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Environmental Technology Verification Report

Photoacoustic Infrared Monitor

Innova AirTech Instruments Type 1312 Multi-gas Monitor

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Innova AirTech Instruments Type 1312 Multi-gas Monitor

by

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Notice

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

ET✔

ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**PHOTOACOUSTIC INFRARED MONITOR**
APPLICATION:	**MEASUREMENT OF CHLORINATED VOLATILE ORGANIC COMPOUNDS IN WATER**
TECHNOLOGY NAME:	**Type 1312 Multi-gas Monitor**
COMPANY ADDRESS:	**Innova AirTech Instruments Energivej 30 2750 Ballerup, Denmark**
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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 Innova AirTech Instruments Type 1312 Multi-gas Monitor.

DEMONSTRATION DESCRIPTION

The field demonstration of the Type 1312 photoacoustic infrared monitor 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 McClellan Air Force Base, the target compounds were trichloroethene, tetrachloroethene, 1,2-dichloroethane, 1,1,2-trichloroethane, 1,2-dichloropropane, and *trans*-1,2-dichloropropene. These sites were chosen because they contain varied concentrations of chlorinated VOCs and exhibit different climatic and geological conditions. The conditions at these sites are typical, but not inclusive, of those conditions 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, Photoacoustic Spectrophotometer, Innova AirTech Instruments, Type 1312 Multi-gas Monitor*. (EPA/600/R-98/143).

TECHNOLOGY DESCRIPTION

The Type 1312 utilizes photoacoustic spectroscopy for the detection of chlorinated VOCs in the headspace of a water sample. The vapors from the equilibrium headspace of a stirred water sample are circulated through the instrument's measurement cell. When a gas in the cell is irradiated with electomagnetic energy at frequencies that correspond to resonant vibration frequencies of VOC compounds in the gas, a portion of the incident energy is absorbed, causing some of the molecules of the gas to be excited to a higher vibrational energy state. These molecules subsequently relax back to the lower-energy, vibrational state through a combination of radiative and kinetic processes. The kinetic energy decay process results in increased heat energy of the gas molecules and a corresponding temperature and pressure increase in the gas. The incident infrared source is modulated and the resulting pressure is also modulated. The varying pressure in the cell produces an acoustic wave that is detected with a high-sensitivity microphone. Compound specificity is achieved by using bandpass filters tuned to the energy absorption bands of target compounds, and quantification is done by measuring the intensity of the resulting acoustic signal.

The Type 1312 is a commercially available measurement system that provides groundwater analysis capabilities in a field-portable package. The instrument weighs 30 pounds with accessories and is encapsulated in a weather-resistant case. Required accessories include a motorized stir plate, a 2-L flask, and assorted connecting tubing. The system can be easily transported and operated in the rear compartment of a minivan. Instrument detection limits for TCE and PCE in water are in the vicinity of 5 μg/L. Sample composition must be known since the measurement technique is susceptible to interference from unknown VOCs in the sample. Sample processing and analysis can be accomplished by a technician; however, method development and periodic instrument calibration require a higher level of operator experience and training. About 1 day of training is recommended for a technician to be able to perform routine sample processing. At the time of the demonstration, the baseline cost of the Type 1312 was $28,000. Maintenance costs are less than $100 per year. And with the exception of a disposable inlet air filter, the instrument uses no consumable items, such as carrier gases or calibration standards.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the Type 1312 were observed:

Sample Throughput: Throughput was approximately one to two water samples per hour.

Completeness: The Type 1312 reported results for all but one of the 141 PE and groundwater samples provided for analysis at the two demonstration sites. One PE sample was dropped by the Innova team during preparation and handling.

Analytical Versatility: The Type 1312 was calibrated for and reported results for TCE and PCE. The Type 1312 reported results for 29 of 31 detects of TCE and PCE in groundwater samples from both sites that were reported by the reference laboratory. The instrument also reported results for carbon tetrachloride, chloroform, and *cis*-1,2-dichloroethene under appropriate circumstances. The instrument can report results for up to five compounds from a single analysis; however, sample composition must be known to account for possible spectral interferences from all sample components.

Precision: Instrument precision was determined by analysis of sets of four replicate samples from a variety of PE mixtures containing known concentrations of TCE and PCE. The range of relative standard deviations (RSDs) for TCE was 4 to 22%, and 5 to 46% for PCE. The distribution of RSD values for combined TCE and PCE measurements from both sites had a median value of 15% and a 95th percentile value of 34%. By comparison, the compiled RSDs for TCE and PCE from the reference laboratory had a median value of 9% and a 95th percentile value of 18%.

