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Environmental Technology Verification Report

Field-Portable Gas Chromatograph

Electronic Sensor Technology, Model 4100

by

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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:	**Model 4100**
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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's 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 Electronic Sensor Technology (EST) Model 4100 field-portable gas chromatograph (GC).

DEMONSTRATION DESCRIPTION

The field demonstration of the Model 4100 portable GC was held in September 1997. The demonstration was designed to assess the instrument's ability to detect and measure chlorinated volatile organic compounds 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

The accompanying notice is an integral part of this verification statement

McClellan Air Force Base, the target compounds were trichloroethene, tetrachloroethene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, and *trans*-1,3-dichloropropene. These sites were chosen because they contain varied concentrations of chlorinated VOCs and exhibit different climatic and geologic 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, Electronic Sensor Technology, Model 4100*. (EPA/600/R-98/141).

TECHNOLOGY DESCRIPTION

Gas chromatography is a proven analytical technology that has been used in environmental laboratories for many years. The Model 4100 GC incorporates a purge-and-trap sample introduction method for the analysis of VOCs in water. The instrument is a single-column GC with programmable temperature control and a surface acoustic wave detector. The system uses short, capillary GC columns and a fast-response detector to produce a complete chromatogram in 30 seconds or less. A room-temperature water sample is sparged with a small volume of air and the entrained VOCs are transferred to a small adsorbent trap, which is subsequently thermally desorbed and injected onto the GC column of the Model 4100. The chromatographic column separates the sample mixture into individual components. Compounds exiting the column momentarily stick to the detector surface, causing a frequency change in an oscillating crystal.

Compounds are identified by column retention time and are quantified by comparing detector response to that of standards run under similar conditions. A gas chromatograph offers some limited potential for identification of unknown components in a mixture; however, a confirmational analysis by an alternative method is often advisable. A field-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 Model 4100 weighs 35 pounds and is about the size of a large briefcase. The unit can be easily transported and operated in the rear compartment of a minivan. Instrument detection levels for many chlorinated VOCs in water range from 10 to 100 µg/L. Sample processing and analysis can be accomplished by a chemical technician; however, instrument method development, instrument calibration, and data processing may require a higher level of operator experience and training. At the time of the demonstration, the baseline cost of the Model 4100 with laptop computer was $25,000.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the Model 4100 were observed:

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

Completeness: The Model 4100 reported results for all of the 165 PE and groundwater samples provided for analysis at the two demonstration sites.

Analytical Versatility: The Model 4100 was calibrated for and detected 25 of the 32 (78%) PE sample VOCs provided for analysis at the demonstration. Six pairs of coeluting compounds were reported. For the groundwater contaminant compounds for which it was calibrated, the Model 4100 detected 42 of the 66 compounds detected 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 organic compounds. The results are reported in terms of a relative standard deviation (RSD). The distribution of RSD values compiled for all reported compounds from both sites had a median value of 15% and a 95th percentile value of 46%. By comparison, the compiled RSDs from the reference laboratory had a median value of 7% and a 95th percentile value of 25%. The ranges of Model 4100 RSD values for specific target compounds were as follows: trichloroethene, 2 to 28% (reported as coeluter with 1,2-dichloropropane); tetrachloroethene, 6 to 22%; 1,2,3-trichloropropane, 4 to 41%; and *trans*-1,3-dichloropropene, 4 to 55%.

Accuracy: Instrument accuracy was evaluated by comparing Model 4100 results with the known concentrations of chlorinated organic compounds in PE mixtures. Absolute percent difference (APD) values from both sites were calculated for all analytes in the PE mixtures. The APDs for all reported compounds from both sites had a median value of 44% and a 95th percentile value of 100%. By comparison, the compiled APDs from the reference laboratory had a median value of 7% and a 95th percentile value of 24%. The ranges of Model 4100 APD values for target compounds were as follows: trichloroethene, 25 to 42% (reported as coeluter with 1,2-dichloropropane); tetrachloroethene, 32 to 66%; 1,2-dichloroethane, 2 to 20%; 1,2,3-trichloropropane, 12 to 74%; 1,1,2-trichloroethane, 8 to 43%; and *trans*-1,3-dichloropropene, 2 to 45%.

***Comparability*:** A comparison of Model 4100 and reference laboratory data was based on 33 groundwater samples analyzed at each site. The correlation coefficients (r) for all compounds detected by the Model 4100 and laboratory, at or below the 100 μg/L concentration level, were 0.967 at Savannah River and 0.816 at McClellan. The r values for compounds detected at concentration levels in excess of 100 μg/L were 0.969 for Savannah River and 0.968 for McClellan. These correlation coefficients reveal a highly linear relationship between Model 4100 and laboratory data. The median absolute percent difference between groundwater compounds mutually detected by the Model 4100 and reference laboratory was 30%, with a 95th percentile value of 100%.

Deployment: The system was ready to analyze samples within 30 minutes of arrival at the site. At both sites, the instrument was transported in a minivan and operated from its rear compartment. The instrument was powered with line ac obtained from a small dc-to-ac inverter connected to the vehicle's battery.

Under appropriate applications, the Model 4100 field-portable gas chromatograph with surface acoustic wave detector can provide useful, cost-effective data for environmental site characterization and routine monitoring. The results of this demonstration show that the instrument is best suited for routine monitoring of water samples contaminated with relatively few chlorinated VOCs. In the selection of a technology for deployment at a 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 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 (EST), 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 Electronic Sensor Technology, Model 4100 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, and the demonstrations were designed to evaluate the capabilities of each field-transportable system. They 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 Model 4100. Instrument precision and accuracy were determined from analysis of replicate samples from 16 multicomponent standard mixtures of known composition. The relative standard deviations (RSD) from four replicate samples from each of the 16 standard mixtures were used as measures of precision. Pooled RSDs from all compounds had a median value of 15% and a 95th percentile value of 46%. Accuracy was expressed as the absolute percent difference between the Model 4100 measured value and the true value of the component in the standard mixtures. Pooled absolute percent difference values for all compounds had a median value of 44% and a 95th percentile value of 100%. A comparison of Model 4100 and reference laboratory results from 33 groundwater samples at each site produced a median absolute percent difference of 30% with a 95th percentile value of 100% for mutually detected compounds. The Model 4100 reported results for 42 of 66 groundwater compounds detected by the laboratory at concentration levels greater than 1 µg/L and for which the Model 4100 was calibrated. Correlation analysis between Model 4100 and laboratory results produced correlation coefficients (*r*) in the range of 0.82 to 0.97 at low (≤100 µg/L) contaminant concentrations. Correlation coefficients were 0.97 or greater at high (>100 µg/L) concentrations. Model 4100 sample throughput rates were 2 to 3 samples per hour.

Under appropriate applications, the Model 4100 field-portable 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 for the application by taking into account the 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
°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
EPA	Environmental Protection Agency
EST	Electronic Sensor Technology
ETV	Environmental Technology Verification Program
GC	gas chromatograph
GW	groundwater
GC/MS	gas chromatograph/mass spectrometer
Hz	hertz, cycles per second
i.d.	inside diameter
L	liter
m	meter
mg	milligram
mg/L	milligram per liter
mL	milliliter
mm	millimeter
MAFB	McClellan Air Force Base
MCL	maximum concentration level
MDL	method detection limit
MHz	megahertz
MS	mass spectroscopy
NA	not available

ND	not detected
NERL	National Exposure Research Laboratory
NR	not reported
PCB	polychlorinated biphenyls
PC	personal computer
PCE	tetrachloroethene (perchloroethene)
PE	performance evaluation
ppb	parts per billion
ppm	parts per million
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
SAW	surface acoustic wave
SPCC	system performance check compounds
SRS	Savannah River Site
TCA	trichloroethane
111TCA	1,1,1-trichloroethane
TCE	trichloroethene
V	volts
V ac	volts alternating current
VOA	volatile organics analysis
VOC	volatile organic compound
µg	microgram
µg/L	microgram per liter
µL	microliter

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 Electronic Sensor Technology in this technology demonstration is also acknowledged. Gary Watson and David McGuire operated the instrument during the demonstrations.

For more information on the wellhead monitoring demonstration, contact:

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For more information on the Electronic Sensor Technology Model 4100 gas chromotograph/mass spectrometer technology, contact:

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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 (GW) 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 Electronic Sensor Technology (EST) Model 4100 field-portable 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 EPA approval or endorsement.

Technology Overview

The Electronic Sensor Technology Model 4100 is a fast, field-portable gas chromatograph that utilizes a surface acoustic wave (SAW) detector. The instrument can be operated from ac power or a battery, using a dc-to-ac inverter. The 4100 is designed to separate and detect headspace vapors in the parts-per-billion (ppb) to parts-per-million (ppm) range and speciate the analytes of interest via gas chromatography in less than 30 seconds. The 4100 has multiple applications in environmental measurement of analytes of interest in an air, water, or soil matrix. Air samples can be injected into the instrument from Tedlar bags or from the headspace of closed containers using a gas-tight syringe. Volatile organic compounds in water can be analyzed using a purge-and-trap accessory. A water trap is also available as an option, to remove high levels of water vapor from the sample under analysis.

The 4100 consists of a head unit, a chassis, and a laptop computer. The chassis contains the electronic circuitry and helium storage for up to 5 days of operation, while also serving as a carrying case for the 4100. The head unit contains the column, the adsorbent trap, a six-way valve, and the detector. The laptop personal computer (PC) contains the proprietary software that controls the 4100 through all operations. It also records all chromatograms and data for export and report generation. The 4100 is fully field-portable and requires approximately 20 minutes from setup to full operation. Analytes of interest are calibrated using standard water solutions, standard gases in pressurized tanks, or Tedlar bags spiked at the concentration levels of interest. The unit is field-portable and weighs 35 pounds.

Principle of Operation

For the detection of volatile organic compounds in air, the air sample is pumped through a Tenax-packed trap for a preselected time. The trap is then heated and the desorbed vapors are directed, via a temperature-controlled rotary valve, to a short GC column. The GC column is thermally ramped and the separated effluent vapors are directed onto the surface of the SAW. The SAW is a 500-MHz resonator that is highly sensitive to any impinging vapors. The corresponding change in frequency caused by surface loading of the SAW oscillator is recorded and displayed in the form of an integram by proprietary software adapted to run on the system PC. The computer simultaneously displays an evolving chromatogram produced from the differential of the integram.

The differential mimics the form of a traditional chromatogram but will usually display a negative inflection following each chromatographic peak. This physically corresponds to the desorption of the analyte from the SAW's surface.

History of the Technology

The 4100 was developed under a Department of Energy research and development contract. As a fully temperature-programmable instrument, it has potential applications in the analysis of semivolatiles, including polychlorinated biphenyls (PCBs), dioxins, and dibenzofurans. The 4100 has also been employed in the detection of narcotics, controlled substances, explosives, and nerve agents.

Applications

The 4100 is designed to address the requirements of separating and quantifying volatile and semivolatile compounds in water, soil, and air. The technology meets the needs of site investigation, characterization, continuous monitoring, and postclosure compliance. Because of its wide dynamic range (greater than 10^4 in concentration) and fast throughput (less than 30-second chromatography total elution time), the 4100 can also be used in laboratories to prescreen samples for concentration measurements before injection into laboratory gas chromotograph/mass spectroscopy (GS/MS) instruments.

Advantages

The 4100 offers on-site, real-time speciation and quantification of analytes. Managers can make decisions based upon data that minimize drilling requirements or the movement of expensive personnel and equipment. A 4100 is half the cost of a laboratory GC/MS system and may provide a level of accuracy that meets regulatory requirements. Studies have indicated that the Model 4100 can save over 50% in laboratory analysis fees while providing real-time site characterization or monitoring data.

Limitations

As with gas chromatographs in general, the Model 4100 can encounter possible situations of coeluting analytes. Analytical method parameters such as column temperature or column coating can often be adjusted to minimize overlapping peaks from coeluting compounds.

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 of a particular compound; however, as with most GC systems, an additional data dimension such as mass spectra, provided by GC/MS systems, is not available.

The Model 4100 utilizes an equilibrium headspace method to determine VOCs in water. Thus it is only able to analyze for those compounds with solubilities and vapor pressures that promote the formation of headspace concentrations detectable by the instrument.

Performance Characteristics

Method Detection Limits and Practical Quantitation Limit

Developer-provided estimates of instrument method detection limits (MDLs) and maximum concentration levels (MCLs) for selected hydrocarbon compounds are given in Table 2-1.

