. Only one person is needed to operate the instrument. With 1 hour of training, an experienced chemical technician could operate the system. A novice technician operator would require 1 day of training. Experience with GC data processing is required to do method development and analysis of complex mixtures.

Data Processing and Output

A real-time chromatogram is displayed on the Voyager's display panel and on the PC's SiteChart software, if connected. Hardcopy output is available immediately after analysis. The analysis report, available as a monitor display or hard copy, includes the following:

- chromatogram;
- analysis parameters;
- analysis method;
- integration method; and
- peak report (compounds identified, compound concentration, peak area and height, retention time, and status).

Compounds Detected
The system was calibrated for 24 compounds at the SRS site and utilized two different methods and two columns. To reduce analysis time and increase sample throughput, at the MAFB site the system was calibrated for 17 compounds on a single column. The calibrated compounds are given in Table 5-1.

Initial and Daily Calibration
A three-point calibration for each target compound was completed at Photovac facilities prior to the demonstration period. The software will accommodate up to a five-point calibration, with the lowest point being a blank sample. The user can choose a linear calibration curve or a quadratic fit curve. The linear curve selection produces a point-to-point line based on the calibration data. A standard mixture of target compounds at an intermediate concentration (100 µg/L) was analyzed at the beginning of each demonstration day to update compound retention times and detector response factors in the calibration file.

QC Procedures and Corrective Actions
Standard mixtures of chlorinated VOCs in methanol were used in a single daily calibration run. Injection syringes were decontaminated between uses by heating them in sunlight. Carrier gas flow was controlled by an automatic pressure regulator to permit analysis at varying atmospheric pressures with no mathematical data manipulation. No internal standards or surrogate standards were used to monitor sample matrix effects.

Sample Throughput
Chromatographic analysis run time was observed to be approximately 60 minutes for a multicomponent PE sample, and 10 minutes for a groundwater sample containing only TCE and PCE. Preliminary hardcopy data were available at the end of the day and final data in spreadsheet format were available the following day. Typical throughput rates were one to three samples per hour.

Problems Observed During Audit
The auditors observed that sample handling procedures used by the Voyager team at the SRS may have contributed to imprecise or inaccurate results. The PE and groundwater samples were heated to 30 °C and then uncapped and poured. Handling warm samples in this manner could result in volatile losses of target compounds, with resulting degraded instrument recovery and precision. The method was changed at MAFB so that warm samples were never opened. The precision data presented in Chapter 5 reveal improvement at MAFB compared with the SRS, particularly for groundwater samples (see Tables 5-7 and 5-8). A moderate improvement in Voyager accuracy at MAFB for groundwater samples was also noted (see Table 5-9).

The Voyager team encountered problems with the laptop computer during the latter portion of the MAFB demonstration. This delayed delivery of hardcopy data until the computer could be repaired. The Voyager GC performed acceptably throughout the demonstrations at both sites.

Data Availability and Changes
Preliminary data from the Voyager were obtained at the end of each demonstration day in hardcopy format. Data were provided in spreadsheet format at the conclusion of each demonstration week. Several typographical and transcription errors were corrected at the final data review. The concentration levels of several compounds were

reevaluated and changed after the final demonstration period when it was discovered that incorrect compound response factors in the original calibration file were applied to several compounds. A software change has since been made to remedy this situation in future use.

Instrument Transport

The Voyager can either be carried on or checked as luggage on airline flights provided that the internal carrier gas cylinder is emptied. The GC is equipped with a purge valve so that the cylinder can be easily discharged. Drop shipment is the preferred method for transporting the external carrier gas cylinder since carrying compressed gases on commercial flights is not permitted. A hard-sided shipping case is available as an instrument option. When shipping a Voyager equipped with an ECD, no special shipping papers are required since the radiation level of the detector falls within the International Air Transportation Association level for exempt packages. A 2-week prior notification is required to bring the Voyager to a particular state in the United States. There is usually no fee associated with this notification and typically it is valid for 1 year.