Accuracy: Instrument accuracy was evaluated by comparing Type 1312 results with the known concentrations of TCE and PCE in PE mixtures. The range of absolute percent differences (APD) for TCE was 4 to 48%, and 2 to 48% for PCE. The distribution of APD values for combined TCE and PCE measurements at both sites had a median value of 29% and a 95th percentile value of 47%. By comparison, the compiled APDs for TCE and PCE from the reference laboratory had a median value of 10% and a 95th percentile value of 25%.

Comparability: A comparison of Type 1312 and reference laboratory data was based upon 33 groundwater samples analyzed at each site. The correlation coefficient (r) for TCE and PCE detected by both the Type 1312 and the reference laboratory below the 300 µg/L concentration level was 0.984 at Savannah River and 0.892 at McClellan. The number of data pairs above the 300 µg/L concentration level was insufficient for a meaningful correlation analysis. The observed correlation coefficients reveal a linear relationship between the Type 1312 and laboratory data at both sites. The median absolute percent difference between mutually detected TCE and PCE by the Type 1312 and the reference laboratory was 29% with a 95th percentile value in excess of 2000%.

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 rental vehicle and was powered by line or generator ac power. During this demonstration, the system was set up and operated on a table. It can also be set up and operated in the rear luggage compartment of a minivan or station wagon.
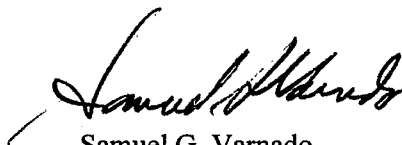
The results of the demonstration show that the Innova AirTech Instruments Type 1312 Multi-gas Monitor can provide useful, cost-effective data for routine groundwater monitoring when the composition of the samples is known. Since the composition of the sample must be known to avoid spectral interference, the instrument is not well suited for site characterization applications where the VOC content of the samples is unknown. 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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Foreword

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

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

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

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Executive Summary

The U.S. Environmental Protection Agency, through the Environmental Technology Verification Program, is working to accelerate the acceptance and use of innovative technologies that improve the way the United States manages its environmental problems. As part of this program, the Consortium for Site Characterization Technology was established as a pilot program to test and verify field monitoring and site characterization technologies. The Consortium is a partnership involving the U.S. Environmental Protection Agency, the Department of Defense, and the Department of Energy. In 1997 the Consortium conducted a demonstration of five systems designed for the analysis of chlorinated volatile organic compounds in groundwater. The developers participating in this demonstration were Electronic Sensor Technology, Perkin-Elmer Photovac, and Sentex Systems, Inc. (portable gas chromatographs); Inficon, Inc. (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 Innova Type 1312 Multi-gas Monitor. Reports documenting the performance of the other technologies have been published separately.

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

The demonstration provided adequate analytical and operational data with which to evaluate the performance of the 1312 Multi-gas Monitor (hereafter, the Type 1312 or 1312). Instrument precision and accuracy were determined from analysis of replicate samples from 13 standard mixtures containing trichloroethene (TCE) and tetrachloroethene, also known as perchloroethene (PCE). The relative standard deviations obtained from an analysis of replicate samples from each of the 13 two-component mixtures were used as measures of precision. The distribution of relative standard deviations for combined results from TCE and PCE had a median value of 15% and a 95th percentile value of 34%. Accuracy was expressed as the absolute percent difference between the 1312 measured value and the true value of the component in the standard mixtures. The distribution of absolute percent difference values for TCE and PCE in all mixtures had a median value of 29% and a 95th percentile value of 47%. A comparison of Type 1312 and reference laboratory TCE and PCE results from 33 groundwater samples at each site resulted in a median absolute percent difference of 29% with a 95th percentile value in excess of 2000%. The Type 1312 reported results for 29 of 31 detects of either TCE or PCE reported by the reference laboratory in all groundwater samples from both sites. A correlation analysis of 1312 and laboratory TCE and PCE groundwater results revealed a relatively high degree of linear correlation for Savannah River data ($r > 0.98$) and McClellan data ($r > 0.89$).