Table 2-1. Method Detection Limit and Maximum Concentration Levels in Water

Analyte	Method Detection Limit (Water) (μg/L)	Maximum Concentration Level (Water) (μg/L)
Carbon tetrachloride	70	100,000
cis-1,2-Dichloroethene	110	186,000
Chloroform	65	182,000
Trichloroethene	10	75,000
Tetrachloroethene	3	18,000
1,1,2,2-Tetrachloroethane	1	6300
Benzene	45	107,000
Toluene	5	29,000
Ethyl benzene	2	98,000
ortho-Xylene	2	6000

The practical quantitation limit (PQL) is the lower bound of the calibration range and represents a peak-to-peak, signal-to-noise ratio of 12:1. The signal level provides acceptable and reproducible signal integration with the 4100 Microsense software. The vendor estimates the practical quantitation limit to be 5 times the method detection limit.

Precision and Accuracy

Precision for the Electronic Sensor Technology 4100 instrument, as represented by the relative standard deviation (RSD)[1] on replicate measurements, is generally less than 10% for the compounds shown in Table 2-1. Accuracy, as represented by percent difference, is also generally 10% or better.

Instrument Working Range

The Model 4100 is equipped with a number of user-selected settings, such as purge duration and column temperature settings, which are components of an analytical method. The limit of detection for an analyte is determined by the sampling time input and the retention volume of the inlet preconcentrator trap. The EST 4100 is capable of performing measurements up to the maximum vapor concentration as given by the saturation vapor concentration for each analyte. Saturated vapor measurements are made using methods with short sampling times and elevated detector temperatures. Typical upper limit concentrations are shown in Table 2-1.

Comparison with Reference Laboratory Analyses

The 4100 GC/SAW analytical results for volatile organics in a water matrix are expected to be within 20% or better of a reference laboratory instrument.

Specificity

The possibility of coeluting compounds provides the most common cause of interference. It is not generally possible to be certain that an unknown analyte is present as a coeluting compound based only on retention time

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

data. An understanding of the sampling environment and the potential target analytes is necessary to reduce the likelihood of interference.

Other Field-Performance Characteristics

Instrument Setup and Disassembly Time

The instrument setup and disassembly time is 20 minutes.

Instrument Calibration Frequency During Use

Normally, a calibration mixture is run every 10 chromatographic runs. Based on typical sample throughput rates, this corresponds to about 3 calibration checks per hour.

Ancillary Equipment Requirements

The instrument requires 110 V ac, which can be supplied via line connection, generator, or from a dc-to-ac inverter connected to a 12-V car battery.

Sample Throughput Rate

The throughput rate ranges from 2 to 3 samples per hour and is largely dependent upon sample complexity. Samples with few components can be processed quickly, while complex samples require additional data analysis time.

Operator Training Requirements

A laboratory or field technician with some previous GC experience can become proficient after about 1 day of training. The operator must also be proficient in the operation of a laptop computer using a graphical user interface such as Windows 95.

Ease of Operation

The instrument can be operated by a single technician. A second technician doing sample handling can expedite sample throughput.

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

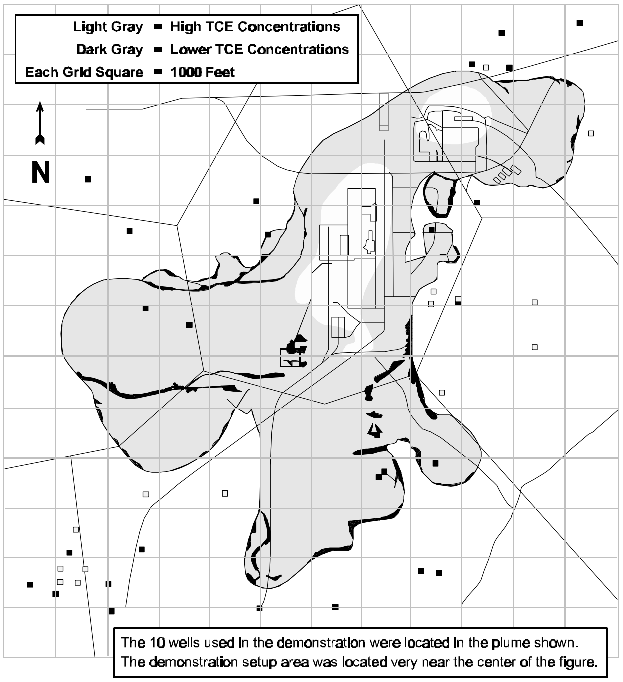
The SRS is located on the upper Atlantic Coastal Plain. The site is underlain by a thick wedge (approximately 1000 feet) of unconsolidated Tertiary and Cretaceous sediments that overlie Precambrian and Paleozoic metamorphic rocks and consolidated Triassic sediments (siltstone and sandstone). The younger 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.

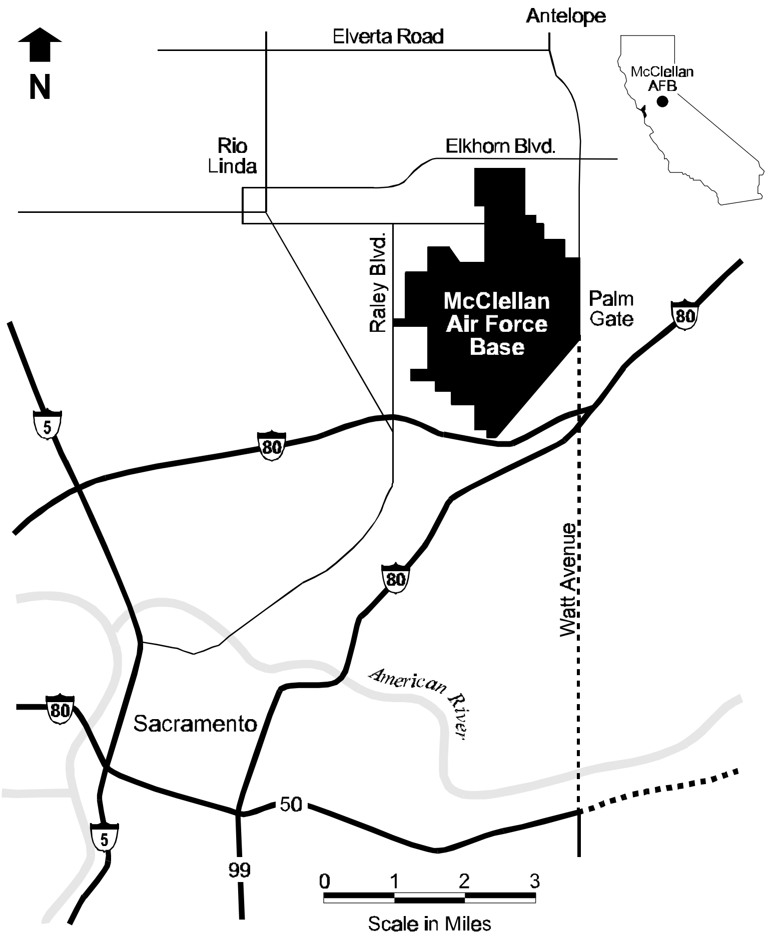


Figure 3-3. A map of Sacramento and vicinity showing the location of McClellan Air Force Base.

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.

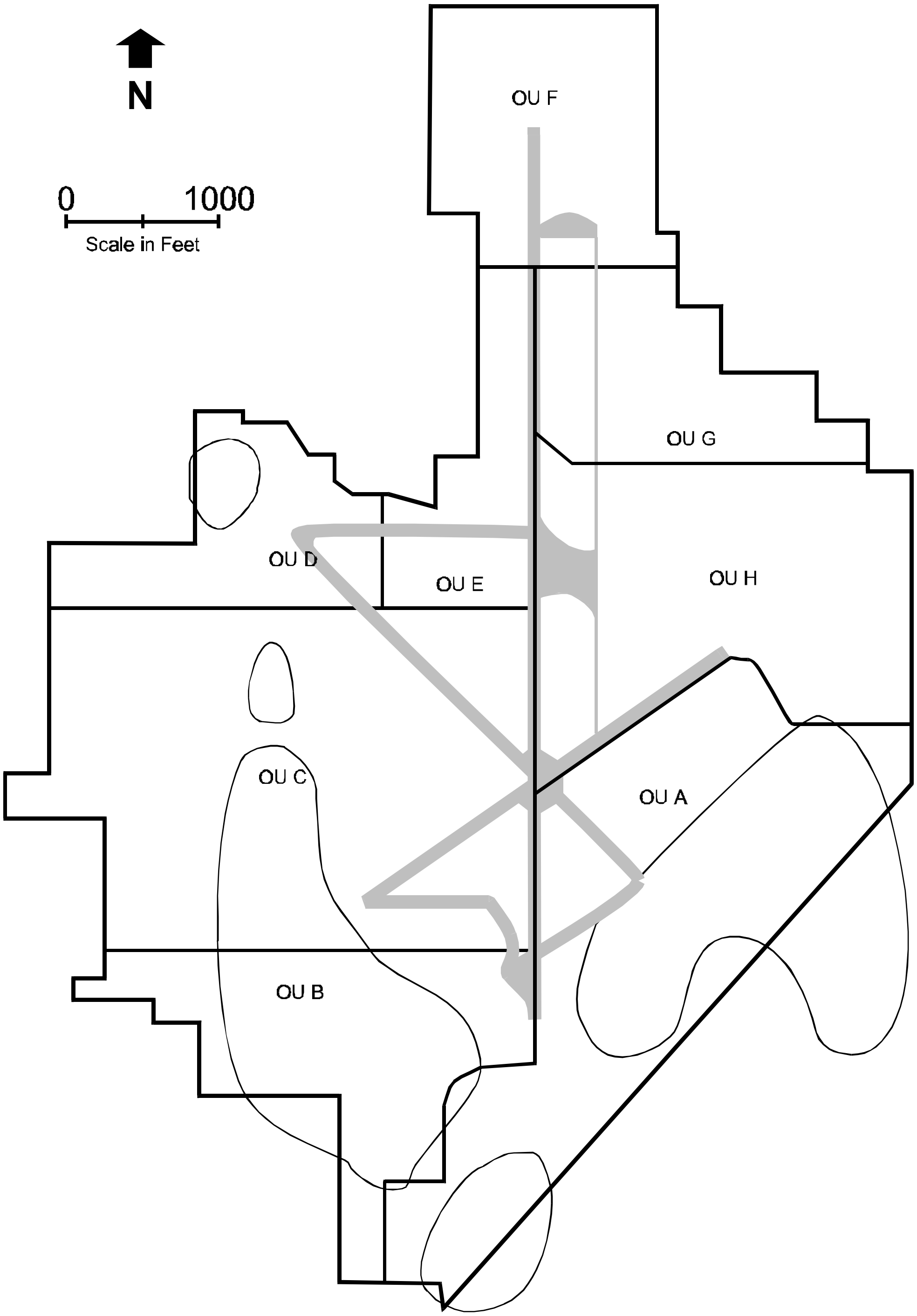


Figure 3-4. Subsurface TCE plumes at McClellan Air Force Base in the shallowest (A) aquifer layer. The circular lines enclose plume concentrations in excess of 5 µg/L TCE. OU refers to operational units. Monitoring wells used in the demonstration were primarily in OUs A and B. The demonstration setup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

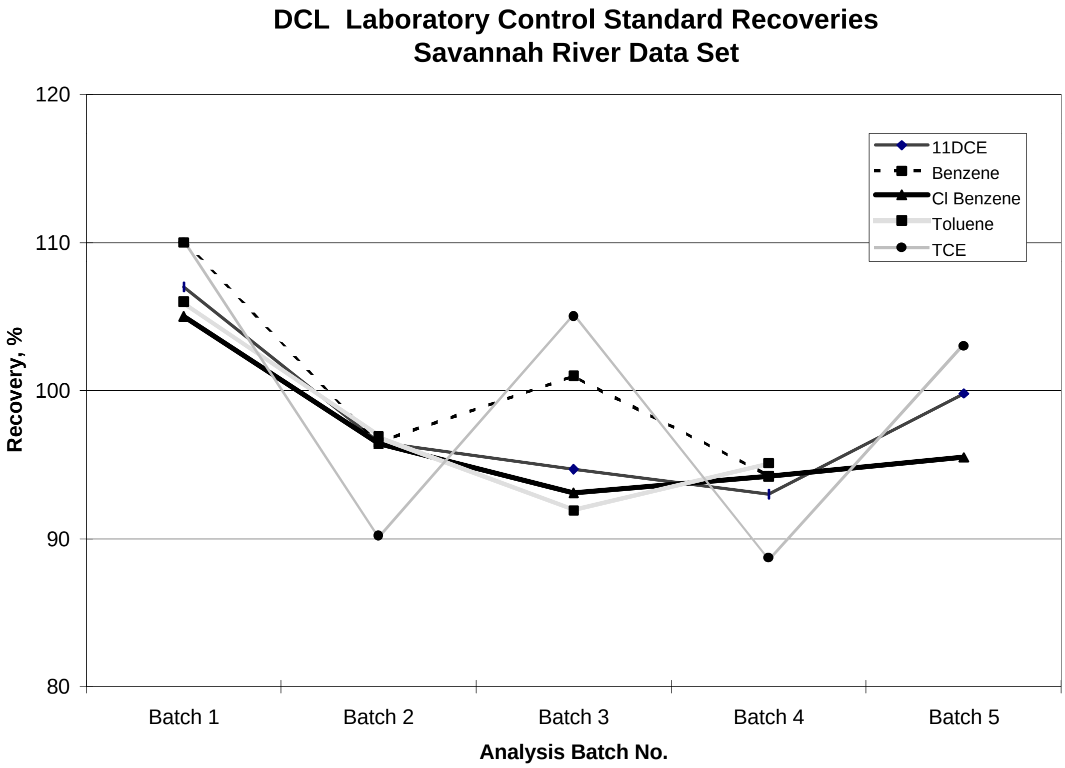

Figure 4-1. Laboratory control standard recovery values for SRS analyses.