Applications Assessment

This demonstration was intended to provide an assessment of the instrument's suitability for analytical tasks in site characterization and routine site monitoring. Site characterization refers to those instances where subsurface contamination is suspected but information on specific compounds and their concentration level is not available. The instrument best suited for this application is one that can screen a wide array of compounds in a timely and cost-effective manner. Analytical precision and accuracy requirements may be relaxed in these instances since a general description of the site characteristics is adequate for remediation planning. At the other end of the spectrum is a monitoring application where contaminant compounds and their subsurface concentrations are known with some certainty. Periodic monitoring requirements imposed by local regulatory agencies may specify that analyses be carried out for specific contaminant compounds known to be present in the water. Quarterly well monitoring programs fall into this category.

Based on its performance in this demonstration, the Voyager is most applicable to routine monitoring applications where sample composition is known. It could also be successfully used in sample screening situations where the contaminants and their approximate concentration in the water are known. Chromatographic methods utilized with the Voyager may require specific tailoring for a given routine monitoring application.

The Voyager team has observed that their method of sample preparation could be improved. One suggested improvement is to inject an internal standard in the water sample prior to temperature equilibration and withdrawal of the headspace gas sample. The internal standard would yield a QC check on every sample and would reveal such conditions as a plugged syringe or sample matrix effects. A low or high recovery of the internal standard would prompt the analyst to flag the data and further investigate or reanalyze the sample. See Chapter 7 for a vendor discussion of a modified method that incorporates an internal standard.

Chapter 7
Technology Update

Note: The following comments were submitted by the technology developer. They have been edited for format consistency with the rest of the report. The technical content in the following comments has not been verified by the verification organization.

Introduction

Perkin-Elmer Photovac personnel reviewed the Environmental Technology Verification Report and found the document to be written in a well-organized and objective manner. Since our participation in the ETV demonstration, we have improved the method of sample preparation and handling. The revised method specifies the injection of an internal standard into the water sample prior to temperature equilibration, headspace sampling, and analysis with the Voyager GC. In addition, a heater block is now used instead of a water bath to provide more uniform warming of the samples. In accordance with the applications assessment section in Chapter 6, the revised data review process now includes a QC check based upon analytical results using an internal standard. These results will help to identify abnormal conditions such as a plugged syringe or unusual sample matrix effects.

Additional Performance Testing

A summary of accuracy and precision results from limited additional testing using the improved methodology is included in this chapter. This testing was carried out by Perkin-Elmer Photovac without verification organization oversight and followed a design similar to that used during the field demonstrations.

Voyager Configuration and Method Improvements

Optimum separation of eight chlorinated and nonchlorinated VOC analytes examined in this test was achieved utilizing two of the three columns in the Voyager’s analytical engine. The columns are described below:

Column B: 20 m × 0.32 mm × l µm Supelcowax 20 (PEG)

Column C: 25 m × 0.32 mm × 12 µm Quadrex 007-l

Improvements in the analytical protocol include:

- a modified headspace equilibration system using a heater block to ensure precise, uniform heating of samples at 30 °C;
- use of dibromomethane as an internal standard for both the PID and ECD; and

- a five-point calibration curve stored in the Voyager's built-in assay library instead of the previous two-point (zero and upscale value) calibration protocol.

Sample Preparation and Handling

For the postdemonstration test, standard solutions of the following compounds were prepared from certified stock solutions at concentration levels of 7, 30, 700, and 3000 µg/L: benzene, toluene, ethyl benzene, *meta*-xylene, trichloroethene, tetrachloroethene, bromodichloromethane, and dibromochloromethane. A two-level mixture was also prepared with TCE and PCE at 5000 µg/L levels and the other compounds at 300 µg/L levels.

The standard samples were prepared by serial addition into organic-free water. Each solution was then transferred to a 40-mL volatile organics analysis (VOA) vial with zero headspace. Twelve replicate vials of each concentration were prepared in this manner. Four vials of each concentration were stored upside down in a refrigerator at 4 °C for Voyager analysis. The remaining eight replicates (four samples of each concentration plus four extras in case of breakage) were placed in a cooler with ice packs and shipped to Phoenix Environmental Laboratories, Inc., in Manchester, Connecticut, for analysis using EPA Method 8260A. The sample preparation and handling procedures were essentially the same as those used during the field demonstration.