The Type 1312 costs between $28,000 and $35,000, depending on options, and can be operated by a field technician with minimal training. Method development and analysis of multicomponent samples may require a higher level of operator training and knowledge in use of the instrument. The throughput rate was in the range of one to two samples per hour. Analytical results are available at the conclusion of a sample run. The results of the demonstration show that the 1312 can provide useful, cost-effective data for routine groundwater monitoring in circumstances where the sample composition is known. As with any technology selection, the user must determine what is appropriate for the application by taking into account instrument performance and the project's data quality objectives.

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Acronyms and Abbreviations

ac	alternating current
APD	absolute percent difference
BNZN	benzene
°C	degrees centigrade
CCC	calibration check compounds
CCL4	carbon tetrachloride
CLFRM	chloroform
cm^{-1}	one per centimeter (wave number)
cm^3	cubic centimeters
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
ETV	Environmental Technology Verification Program
°F	degrees Farenheit
FTIR	Fourier-transform infrared
eV	electron-volt
GC	gas chromatograph
GW	groundwater
GC/MS	gas chromatograph/mass spectrometer
L	liter
m	meter
mg	milligram
mg/L	milligrams per liter
mL	milliliter
mm	millimeter
MAFB	McClellan Air Force Base
MCL	maximum concentration level
MDL	method detection limit
MS	mass spectroscopy
NERL	National Exposure Research Laboratory

NR	not reported
PC	personal computer
PCE	tetrachloroethene (perchloroethene)
PE	performance evaluation
ppb	parts per billion
ppbv	parts per billion volume
ppm	parts per million
ppmv	parts per million volume
PQL	practical quantitation limit
PVC	poly (vinyl chloride)
QA	quality assurance
QC	quality control
r	correlation coefficient
RPD	relative percent difference
RSD	relative standard deviation
SPCC	system performance check compounds
SRS	Savannah River Site
TCA	trichloroethane
111TCA	1,1,1-trichloroethane
TCE	trichloroethene
V	volts
V-A	volts-ampere
V ac	volts alternating current
V dc	volts direct current
VOA	volatile organics analysis
VOC	volatile organic compound
μg	microgram
μg/L	micrograms per liter
μL	microliter

Acknowledgments

For more information on the wellhead monitoring demonstration, 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

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- 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 photoacoustic infrared spectrometer from Innova AirTech Instruments. 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 Innova Type 1312 Multi-gas Monitor (hereafter referred to as the Type 1312 or the 1312) is a field-portable, photoacoustic spectrophotometer designed for monitoring volatile organic compounds in the vapor phase. A headspace sampling accessory extends the measurement capabilities of the instrument to water matrices as well. The instrument's measurement technique utilizes a photoacoustic effect, which is based on the conversion of light energy into sound energy by a gas, liquid, or soil. This effect was discovered and investigated by Alexander Graham Bell in the late 1800s, but was little more than a curiosity until the 1970s, when interest in the technique was renewed following the development of lasers and very sensitive detection techniques. Since that time, instruments employing photoacoustic principles have been used to monitor a wide variety of chemicals in stack and vent emissions, ambient air, and in the troposphere.

Principle of Operation

When a gas is irradiated with electromagnetic energy at a frequency that corresponds to a resonant vibration frequency of the gas, some of the energy will be absorbed by the gas. The absorption causes some of the molecules of the gas to be excited to a higher vibrational energy state. These molecules subsequently relax back to the initial vibrational state through a combination of radiative and nonradiative processes. For vibrational excitation, the primary relaxation process is a nonradiative, vibrational-to-translational energy transfer. An increase in the translational energy of the gas molecules corresponds to a temperature and pressure increase in the gas. The irradiating source is modulated, and the temperature and pressure response of the gas is also modulated. The modulated pressure will result in an acoustic wave, which can be detected with a sound measuring device, such as a microphone. The amplitude of the acoustic wave depends upon such factors as the geometry of the gas cell, the incident light intensity, the absorbing gas concentration, the absorption coefficient, and the background gas. For a nonresonant spherical gas cell under steady-state conditions, the amplitude of the acoustic wave can be determined from the following equation:

$$P = K\left[\left(C_p / C_v\right) - 1\right] I_0 c (1/f)$$

In the above, P is the sound pressure—the measured parameter, I_0 is the incident light intensity, c is the absorbing gas concentration, f is the modulation frequency, C_p and C_v are heat capacities, and K is a cell- and gas-dependent constant.