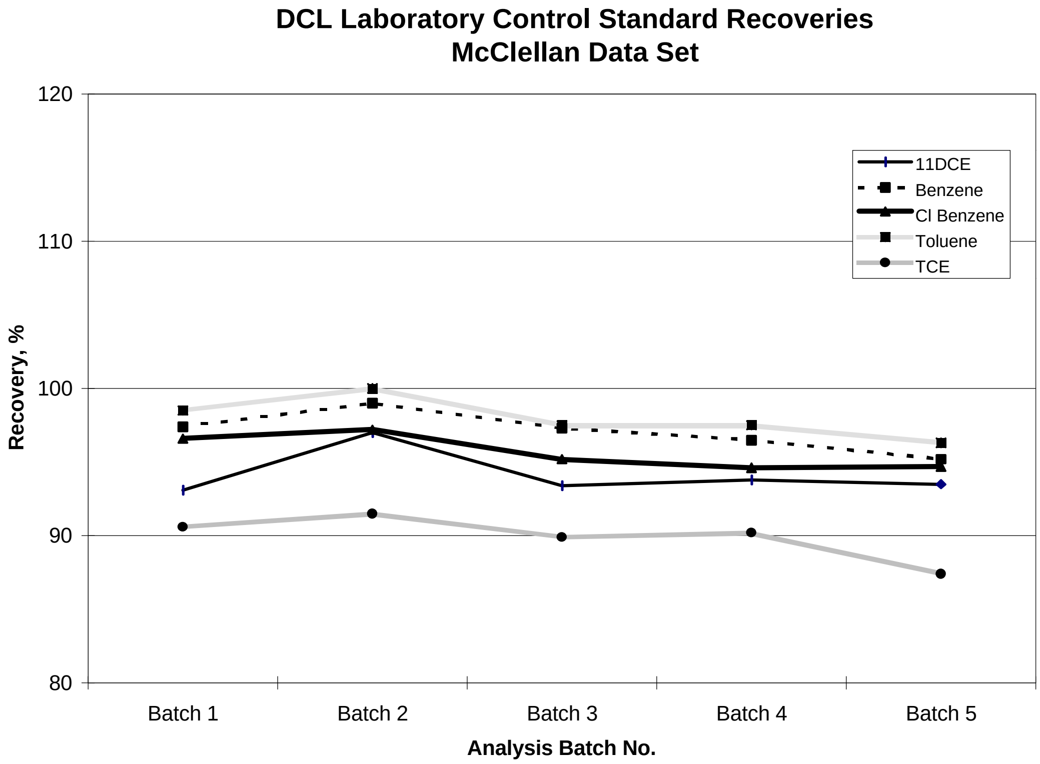

Figure 4-2. Laboratory control standard recovery values for MAFB analyses.

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 4-1. 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.

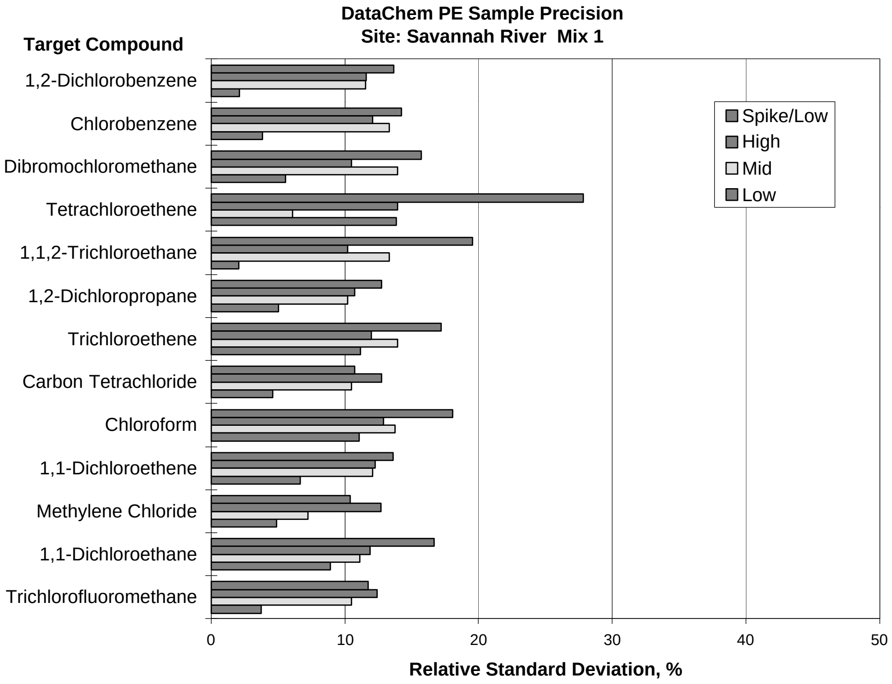

Figure 4-3. Laboratory precision on SRS PE samples containing mix 1. Trichloroethene was spiked into the spike/low samples.

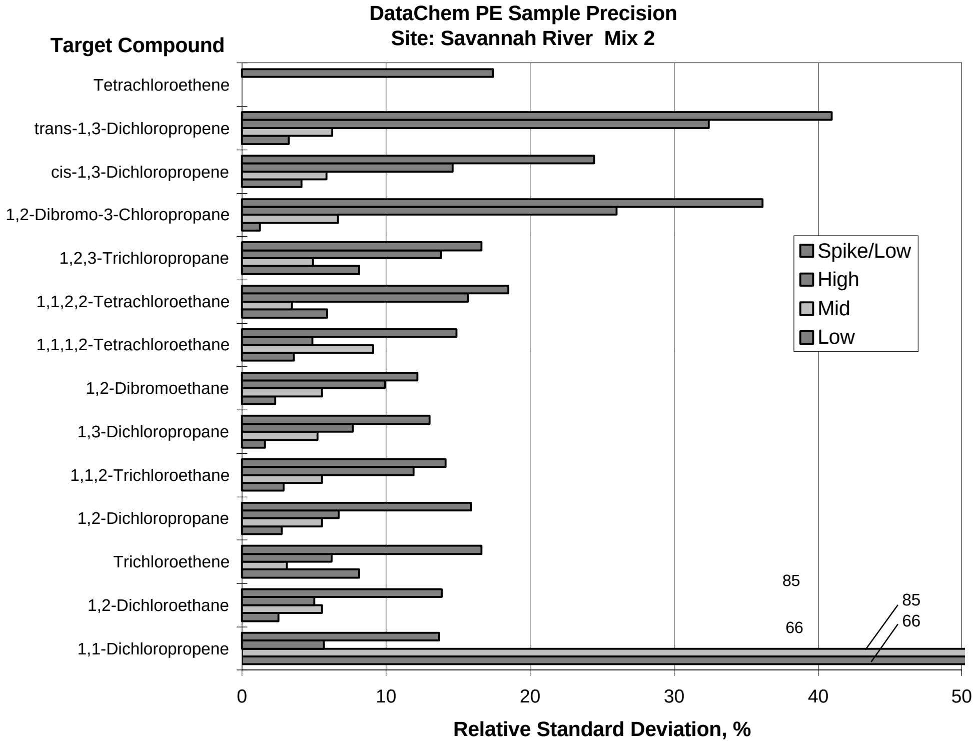

Figure 4-4. Laboratory precision on SRS PE samples containing mix 2. Tetrachloroethene was spiked into the mix 2 samples. Trichloroethene and tetrachloroethene were spiked into the spike/low samples.

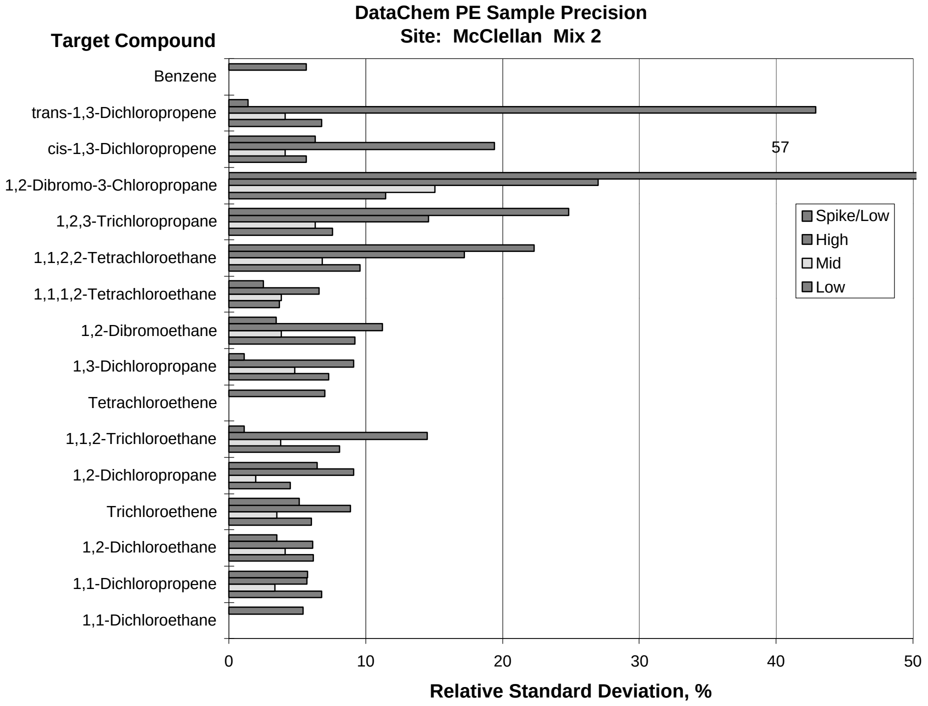

Figure 4-5. Laboratory precision on MAFB PE samples containing mix 2. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

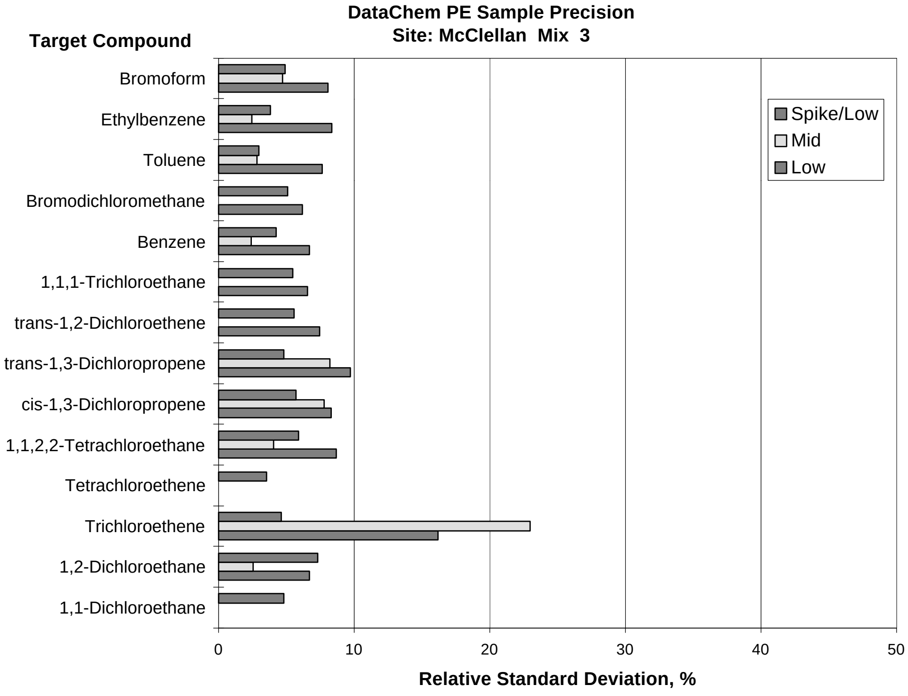

Figure 4-6. Laboratory precision on MAFB PE samples containing mix 3. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