Sample handling during Voyager analysis was conducted by withdrawing a 20-mL portion of the water sample from the 40-mL VOA through the septum using a syringe. The withdrawn sample aliquot was discarded. A 100-µL volume of the dibromomethane internal standard was then injected through the septum to produce a final solution concentration of 1000 µg/L. The vial was gently agitated for 30 seconds and placed in a heater block at 30 °C for 15 minutes. The vial was then removed from the heater block and a 100-µL volume of headspace gas was manually withdrawn from the vial and injected into the Voyager with a gas-tight syringe.

Reference Laboratory

For consistency with the field demonstration design plan, Phoenix Environmental Laboratories was used as a reference laboratory for verification of sample concentrations using EPA Method 8260A. A total of 24 samples (4 replicates of 5 different mixtures and 4 blanks) were analyzed by the reference laboratory for verification of mixture composition and concentration.

Test Results

Calculation of Concentrations

Analytical results obtained using chromatograph column B were manually calculated from response factors derived from peak area and weight ratios of earlier calibration runs of the dibromomethane internal standard and 500 µg/L standards of each target analyte. The results for toluene and PCE on chromatograph column C were calculated using Voyager internal software and a five-point calibration curve. The dibromomethane internal standard was not used for these two compounds since it coelutes with toluene on this particular column.

Precision and Accuracy

Relative standard deviations for the nine compounds and six (five and a blank) concentration levels investigated in this study are provided in Tables 7-1 to 7-6. The RSD values were computed from four replicate samples analyzed at each concentration level. The average percent recovery of each compound, also computed from the replicate samples, is also shown in Tables 7-1 to 7-6. In each table, three different recovery values are given: (1) the percent ratio of the Voyager result to the laboratory result; (2) the percent ratio of the Voyager result to the "true" value; and (3) the percent ratio of the laboratory value to the "true" value. The mean percent recoveries for each target compound over all concentration ranges are given in Table 7-7.

Table 7-1. Blank Sample Results

Compound	Voyager Avg. (µg/L)	Voyager RSD (%)	True Conc. (µg/L)	Lab. Avg. (µg/L)
Benzene	No detect		<0.5	No detect
Trichloroethene	No detect		<0.5	No detect
Toluene	No detect		<0.5	No detect
Tetrachloroethene	13	84.8	<0.5	No detect
Dibromomethane	1007	6.7	1000	NA
Ethyl benzene	No detect		<0.5	No detect
meta-Xylene	No detect		<0.5	No detect
Dibromochloromethane	No detect		<0.5	No detect
Bromodichloromethane	No detect		<0.5	No detect

Notes: In this table and the following five tables, average and RSD values are computed from four replicate samples.
NA = not analyzed.

Table 7-2. Very Low-Level Sample (7 µg/L) Results

Compound	Voyager Avg. (µg/L)	Voyager RSD (%)	True Conc. (µg/L)	Lab. Avg. (µg/L)	Percent Recovery		
					Voyager to Lab.	Voyager to True	Lab. to True
Benzene	6.0	32.9	7	15	38	82	214
Trichloroethene	6.0	27.3	7	12	52	89	171
Toluene	10.0	46.2	7	13	75	139	186
Tetrachloroethene	10.0	47.5	7	10	95	136	143
Dibromomethane	980	18.6	1000	NA	NA	98	NA
Ethyl benzene	1.0	66.7	7	19	4	11	271
meta-Xylene	1.0	66.7	7	11	7	11	157
Dibromochloromethane	9.0	200.0	7	14	61	121	200
Bromodichloromethane	6.5	115.5	7	16	41	93	229

Note: NA = not analyzed.

Table 7-3. Low-Level Sample (30 μg/L) Results

Compound	Voyager Avg. (μg/L)	Voyager RSD (%)	True Conc. (μg/L)	Lab. Avg. (μg/L)	Percent Recovery		
					Voyager to Lab.	Voyager to True	Lab. to True
Benzene	42	10.2	30	40	104	139	133
Trichloroethene	44	4.8	30	44	99	145	147
Toluene	35	23.8	30	40	86	115	133
Tetrachloroethene	17	58.2	30	39	43	56	130
Dibromomethane	846	10.9	1000	NA	NA	85	NA
Ethyl benzene	47	10.0	30	42	111	155	140
meta-Xylene	47	7.4	30	42	112	157	140
Dibromochloromethane	23	72.8	30	46	49	75	153
Bromodichloromethane	62	3.8	30	41	151	206	137

Note: NA = not analyzed.