The monitor, shown in Figure 2-1, is known as the Innova (formerly Brüel & Kjaer) Type 1312 Multi-gas Monitor. The instrument uses a heated nichrome wire as its infrared radiation source. The light from the source is focused by an ellipsoidal mirror, modulated with a mechanical chopper, and passed through an optical filter before entering the photoacoustic gas cell. The acoustic signal is detected with a pair of condenser microphones. The electrical signals from the microphones are amplified by preamplifiers mounted directly on the back side of the microphones and added in a summation amplifier before being sent to an analog-to-digital converter for further processing. The digitized signal is then converted to a concentration reading using a calibration factor that is stored in the instrument.

The 1312 measures $6.9 \times 15.6 \times 11.8$ inches and weighs 20 pounds. Its power consumption is 100 V-A and power can be supplied by either a 110-V ac or a 12-V dc source. The cost of the system depends on the intended use and expected sample matrix, but will fall in the range of $28,000 to $35,000.

The 1312 is a newer version of the Type 1302 that was previously tested at the Savannah River Site for the measurement of chlorinated VOC compounds in air. The Type 1312 has a signal-to-noise ratio that is improved over the 1302, resulting in lower detection limits. The 1312 can also work with lower sample volumes, making it more suitable for headspace monitoring applications. During this demonstration, the instrument was connected to a stirred recirculation flask, as shown in Figure 2-1, for improved response time.
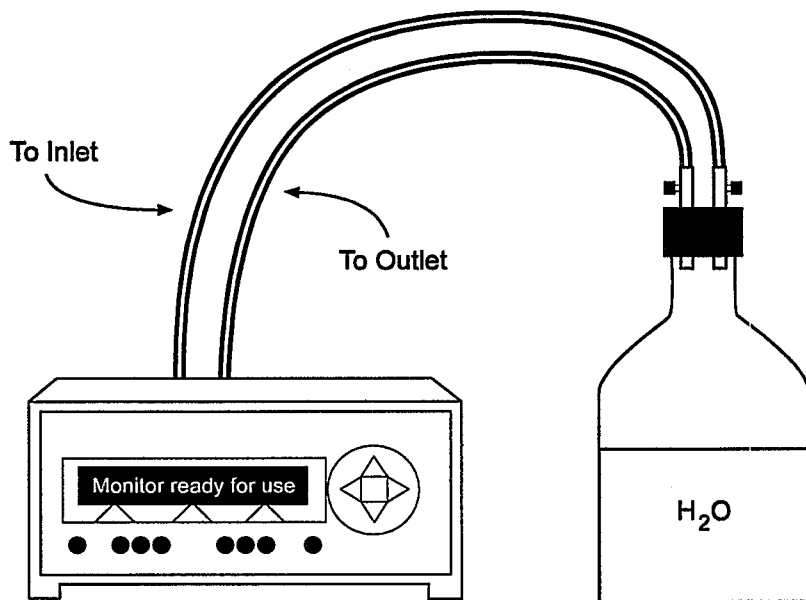
Figure 2-1. A diagram of the Innova Type 1312 Multi-gas Monitor configured for headspace monitoring.

History of the Technology
Both optical filter and Fourier-transform infrared (FTIR) photoacoustic instruments have been used and evaluated for monitoring chlorinated volatile organic compounds in the air at soil remediation sites and from gas wells and boreholes at contaminated sites. They have also been used to analyze chlorinated VOCs purged from soil and water samples.

One application of chlorinated VOC monitoring with the 1312 is the analysis of perchloroethene (tetrachloroethene) (PCE) and trichloroethene (TCE) mixtures. The ability of the instrument to monitor the compounds simultaneously has been evaluated in the laboratory and in the field at the Savannah River Site in South Carolina. TCE and PCE are monitored using the 861 cm^{-1} and 900 cm^{-1} spectral regions, respectively. The optical bandpass of the filters used for these regions is approximately 60 cm^{-1}. Since some interfering absorbance from each compound is encountered in these spectral regions, a matrix method is used to determine each concentration. In this method, the matrix equation $KC = S$ is solved for C, where S is a column vector containing the measured signals for each optical region, K is a matrix containing the response factors for each gas in each of the different spectral regions, and C is a column vector containing the concentrations of each chemical.

Laboratory work has shown a linear photoacoustic sensor response for both PCE and TCE up to approximately 700 parts per million volume (ppmv) with a detection limit of approximately 0.07 ppmv for each. Above 700 ppmv, the response becomes nonlinear. Measurements on mixtures of TCE and PCE indicate that accurate results can be obtained using the above matrix method.