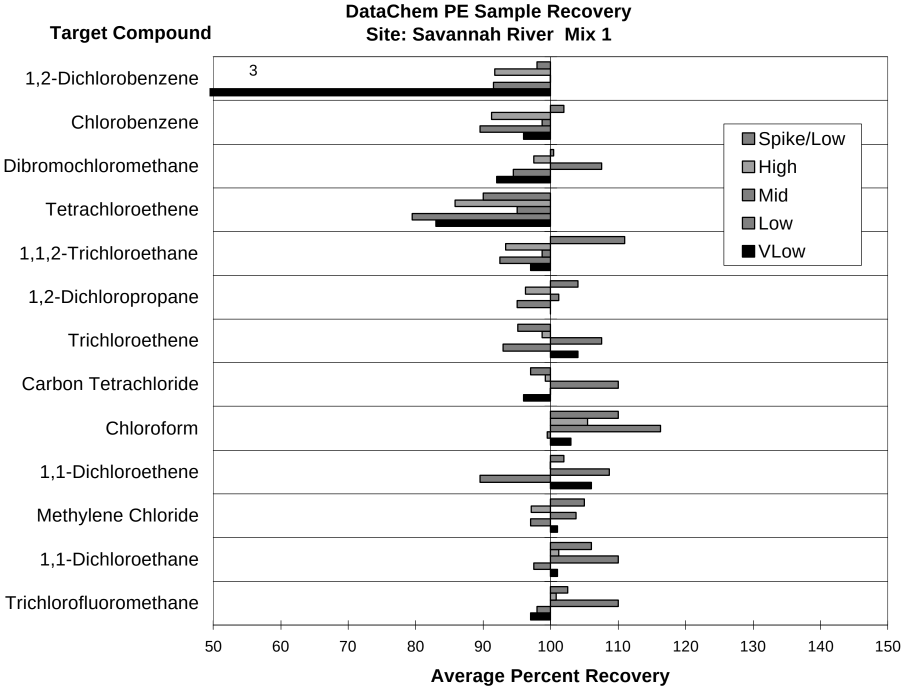

Figure 4-7. Laboratory mean recoveries for SRS PE samples containing mix 1. Trichloroethane was spiked into the spike/low samples.

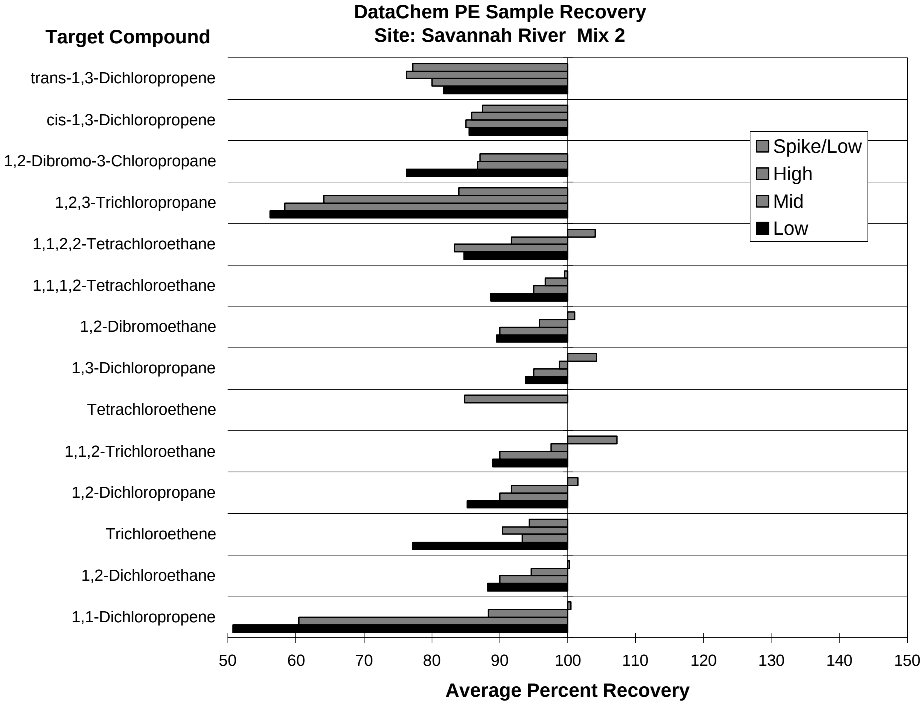

Figure 4-8. Laboratory mean recoveries for SRS PE samples containing mix 2. Trichloroethane and tetrachloroethene were spiked into the spike/low samples.

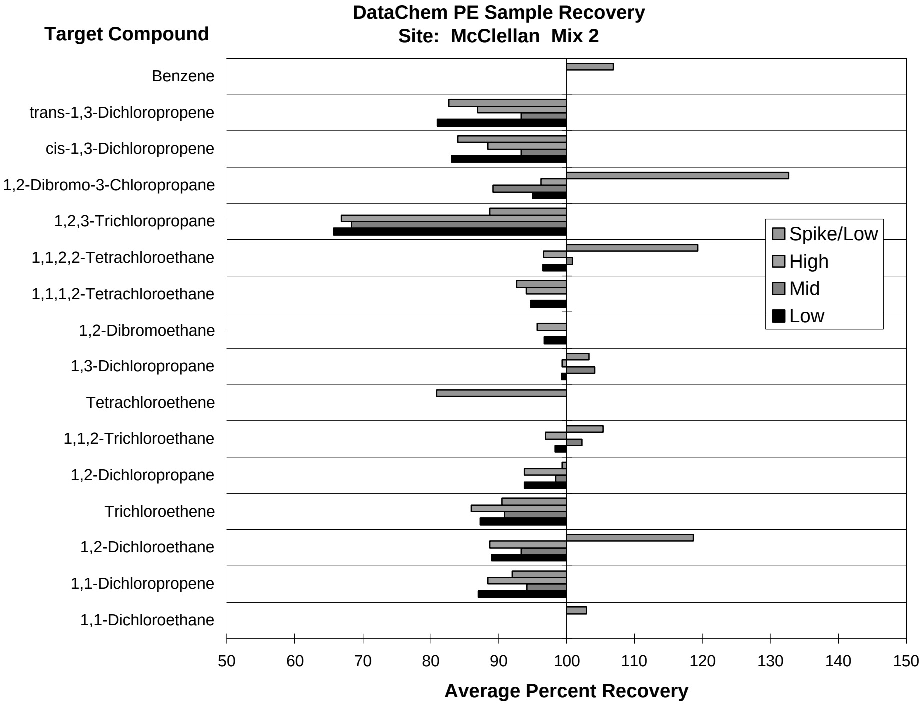

Figure 4-9. Laboratory mean recoveries for MAFB PE samples containing mix 2. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

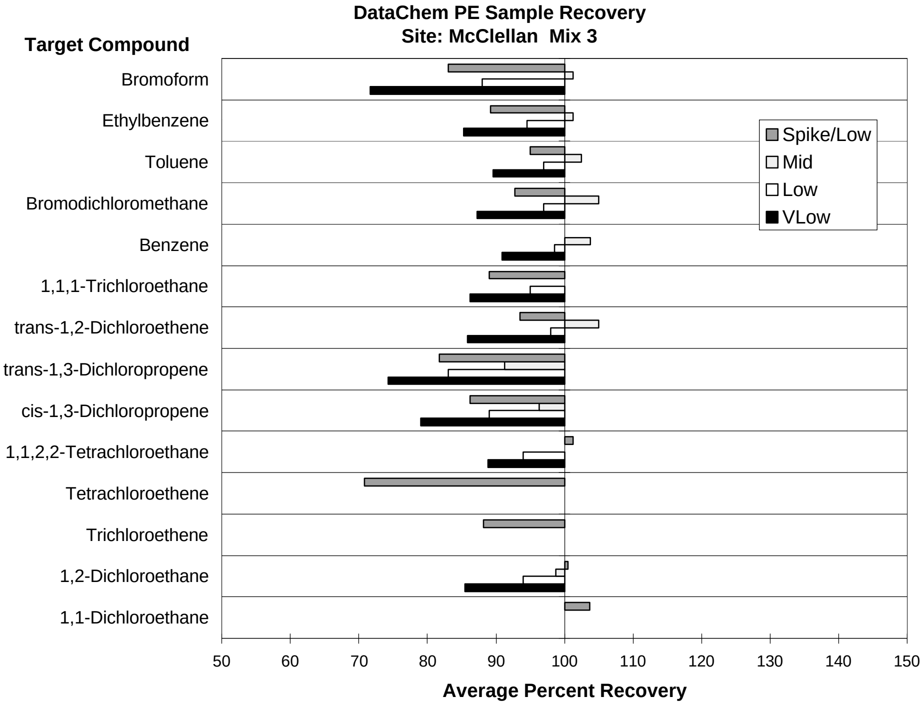

Figure 4-10. Laboratory mean recoveries for MAFB PE samples containing mix 3. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

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

Model 4100 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 preparation for predemonstration instrument calibration. The Model 4100 was calibrated for and reported results for 31 compounds at both demonstrations. Six pairs of coeluting compounds were included in the list, as shown in Table 5-1. Note that some calibrated and reported compounds were not in the demonstration PE mixtures. A total of 32 chlorinated and nonchlorinated hydrocarbon compounds were included in the PE mixtures noted in Table 3-4. Results were submitted for 26 of these compounds. No results from the Model 4100 were reported for the following 6 PE compounds: trichlorofluoromethane, methylene chloride, dibromochloromethane, 2-chloroethyl vinyl ether, 1,2-dichloroethene, and bromodichloromethane.

Table 5-1. Model 4100 Calibrated and Reported Compounds

Reported Compounds at Both Demonstrations	
1,1-Dichloroethane	1,2-Dibromoethane(d)
1,1-Dichloroethene	1,1,1,2-Tetrachloroethane
Chloroform(a)	1,2,3-Trichloropropane(f)
Carbon tetrachloride(b)	1,2-Dibromo-3-chloropropane
Trichloroethene(c)	*cis*-1,3-Dichloropropene
Tetrachloroethene(d)	*trans*-1,3-Dichloropropene
Chlorobenzene	Hexachlorobutadiene
1,2-Dichlorobenzene	1,1-Dichloropropene(b)
1,3-Dichloropropane	Benzene(e)
Dichloromethane	Toluene
Bromochloromethane(a)	Ethyl benzene
1,2-Dichloroethane(e)	Bromoform
1,1,2,2-Tetrachloroethane(f)	1,3-Dichlorobenzene
1,2-Dichloropropane(c)	1,1,1-Trichloroethane
1,1,2-Trichloroethane	Dibromomethane
trans-1,2-Dichloroethene	

Note: Compounds marked with letters in parentheses denote coeluting compound pairs.

Preanalysis Sample Information

Groundwater and PE samples were provided to the Model 4100 team without additional information on the number of compounds in the samples or compound concentration levels.

Sample Completion

A total of 165 PE and groundwater samples were submitted for analysis to the Model 4100 team. All samples were successfully analyzed and the results reported at both demonstration sites. One of the replicate groundwater samples was inadvertently omitted from the sample set for Electronic Sensor Technology.

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. No false positive detects were obtained for the compounds shown in Table 5-1 in blank samples analyzed at SRS and MAFB.

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 5-2. Vendor-provided method detection limits, where available, are also shown in the table for comparison.