Table 7-4. Midlevel Sample (700 μg/L) Results

Compound	Voyager Avg. (μg/L)	Voyager RSD (%)	True Conc. (μg/L)	Lab. Avg. (μg/L)	Percent Recovery		
					Voyager to Lab.	Voyager to True	Lab. to True
Benzene	787	4.1	700	585	134	112	84
Trichloroethene	717	1.0	700	633	113	102	90
Toluene	743	7.1	700	528	141	106	75
Tetrachloroethene	808	11.3	700	628	129	115	90
Dibromomethane	1058	3.6	1000	NA	NA	106	NA
Ethyl benzene	686	6.3	700	648	106	98	93
meta-Xylene	520	2.2	700	403	129	74	58
Dibromochloromethane	705	10.1	700	733	96	101	105
Bromodichloromethane	680	7.5	700	655	104	97	94

Note: NA = not analyzed.

Table 7-5. Mid- to High-Level Sample (300 and 5000 µg/L) Results

Compound	Voyager Avg. (µg/L)	Voyager RSD (%)	True Conc. (µg/L)	Lab. Avg. (µg/L)	Percent Recovery		
					Voyager to Lab.	Voyager to True	Lab. to True
Benzene	197	12.6	300	135	146	66	45
Trichloroethene	3300	12.9	5000	3025	109	66	61
Toluene	254	11.4	300	95	267	85	32
Tetrachloroethene	4749	12.2	5000	2850	167	95	57
Dibromomethane	597	8.9	1000	NA	NA	60	NA
Ethyl benzene	182	13.0	300	123	148	61	41
meta-Xylene	157	19.9	300	135	117	52	45
Dibromochloromethane	238	18.1	300	98	243	79	33
Bromodichloromethane	219	13.1	300	125	175	73	42

Note: NA = not analyzed.

Table 7-6. Very High-Level Sample (3000 µg/L) Results

Compound	Voyager Avg. (µg/L)	Voyager RSD (%)	True Conc. (µg/L)	Lab. Avg. (µg/L)	Percent Recovery		
					Voyager to Lab.	Voyager to True	Lab. to True
Benzene	2825	6.0	3000	2200	128	94	73
Trichloroethene	2675	16.3	3000	1625	165	89	54
Toluene	2765	16.1	3000	2175	127	92	73
Tetrachloroethene	2948	16.3	3000	1375	214	98	46
Dibromomethane	748	31.5	1000	NA	NA	75	NA
Ethyl benzene	2775	16.5	3000	1950	142	93	65
meta-Xylene	2800	15.4	3000	1950	144	93	65
Dibromochloromethane	3050	1.9	3000	2375	128	102	79
Bromodichloromethane	3050	4.2	3000	2325	131	102	78

Note: NA = not analyzed.

Table 7-7. Summary Mean Percent Recoveries

Compound	Mean Percent Recovery at Concentration Level (µg/L)					Overall Mean Percent Recovery
	7	30	700	3000	300/5000	
Benzene	82	139	112	94	66	99
Toluene	139	115	106	92	85	107
Ethyl benzene	11	155	98	93	60	83
meta-Xylene	11	157	74	93	52	77
Trichloroethene	89	145	102	89	66	98
Tetrachloroethene	136	56	115	98	95	100
Dibromochloromethane	121	75	101	102	79	96
Bromodichloromethane	93	206	97	102	73	114

Chapter 8
Previous Deployments

Note from vendor: The names and companies listed below are current Perkin-Elmer Photovac Voyager users. The individuals and/or companies are not endorsing the Voyager or its use for a specific application. Questions about the Voyager and its use or application should be addressed to the Perkin-Elmer Photovac Applications group at (203) 761-5040.

Vicky Bliss
Mobil Oil
Joliet, IL
(815) 423-7397
Application: Assay 2 - Petrochemical

Paulette Lane
PSE&G of New Jersey
(201) 761-1188
Application: Assay 2 - Petrochemical

Hilary Eustace
City of Somerville
Somerville, MA
(617) 625-6600
Application: Assay 1 - Environmental

Jan McChesney
Bayer Rubber
Sarnia, Ontario
(519) 337-8251
Application: Assay 4 - ABS Rubber

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