The 1312 has previously been evaluated for field use in several different test scenarios at the Savannah River Site. In one scenario, the instrument was used to monitor the concentration of PCE and TCE in the gas from a horizontal extraction well. Measurement results were compared with the results from a gas chromatograph (HP Model 5890). In general, the two instruments agreed to within 20% for both gases. The average relative percent difference (RPD)[1] for the 1312 compared with the GC was 10.0% (at concentrations less than 250 ppmv) and 11.4% (at concentrations greater than 250 ppmv) for PCE, with accuracy values of 9.8% and 7.4%, respectively, for TCE. The precision (or stability) of the instrument was also evaluated over a 30-day interval by periodically measuring 100 ppmv standards. The relative standard deviation (RSD)[2] for five measurements over this time period was 0.9% for PCE and 1.2% for TCE.

The instrument has also been used to monitor gas from vadose-zone wells, from off-gas treatment systems, and to determine depth-discrete, soil-vapor concentrations of TCE and PCE with a cone penetrometer. A Fourier-transform infrared photoacoustic instrument from Innova has also proven successful for laboratory-based purge-and-trap analysis of PCE, TCE, carbon tetrachloride, and chloroform in water at Ames Laboratory, Iowa State University. These investigations revealed detection limits for these compounds in the very low parts per billion (ppb) range. Photoacoustic spectroscopy monitors from Innova have also been successfully used in indoor air quality measurements (several units have been sold to the U.S. EPA), industrial hygiene applications, fermentation emissions monitoring, and many more applications.

Advantages

Some of the advantages and characteristics of infrared photoacoustic spectroscopy as it pertains to monitoring trace gases are as follows:

- High sensitivities can be obtained. Instruments using conventional infrared light sources, such as heated nichrome wires, have demonstrated detection limits in the low parts per billion volume to parts per million volume range for single gases.

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

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

- Photoacoustic instruments are very stable, primarily as a result of the stability of the microphones. Microphones are some of the most stable transducers known, with output drifts of <10% over hundreds of years.

- A dynamic range of up to six orders of magnitude relative to the detection limit for a particular gas can be achieved. Thus, very low as well as high contaminant concentrations can be measured with a single instrument.

- Cell volume is very small (3 cm^3), thus reducing the amount of sample and calibration gas needed. The small cell volume also results in a compact instrument.

- Simple instrument and optical setups can be used. In particular, multipass gas cells are not needed, thus eliminating the problems of maintaining optical alignment through this type of cell.

- Photoacoustic systems measure the absorbance directly instead of indirectly as in transmission-type instruments. Consequently, a good baseline stability results.

- No consumables are needed, keeping operational costs low.

- The instrument will function in temperatures ranging from 5 to 40 °C.

Limitations

The main limitation of the technology is the fact that most organic gases absorb energy over a wide range of the infrared spectrum, making the measurement susceptible to interferences. The 1312 has a unique cross-compensation algorithm that allows it to compensate for known interferences. Potential interferences include all compounds that are active in the midinfrared region. In a sample matrix with unknown interferences, measurement results could be erroneous. The technology cannot wholly replace laboratory testing, but it can significantly reduce the amount of testing needed.

Improvements

Innova is investigating the use of various semipermeable silicone tubing configurations that will potentially permit measurements to be made directly in the liquid sample, thus eliminating the need to do headspace monitoring.

Applications

Photoacoustic spectroscopy technologies have been successfully used to measure various organic compounds in air. By bringing the analyte of interest into the gas phase, the technology can also be used to monitor various organic compounds in water, soil, and sludge.

As a result of high sensitivity combined with an extremely small sample cell, this technology is the only infrared-based technology that can achieve the low detection limits needed for water and soil analysis applications. Since the technology is extremely easy to use, even unskilled operators can achieve good results. The instrument is best suited for routine monitoring applications where the composition of the contaminants in the water is known.

Performance Characteristics

Method Detection Limits and Practical Quantitation Limit

With this technology, almost any volatile chlorinated species that absorbs in the infrared spectrum can be measured with a headspace sampling technique. In general, chlorinated species have strong infrared absorption

and thus have low detection limits. In this demonstration, measurements were made for TCE, PCE, and chloroform. Detection limits for chlorinated species in air are typically in the range of 50 to 100 ppbv. Detection limits for the same compounds in water range from 1 to 10 ppb. Detection and quantitation limits for PCE and chloroform have been determined for the Type 1302 monitor (a predecessor to the 1312) and are given in Table 2-1. With the newer 1312 monitor, expectations are that the method detection limits (MDLs) and practical quantitation limits (PQLs) will improve by a factor of three without affecting the upper limit of the working range. The practical quantitation limits (defined as 3 × MDL) are also given in Table 2-1.