Table 5-2. 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 (NA)	10 of 10 (100%)	*trans*-1,2-Dichloroethene (NA)	2 of 10 (20%)
Dichloromethane	No calibration	1,2-Dichloroethane (NA)	10 of 10 (100%)
Chloroform (65)	10 of 10 (100%)	Benzene (45)	10 of 10 (100%)
Carbon tetrachloride (70)	10 of 10 (100%)	Bromodichloromethane (NA)	10 of 10 (100%)
1,2-Dichloropropane (NA)	10 of 10	*cis*-1,3-Dichloropropene (NA)	0 of 10 (0%)
Trichloroethene (10)	0 of 10 (0%)	*trans*-1,3-Dichloropropene (NA)	10 of 10 (100%)
1,1,2-Trichloroethane (NA)	10 of 10 (100%)	Toluene (5)	0 of 10 (0%)
Dibromochloromethane	No calibration	Ethyl benzene (2)	0 of 10 (0%)
Tetrachloroethene (3)	0 of 10 (0%)	Bromoform (NA)	0 of 10 (0%)
Chlorobenzene (NA)	0 of 10 (0%)	1,1,2,2-Tetrachloroethane (1)	0 of 10 (0%)
2-Chloroethyl vinyl ether	No calibration	1,1,1-Trichloroethane (NA)	10 of 10 (100%)
Trichlorofluoromethane	No calibration		
1,1-Dichloroethane (NA)	10 of 10 (100%)		
1,2-Dichlorobenzene (NA)	10 of 10 (100%)		

Notes: Method detection limits (in units of µg/L) reported by the vendor are given in parentheses following the compound; NA = not available; detection limits not determined or reported by instrument developer. The Model 4100 was not calibrated for selected compounds, as noted in the table.

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 PE 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 were 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

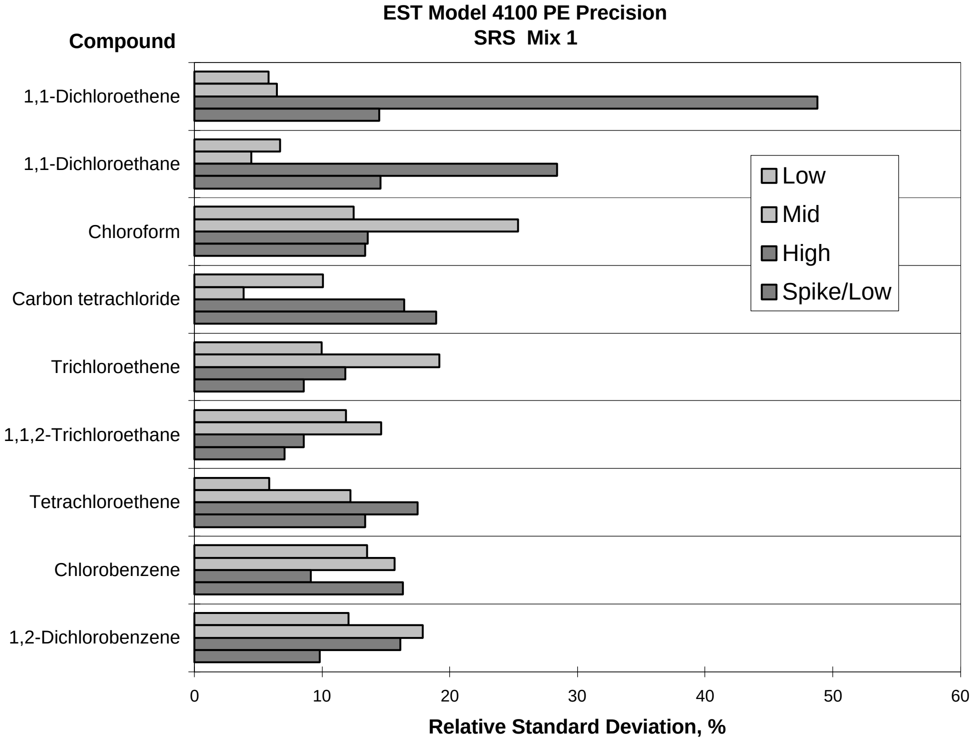

Figure 5-1. Model 4100 precision on PE mix 1 at the SRS. Trichloroethene was spiked into the spike/low sample.

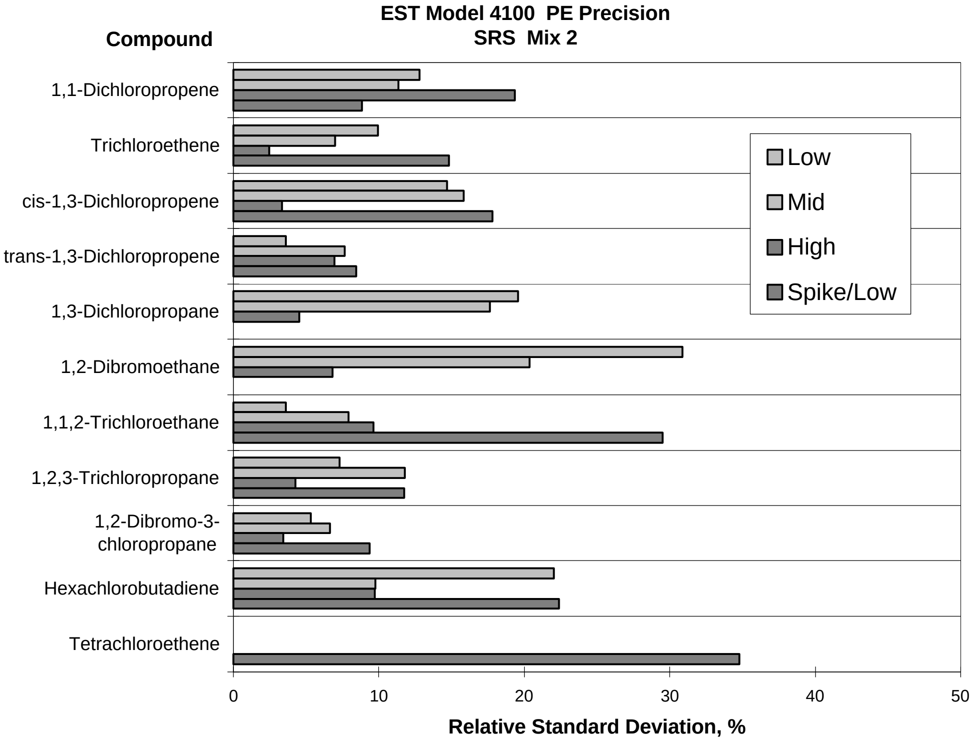

Figure 5-2. Model 4100 precision on PE mix 2 at the SRS. Trichloroethene and tetrachloroethene were spiked into the spike/low sample.

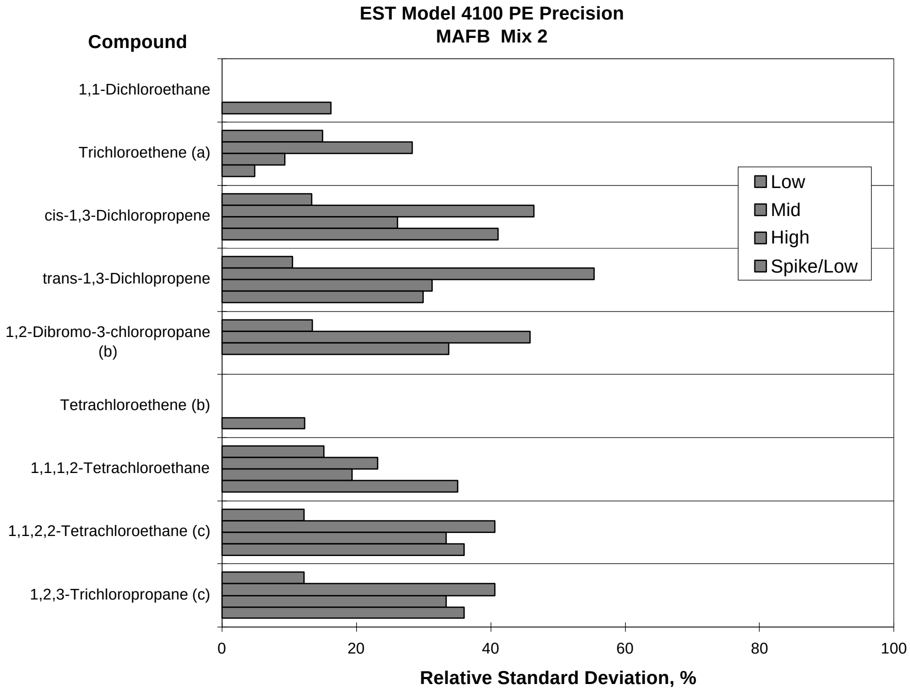

Figure 5-3. Model 4100 precision on PE mix 2 at MAFB. Letters denote coeluting compounds. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

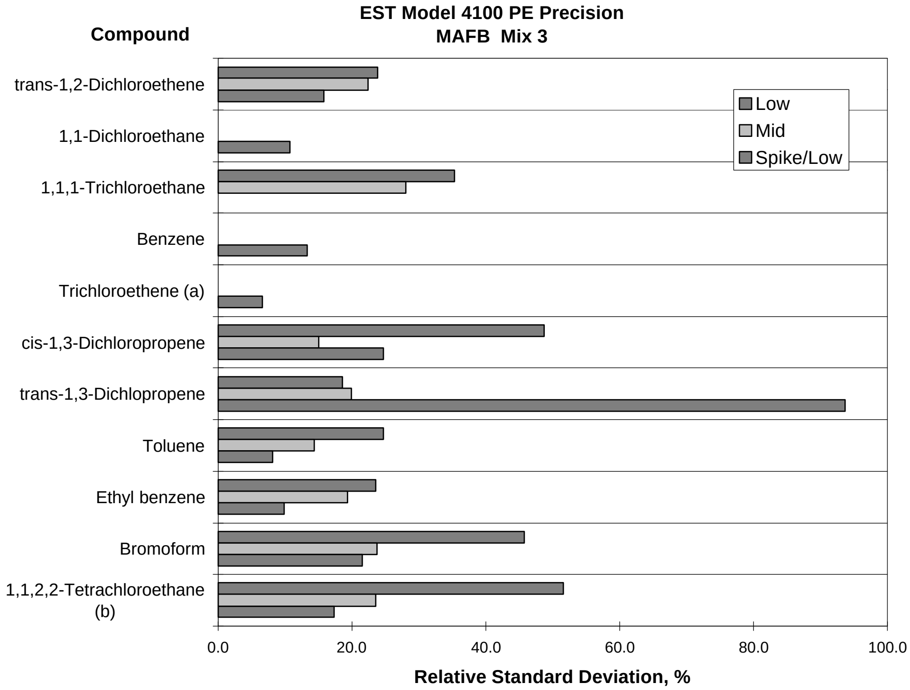

Figure 5-4. Model 4100 precision on PE mix 3 at MAFB. Letters denote coeluting compounds. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

in the study.[1] (The compositions and concentrations of each of these mixtures are given in Table 3-5 for the SRS and Table 3-6 for MAFB.) Relative standard deviations for the coeluting compound pairs, noted in Table 5-1, are shown as reported by the EST analysis team. In some instances both compounds of a coeluting pair were present in a PE mixture. Note that precision and accuracy were not determined for the "very low" concentration mixtures. Instrument precision data for six target compounds that are regulated under the Safe Drinking Water Act are shown in Table 5-3. The RSDs 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 given in the last column of the table.

Table 5-3. Target Compound Precision for PE Samples at Both Sites

Target Compound	Site	Relative Standard Deviation (%)				
		Low	Mid	High	Spike/Low	Range
Trichloroethene[(a)]	SRS	10	7	2	15	2 – 28
	MAFB	15	28	9	5	
1,2-Dichloropropane[(a)]	SRS					5 – 28
	MAFB	15	28	9	5	
1,2,3-Trichloropropane	SRS	7	12	4	12	4 – 41
	MAFB	12	41	33	36	
1,1,2-Trichloroethane	SRS	4	8	10	29	4 – 29
	MAFB					
Tetrachloroethene	SRS	6	12	11	13	6 – 22
	MAFB			22	10	
trans-1,3-Dichloropropene	SRS	4	8	7	8	4 – 55
	MAFB	10	55	31	30	

Notes: Trichloroethene and 1,2-dichloropropane are reported as a coeluting compound pair (a).
Blank cells indicate that no data were reported.

Overall instrument precision is summarized in Table 5-4 for 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.

Table 5-4. Summary of PE Sample Precision and Percent Difference Statistics for 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	12	10	25	21	15
	95th	27	29	46	51	46
	Number in pool	27	39	42	28	136
Absolute percent difference	50th	45	43	45	47	44
	95th	61	64	308	91	100
	Number in pool	27	39	42	28	136

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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.

PE Sample Accuracy

The Model 4100 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 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 assessment of the sign of the difference, the percent recovery data are plotted as either a positive or negative difference from the 100% recovery line. Instrument recovery performance for the target compounds is shown in Table 5-5, which contains the average percent recoveries and associated ranges for each compound.

Table 5-5 contains a summary of overall Model 4100 differences relative to PE mixture true values for both sites. For this summary, percent recoveries were expressed as percent difference (e.g., a 90% recovery is equivalent to a −10% difference; 120% recovery is equivalent to a +20% difference) and all data from PE mixtures were pooled. The median and 95th percentiles of the pooled absolute percent difference (APD) values are shown in Table 5-4.[4]

Table 5-5. Target PE Compound Recovery at Both Sites

Target Compound	Site	Average Recovery (%)				
		Low	Mid	High	Spike/Low	Range
Trichloroethene[(a)]	SRS	61	74	58	75	58 – 75
	MAFB	62	69	67	66	
1,2-Dichloropropane[(a)]	SRS					380 – 5038
	MAFB	380	420	408	5038	
1,2,3-Trichloropropane	SRS	65	60	49	55	49 – 174
	MAFB	144	141	174	112	
1,1,2-Trichloroethane	SRS	118	108	57	59	57 – 118
	MAFB					
Tetrachloroethene	SRS	59	67	67	68	34 – 68
	MAFB			63	34	
trans-1,3-Dichloropropene	SRS	61	66	62	57	57 – 145
	MAFB	79	99	145	59	

Notes: Trichloroethene and 1,2-dichloropropane are reported as a coeluting compound pair (a).
Blank cells indicate that no data were reported.

Comparison with Laboratory Results

For each demonstration site, a total of 33 groundwater 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 Model 4100 results for all groundwater

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[2] Percent recovery is the Model 4100 value divided by the true value, multiplied by 100.

[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 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%.

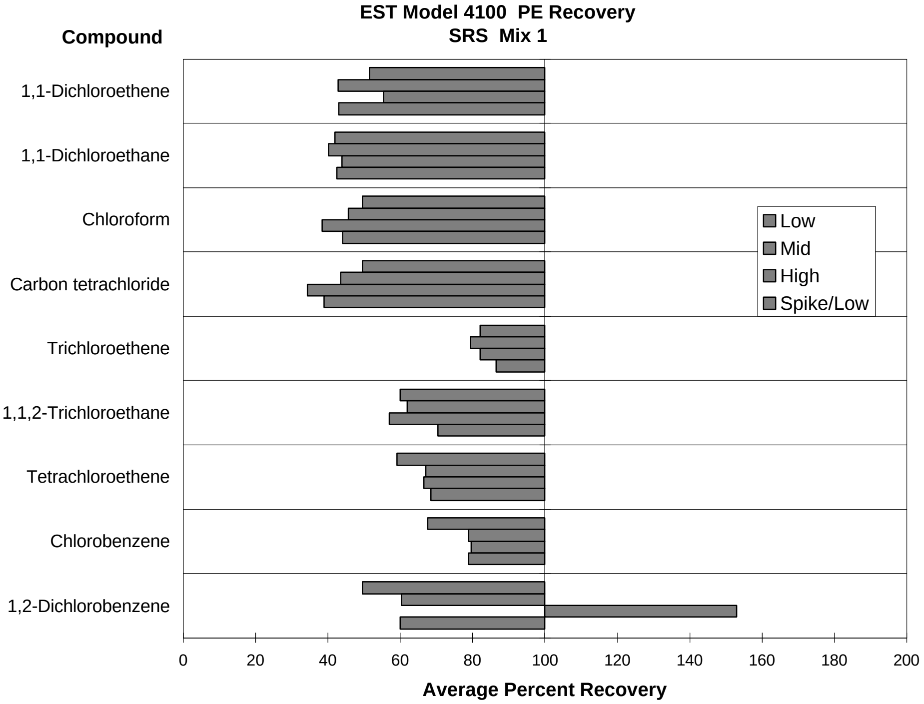

Figure 5-5. Model 4100 recovery on PE mix 1 at the SRS. Trichloroethene was spiked into the spike/low samples.

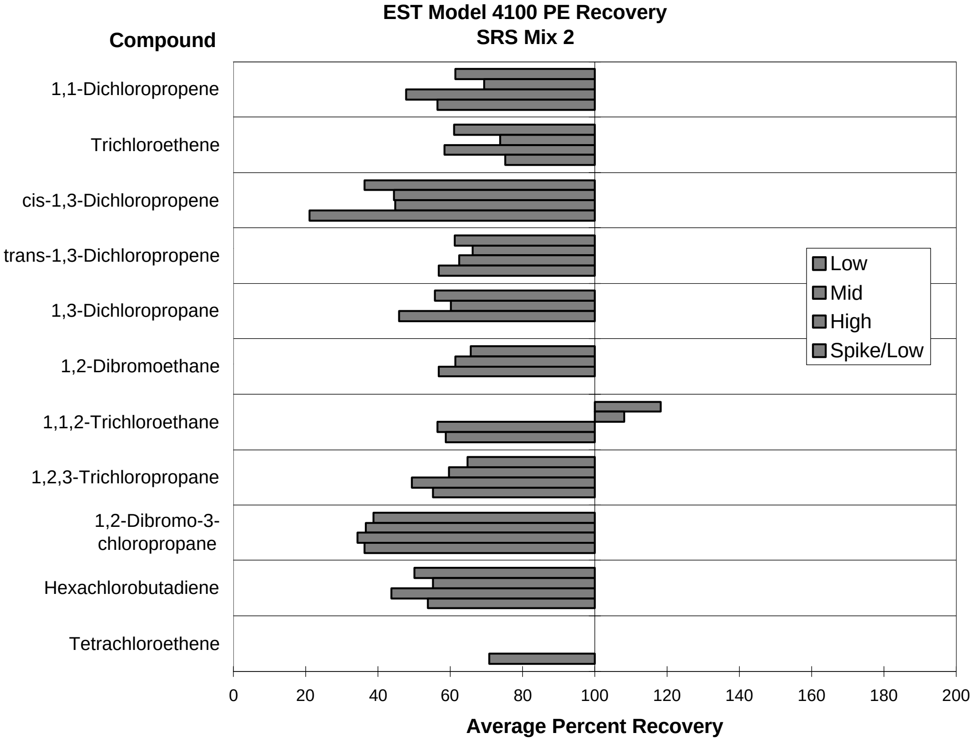

Figure 5-6. Model 4100 recovery on PE mix 2 at the SRS. Trichloroethene and tetrachloroethene were spiked into the spike/low samples.

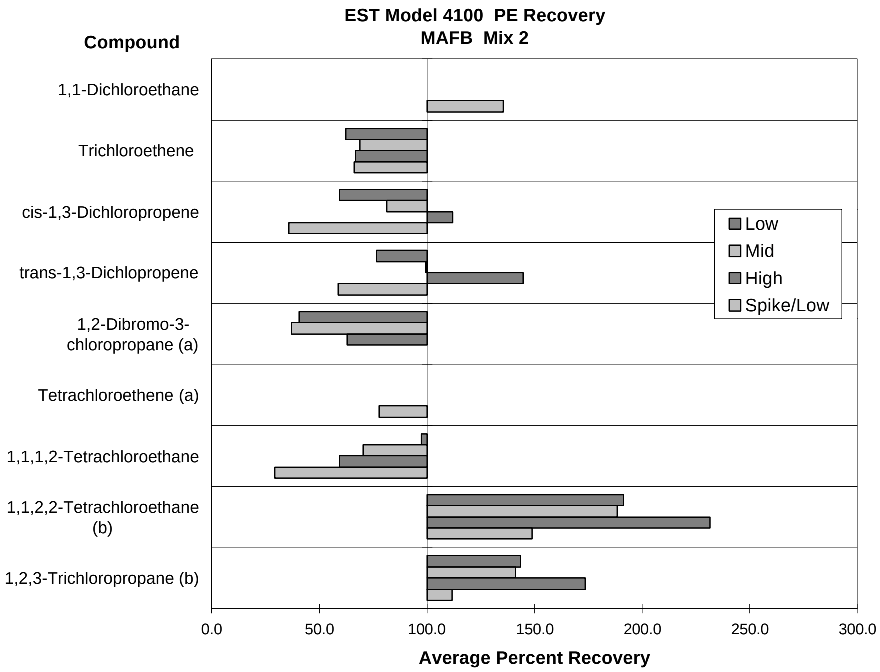

Figure 5-7. Model 4100 recovery on PE mix 2 at MAFB. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/ low samples.

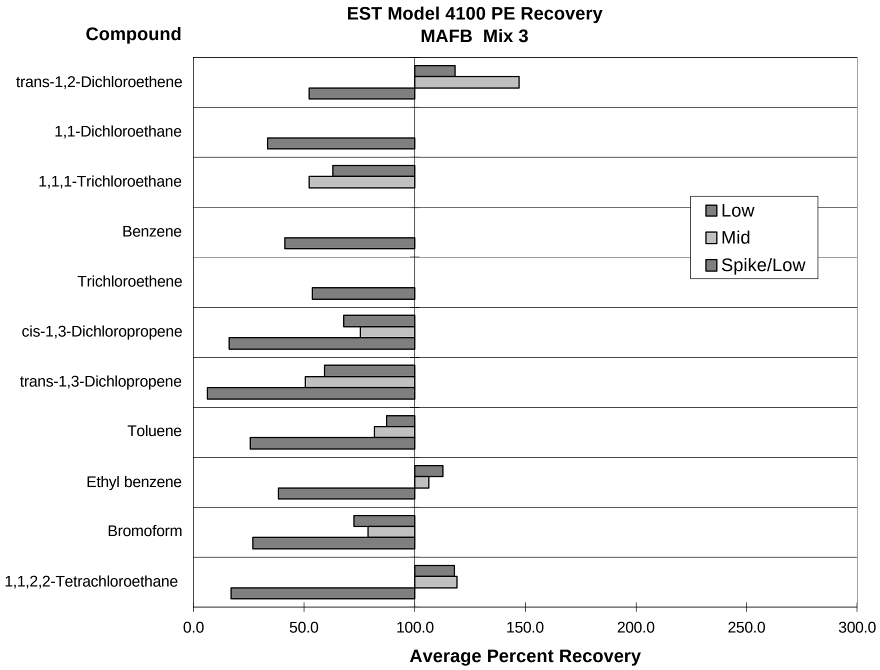

Figure 5-8. Model 4100 recovery on PE mix 3 at MAFB. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/ low samples.

samples is given in Table 5-6 for the SRS and Table 5-7 for the 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 trichloroethene concentration levels; however, other compounds were present in the groundwater samples at concentration levels noted in the tables. The precision of the Model 4100 on replicate groundwater sample sets is also shown in the last column of the tables.

The average percent differences between Model 4100 and laboratory results for the compounds detected in each set of groundwater samples are 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 at the SRS were also contaminated with 1,1-dichloroethene and one well showed chloroform and carbon tetrachloride, as noted in Table 5-6. The groundwater samples at MAFB were more complex, as indicated by the additional compounds shown in Table 5-7 and Figure 5-10. The median and 95th percentile of the distribution of absolute percent differences between Model 4100 and laboratory results for all groundwater samples are given in Table 5-8.

To assess the degree of linear correlation between the Model 4100 and the laboratory groundwater data pairs shown in Tables 5-6 and 5-7, 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 5-9.

Sample Throughput

Model 4100 sample throughput rates ranged from two to three samples per hour. Throughput rates were assessed by using the time lapsed between sample checkout in the morning and delivery of preliminary hardcopy results in the afternoon and the number of samples completed. Model 4100 GC run times were less than 2 minutes per sample and were not significantly influenced by sample complexity during this demonstration. Additional time was required to further process the chromatogram, however. Many of the PE samples provided for analysis in this demonstration were very complex and required additional data processing time. Samples with this level of complexity would very likely not be encountered under typical field conditions. Sample throughput for less complex groundwater samples would be higher than two to three samples per hour.

Performance Summary

Instrument performance parameters and operational features verified in this demonstration for the Model 4100 are summarized in Table 5-10. For groundwater samples, the results from the reference laboratory are given alongside Model 4100 performance results to facilitate comparison of the two methodologies.

Table 5-6. Model 4100 and Laboratory Results for SRS Groundwater Samples

Sample Description	Well Number	Compound	Replicates	Lab. Avg. (µg/L)	Lab. RSD (%)	Model 4100[a] Avg. (µg/L)	Model 4100[a] RSD (%)
Very low 1	MSB 33B	Trichloroethene Tetrachloroethene	3	9.0 3.5	11 14	4.9 1.7	19 10
Very low 2	MSB 33C	Trichloroethene	3	2.4 0.7	34 12	1.7 0.9	NR 52
Low 1	MSB 18B	Trichloroethene Tetrachloroethene	3	11 27	5 6	9.2 27	9 25
Low 2	MSB 37B	Trichloroethene Tetrachloroethene Chloroform Carbon tetrachloride	4	27 22 1.0 1.3	7 9 15 0	31 28 NR NR	18 14 NR NR
Mid 1	MSB 4D	Trichloroethene Tetrachloroethene	4	150 87	9 12	117 65	25 2
Mid 2	MSB 64C	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	3	35 240 12	7 4 8	25 161 NR	23 11 NR
High 1	MSB 4B	Trichloroethene Tetrachloroethene	3	747 33	1 2	694 25	26 14
High 2	MSB 70C	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	4	1875 520 32	12 8 8	1502 327 NR	25 11 NR
Very high 1	MSB 14A	Trichloroethene Tetrachloroethene	3	1367 800	8 6	1277 936	22 27
Very high 2	MSB 8C	Trichloroethene Tetrachloroethene	3	4933 3668	6 6	4502 4769	15 30
Range					0 – 34		2 – 52
Median					8		19
95th Percentile					15		32

[a] NR = Not reported.

Table 5-7. Model 4100 and Reference Laboratory Results for MAFB Groundwater Samples

Sample Description	Well Number	Replicates	Compound	Lab. [a] Avg. (µg/L)	Lab. [a] RSD (%)	Model 4100[a] Avg. (µg/L)	Model 4100[a] RSD (%)
Very low 1	EW-86	3	Trichloroethene	4.6	5	1.9	6
			1,1-Dichloroethene	7.7	9	NR	NR
Very low 2	MW-349	3	Trichloroethene	13	0	5.4	13
			Tetrachloroethene	2.0	6	1.1	16
			Chloroform	9.0	1	21	12
			1,1-Dichloroethene	3.8	3	NR	NR
			Carbon tetrachloride	137	4	114	30
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	12	116
			Carbon tetrachloride	7.5	2	NR	NR
			Chloroform	4.8	2	NR	NR
			Trichloroethene	16	4	8.3	67
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	NR	NR
			Carbon tetrachloride	1.4	4	NR	NR
			Trichloroethene	22	5	13	15
Mid 1	EW-87	4	1,1-Dichloroethene	180	12	0.3	11
			1,1-Dichloroethane	3.0	9	NR	NR
			cis-1,2-Dichloroethene	3.3	13	NR	NR
			1,1,1-Trichloroethane	6.8	12	0.4	NR
			Trichloroethene	114	11	106	34
			Tetrachloroethene	1.2	14	1.0	28
Mid 2	MW-341	3	*cis*-1,2-Dichloroethene	15	4	21	49
			Chloroform	3.5	5	NR	NR
			Trichloroethene	280	4	233	3
High 1	MW-209	3	*cis*-1,2-Dichloroethene	38	4	57	21
			Chloroform	6.9	21	NR	NR
			Trichloroethene	238	2	186	14
High 2	MW-330	4	*trans*-1,2-Dichloroethene	7.7	4	NR	NR
			cis-1,2-dichloroethene	66	5	105	11
			Chloroform	42	5	NR	NR
			1,2-Dibromochloropropane	6.1	6	NR	NR
			Trichloroethene	380	5	356	26
Very high 1	MW-334	3	1,1-Dichloroethene	690	3	0.3	24
			cis-1,2-dichloroethene	237	7	176	41
			Chloroform	397	5	NR	NR
			Benzene	283	5	158	11
			Trichloroethene	10,667	5	2474	62
			Carbon tetrachloride	350	5	NR	NR
Very high 2	MW-369	3	*cis*-1,2-Dichloroethene	207	10	674	129
			Chloroform	63	6	NR	NR
			Carbon tetrachloride	51	5	15	90
			Trichloroethene	6167	8	1671	28
Range					0 – 22		3 – 129
Median					5		24
95th Percentile					14		88

[a] NR = Not reported.

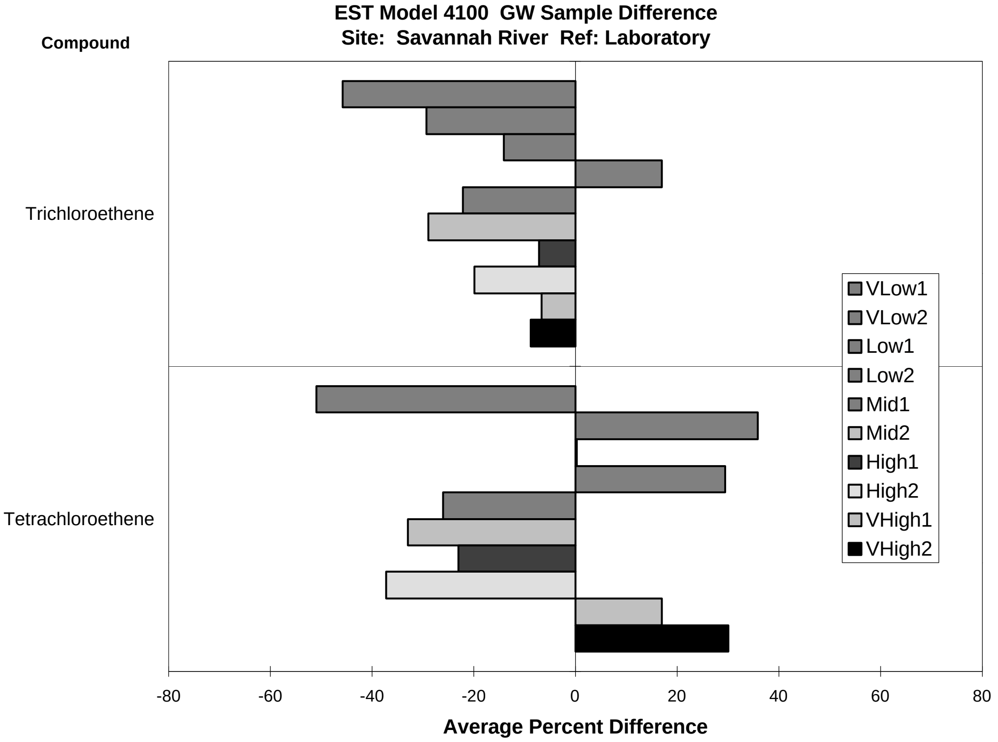

Figure 5-9. Model 4100 groundwater results at the SRS relative to laboratory results.

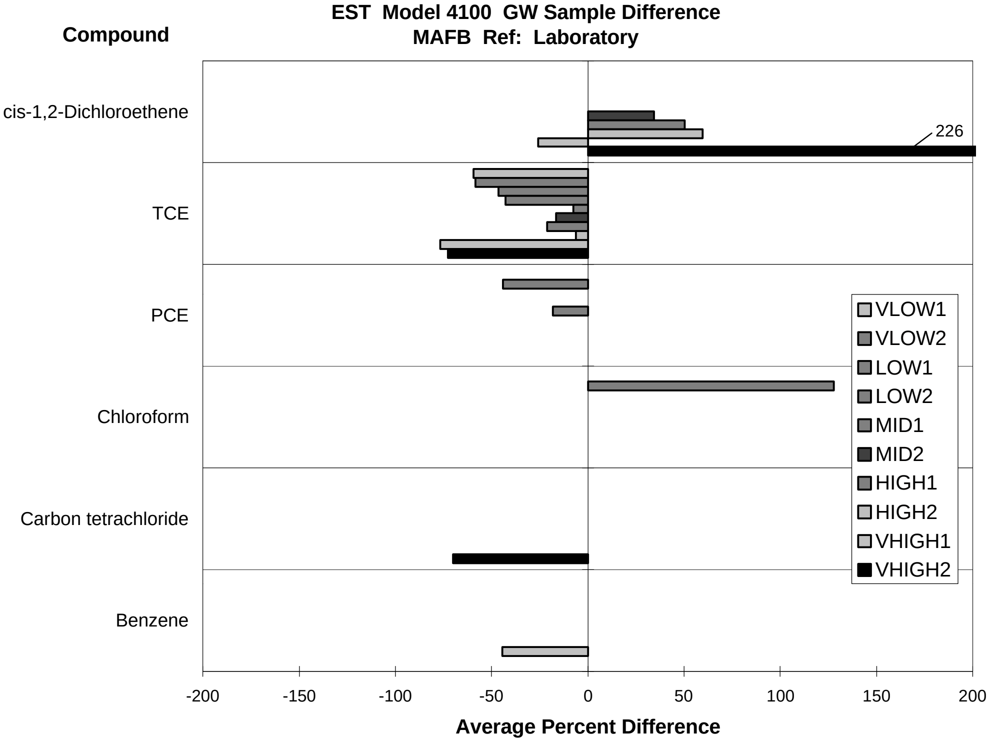

Figure 5-10. Model 4100 groundwater results at MAFB relative to laboratory results.

Table 5-8. Model 4100 Absolute Percent Difference Summary for Pooled Groundwater Results

Percentile	SRS	MAFB	Combined Sites
50th`	25	49	30
95th	46	128	100
Number of samples in pool	20	24	44

Table 5-9. Correlation Coefficients for Laboratory and Model 4100 Groundwater Analyses

Data Set	Correlation Coefficient	Number of Data Pairs
SRS Laboratory (1 through 100 μg/L)	0.967	11
SRS Laboratory (> 100 μg/L)	0.969	9
MAFB Laboratory (1 through 100 μg/L)	0.816	11
MAFB Laboratory (> 100 μg/L)	0.968	12

Table 5-10. Summary of Model 4100 GC Performance

Instrument Feature/Parameter	Performance Summary
Blank sample	No false positives detected for up to 32 calibrated compounds
Detection limit sample	False negatives reported at rates between 10 and 100% for 13 of 21 target compounds at 10-μg/L concentration levels
PE sample precision	Target compounds, RSD range: 2 to 55% All compounds: Model 4100 median RSD: 15%; 95th percentile RSD: 46% All compounds, laboratory median RSD: 7%; 95th percentile RSD: 25% (Target compounds: tetrachloroethene, 1,2,3-trichloropropane, 1,1,2-trichloroethane, 1,2-dichloropropane, and *trans*-1,3-dichloropropene)
PE sample accuracy	Target compounds, absolute percent difference range: 18 to >500% All compounds, Model 4100 median APD: 44%; 95th percentile APD: 100% All compounds, laboratory median APD = 7%; 95th percentile APD: 24% (Target compounds same as those for sample precision)
Model 4100 comparison with laboratory results for groundwater samples	Model 4100 median RSD: 22% Laboratory median RSD: 6% Model 4100 95th percentile RSD: 67% Laboratory 95th percentile RSD: 14% Model 4100: laboratory median APD: 30%; 95th percentile APD: 100% Model 4100: laboratory correlation: SRS low conc. (≤100 μg/L) *r* = 0.967 SRS high conc. (>100 μg/L) *r* = 0.969 MAFB low conc.(≤100 μg/L) *r* = 0.816 MAFB high conc. (>100 μg/L) *r* = 0.968

Table 5-10. Summary of Model 4100 GC Performance (Continued)

Instrument Feature/Parameter	Performance Summary
Analytical versatility	PE samples: calibrated for 25 of 32 PE compounds (78%) Six coeluting compound pairs were reported. GW samples: The reference laboratory detected 68 compounds at concentration levels of 1 µg/L or greater in all groundwater samples. The Model 4100 was calibrated to report 66 of these compounds. The Model 4100 reported values for 42 of the 66 compounds.
Sample throughput	2 to 3 samples per hour
Support requirements	110-V ac or 12-V dc power supply
Operator requirements	Sample processing: field technician Data processing and review: experienced GC chemist
Total system weight	35 pounds
Portability	GC and accessories are field-portable
Total system cost	$25,000 (with notebook computer); printer is optional
Shipping requirements	Air freight, hand carry, luggage check Carrier gas recharge cylinder shipped noncommercial

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 also provided.

Method

The Model 4100 GC uses a purge-and-trap method. A room-temperature water sample is sparged with a volume of air and the entrained VOCs are transferred to a small adsorbent trap. The VOCs are subsequently thermally desorbed and injected onto the column of the Model 4100. The instrument is a single-column GC with programmable temperature control and a surface acoustic wave detector. Compounds eluting from the column momentarily stick to the detector surface, causing a frequency change in an oscillating crystal. The compound is identified by column retention time and quantitation is determined by detector response. An internal standard is used to normalize compound retention times.

Equipment

The Model 4100 is 20 inches wide, 14 inches deep, and 10 inches high. It weighs 35 pounds. A notebook computer is an integral part of the system, as shown in Figure 6-1. A field-portable printer (5 pounds) was also used during the demonstration to print data. The unit was deployed on the folded-down middle seat of a minivan. The Model 4100 is field-portable and could be hand carried and deployed at a wellhead. The equipment weight includes a self-contained helium carrier gas. A small cylinder of compressed helium gas is used for periodic recharge of the internal carrier gas cylinder. The system was powered by 120-V ac through a dc-to-ac inverter that was connected to the vehicle's battery.

Additional equipment included 250-mL screw-cap septa sample vials, standards mixtures, microliter syringes and needles, and Teflon tubing for transferring samples. The unit is contained in a fiberglass shipping container and was transported to the sites as checked or carry-on luggage. The external carrier gas refill cylinder cannot be transported on commercial passenger aircraft and must be drop shipped to its destination.

Sample Preparation and Handling

Sample handling at both sites was as follows: 50 mL of the cold, 250-mL zero-headspace sample were discarded. The capped sample was then allowed to warm to room temperature. A sparge- and a sample-transfer needle

Figure 6-1. The Model 4100 GC/SAW.

were then inserted through the septum cap. The sparge needle was immersed into the water and the transfer needle was positioned in the bottle's headspace. About 5–15 mL of air were bubbled through the water over a period of 10 to 30 seconds. The VOC-laden air was transferred to small adsorbent trap containing a few milligrams of Tenax. An integral membrane dryer with a concentric-tubing configuration was positioned in front of the trap to remove water vapor from the sample. A molecular sieve was used to trap water vapor on the back side of the membrane. The adsorbent trap was heated and the volatile components were swept with helium carrier gas onto the column through an automatic gas sampling valve. The GC run time was about 30 seconds, during which the column temperature was ramped from 40 to 80 °C at 1.5 degrees/second. Following analysis, the SAW detector was momentarily flash heated to 200 °C to remove residual compounds from the detector surface.

Consumables

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

Historical Use

This is the first demonstration of the Model 4100 GC for VOC analysis in water. The instrument has been used for air and soil-gas analysis. See Chapter 8 for a list of previous deployments.

Equipment Cost

The Model 4100, as equipped at the demonstration, has a purchase price of about $25,000. This includes proprietary software, a laptop computer, and connection cables for data processing and instrument control. Instrument costs are summarized in Table 6-1. Laboratory costs for this demonstration were $95 per sample plus shipping costs of about $30 per batch of 12 samples. Sample throughput for the Model 4100 is in the range of 2 to 3 samples per hour.

Table 6-1. Model 4100 GC/MS Cost Summary

Instrument/Accessory	Cost
Instrument (Model 4100, laptop computer, software)	$25,000
Instrument accessories (field-portable printer, optional)	$500
Sample handling accessories (carrier gas, syringes, vials, standards)	$25 per day
Maintenance costs	Undetermined

Operators and Training

The Model 4100 was operated by the same two technicians at both demonstrations. Both had B.S.-level or higher training in either engineering or chemistry. Only one person is required to operate the instrument. With 1 day of training, an experienced chemical technician could operate the system. A novice technician operator would require additional training. Experience and some additional training in GC data processing are required to do method development and analysis of complex mixtures.

Data Processing and Output

The instrument uses proprietary Windows-95-based software with icon-based run events (e.g., purge time, temperature ramps, acquisition time). The results generated from the software are in a standard GC report form (header information, chromatogram, table of compounds listed by retention time, etc.). Data were delivered in the form of a spreadsheet printout.

Compounds Detected

The system was calibrated for and reported a total of 31 compounds at both sites (see Table 5-1). The analytical methods used at MAFB resulted in 6 coeluting compound pairs. The possibility of coeluting pairs requires that some information about sample content be available so that the methods can be adjusted to minimize or avoid compound coelution.

Initial and Daily Calibration

An initial three-point calibration was performed at two detector temperatures by running five replicates at three concentrations. (Two detector temperatures are used to increase the dynamic range of the instrument.) The detector response is not linear, and the compound response factor is based directly on detector response and not on a response factor ratio to the internal standard.

During sample analysis, a calibration mixture was run every 10 samples. Recovery of this standard had to be in the range of 80 to 120% for the calibration to be valid.

QC Procedures and Corrective Actions

At MAFB an internal standard (1,2,4-trimethylbenzene) was injected into each sample using a microliter syringe. This standard was used to normalize compound retention times. A blank sample run was also conducted after every sample run. If compounds were detected in the blank sample, the specified corrective action was to rerun the blank until the signal was below the MDL. The specified corrective action for an unacceptable calibration check sample was a full calibration rerun.

Sample Throughput

Gas chromatographic analysis time was less than 2 minutes; however, additional time was required to further analyze the data prior to their final submission. Preliminary data were generally available on hard copy at the end of the day and final data were available the following day. Throughput was on the order of two to three samples per hour. This includes periodic instrument calibration checks, sample reruns, and all data-processing tasks. Complex samples would likely take longer, whereas samples with only one or two contaminants would be processed much faster.

Problems Observed During Audit

No hardware problems were observed or reported during the two demonstration periods. It was apparent to auditors that considerable effort was expended by the EST team to interpret and analyze the data, particularly for the PE samples. Part of this effort was to allow an entire day's results to be reported in tabular form. Additional effort was required to correctly identify observed peaks in the complex multicomponent PE samples. The system is designed to provide analysis results at the completion of each run. With the 14-component PE mixtures provided in this demonstration, this was not always the case. The numerous peaks required closer examination and in some cases manual treatment of the data for best results. For less complex groundwater samples containing fewer than 5 or 6 contaminants, analysis and data reduction were more straightforward. Based on auditor observations, expertise in the use of spreadsheets and chromatogram data processing would be a useful skill during analysis of complex samples with this instrument.

As a result of the 3-foot column length, the short GC run time generates numerous, nearly coeluting peaks for complex mixtures such as the multicomponent PE samples used in this demonstration. The system does have a fast data acquisition frequency (50 Hz) that allows precise identification of retention times. As noted earlier, six pairs of coeluting compounds were reported at MAFB. Included were TCE, PCE, carbon tetrachloride, and benzene. These compounds do not coelute with each other, but could be masked by other peaks in complex mixtures. Analysis of complex mixtures may require additional care by the analyst in avoiding or interpreting coeluting peaks.

Data Availability and Changes

Preliminary data from the Model 4100 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 errors were corrected at the final data review. The concentration levels of several compounds were reevaluated and changed after the demonstration, when it was discovered that incorrect compound response factors in the original calibration file were applied to several compounds. (See Chapter 7 for additional vendor discussion on this issue.)

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 usually 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 Model 4100 is most applicable to routine monitoring applications where the sample composition is known and not complex. The system could also be successfully used in sample-screening situations where target contaminants are known. The instrument was unable to detect regulated chlorinated VOCs such as carbon tetrachloride and chloroform at concentration levels below about 50 µg/L. Care must also be taken to avoid compound coelution. Chromatographic methods may require special adjustment for a given routine monitoring application.

The observed precision and accuracy of the Model 4100 may be adequate for using this instrument for routine monitoring or screening situations. As with any application of a field instrument, the analyst or site manager must evaluate the performance characteristics of the instrument against the data quality objectives established for the project.

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.

Review of Demonstration and Results

The objective for testing the 4100 was to verify the effectiveness of the instrument as a screening tool. The ability of the 4100 to rapidly analyze samples in the field and achieve moderately accurate answers would be of great benefit to those interested in rapid site characterization. The instrument performed well in the field, and as many as 20 groundwater samples per hour were run. As the tests unfolded, it became clear that high accuracy and the detectability of low-level contaminants in the midst of high spiked analytes were of greater importance than just "screening." Often in measuring unknown samples, nondetects are encountered. These samples take just as long to analyze as the samples that contain analytes. Screening these samples at up to 20 per hour can save many hundreds of dollars in laboratory costs. The 4100 was configured to make these determinations rapidly in a field situation. The complex nature of the evaluation samples made the reporting of the results more challenging than originally envisioned and added somewhat to the final determination of sample throughput.

Summary of the Method

The analysis method adopted for water is a modified purge-and-trap method utilizing sample vial headspace. Bottles containing 200 mL of water are sampled for 2, 10, or 30 seconds, depending on the concentration of analyte. The 4100 traps the vapor in the headspace on a microtrap and injects it into the GC column. Because of the complexity of the samples, each was sampled at least twice. The first run gave the quantitative response. An internal standard was then added and a second run was performed to determine a relative retention time. Many samples were screened multiple times to determine the appropriate sampling time. Each analysis generates a chromatogram that reports the sample concentration in parts per billion for each analyte.

Sample Preparation and Handling

The water samples were received 10 or 20 at a time in 250-mL bottles at 4 °C. The method required that 50 mL of the water be poured off to create 50 mL of headspace in the bottle. It was observed that some loss of the lighter analytes occurs during this step of the procedure. Also, the temperature of the water influences the partitioning of the analytes between the liquid and the headspace. In this demonstration, the water temperature was not monitored during the analysis. The water temperature was generally lower than that of the water used for calibration and this difference may account for the lower than expected recovery figures that were obtained.

Data Processing and Output

The instrument reports the concentration of detected analytes at the end of each run, along with a traditional chromatogram. The postrun data analysis is performed by extracting the peak data and "logging" the stored chromatograms to make a single report that summarizes the results. This analysis is performed in an Excel program and requires a basic knowledge of spreadsheet techniques. A postrun analysis is not required; however, it was used at the SRS and MAFB sites to facilitate reporting results to the program monitors of the verification organization. Data can be analyzed in two ways. Calibration values can be stored in the peak file for each analyte, along with the retention time. If a peak falls within the retention time window established using the calibrated standards, the peak is identified and the concentration value is calculated based on the response factor for that compound. The concentration is then printed, along with the chromatogram. Because of the rapid analysis time, printing the chromatogram becomes a limiting factor for sample throughput. A second data analysis method involves the use of multiple runs collected into a single data file. The postanalysis logging of the data allows the software to list all compounds identified from multiple runs in a single file. Scale factors are then added to the Excel file and the analysis is done in Excel. New software will automate this process and dramatically speed up data processing in the future.

Some of the large observed errors were due to misidentification of peaks. In several cases, closely eluting peaks were misinterpreted and the values reported were therefore in error for both peaks (+100% for one and −100% for the other). This adversely affected the statistics for the determination of absolute percent difference.

QC Procedures and Corrective Actions

During the field tests at MAFB, the addition of an internal standard (1,2,4-trimethylbenzene) to the unknown matrix allowed the instrument to be normalized for compound retention time. The normalization was performed manually. New software will allow the normalization to occur semiautomatically. After each sample run, a blank run was performed to ensure that the trap was clean. If residual compounds existed, they were removed by heating the trap and baking it out. The only compound for which this was necessary was 1,3-hexachlorobutadiene. In the Model 4100, the retention time for this compound was 29.8 seconds. Its presence in the mix had no effect on sample throughput except to require extra trap cleaning cycles.

Sample Throughput

The 4100 has the ability to process relatively noncomplex samples (e.g., several components) at the rate of one every 120 seconds. All the groundwater samples (>30 total) at the SRC were run in a 2-hour period and totally rerun in a demonstration to key SRS personnel in the afternoon. These groundwater samples contained only TCE and PCE and could be processed quickly. The ability to rapidly process samples is the best feature of the 4100.

Data Availability and Changes

The response factors for some of the data were found to be in error when the data from the field were reevaluated. This error was a result of using the wrong version of the software for the field tests. The raw data were not affected and after the proper software version was applied to the data, the response factors were adjusted accordingly. This data-quality issue was addressed and precautions against this inadvertent error have been implemented.

Chapter 8
Previous Deployments

No information on previous deployments was submitted by the vendor.

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