Table 2-1. MDL and PQL in Air and Water Samples for the Type 1302 Multi-gas Monitor

Analyte	MDL Air (ppb)	MDL Water (ppb)	PQL Water (ppb)
Tetrachloroethene	70	2	7
Chloroform	70	3	10

Accuracy
Measurements have not been made on a certified standard with the headspace measurement technique. However, as mentioned earlier, the results of the Type 1302 air sample measurements were within 20% of the gas chromatography results.

Precision
Instrument precision for the Type 1312 is better than 20% RSD for concentrations ranging from the PQL to 0.5 ppm and better than 10% RSD over the upper end of the instrument's working range.

Instrument Working Range
For air samples, the working range for chloroform and tetrachloroethene, with a one-point calibration, is from the PQL (0.2 ppmv) to 700 ppmv.

For water samples, a test of a 1-L volume of water in a 2.5-L flask gave the following results: 1 ppm chloroform in water correlated to 35 ppm in the headspace, and 1 ppm tetrachloroethene in water correlated to 50 ppm in the headspace. These results yielded a working range for chloroform and PCE as shown in Table 2-2, using a one-point calibration of the instrument. With a two-point calibration, the range was extended as shown in Table 2-2.

Table 2-2. Working Range of the Innova Type 1312 Photoacoustic Monitor in Water

Analyte	Single-Point Calibration	Two-Point Calibration
Tetrachloroethene	7 ppb–15 ppm	7 ppb–150 ppm
Chloroform	10 ppb–20 ppm	10 ppb–200 ppm

Comparison with Reference Laboratory Analyses
At the time of the demonstration, the developer had not performed this comparison.

Data Completeness

Analysis and valid results will be reported for 95% or more of the samples presented for analysis during the demonstration, provided that no unknown interferences are present.

Specificity

The Type 1312 has a built-in cross-compensation feature. The instrument can compensate for up to four known interfering species and water vapor. If the instrument is not calibrated to perform compensation for an interfering substance, the signals are added and the measurement result is dependent upon the degree of energy absorption of the interfering substance at the wavelength range of the optical filter in use. Consider the following example:

- 10 ppm of chloroform and 100 ppm of xylene are present in the headspace.
- Without cross-compensation, 100 ppm of xylene are equivalent to 3.5 ppm of chloroform.
- With cross-compensation, the interference is reduced to a positive interference of 0.07 ppm.

Other Field Performance Characteristics

Instrument Setup and Disassembly Time

The setup time for the system is less than 15 minutes. The system can be air shipped in a container or, alternatively, can be transported as a carry-on item.

Instrument Calibration Frequency During Field Use

The recommended instrument calibration interval is 3 months.

Ancillary Equipment and Field Maintenance Requirements

The system requires 110-V ac but can also be operated on 12-V dc through an external dc-to-ac inverter. A fine-particle air inlet filter needs replacement once a month. No other consumables are required for routine field use or maintenance.

Sample Throughput Rate

The expected throughput rate is three samples per hour.

Operator Training Requirements and Ease of Operation

Less than 1 hour of training is required to become proficient in operating the instrument.

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.

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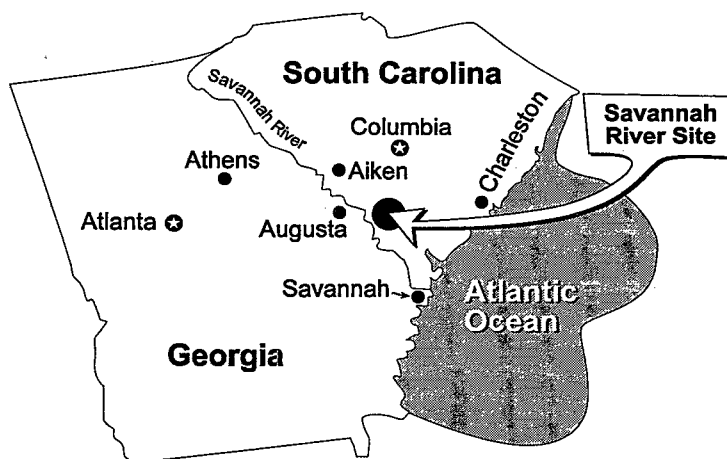
Figure 3-1. The general location of the Savannah River Site in the southeast United States.

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.

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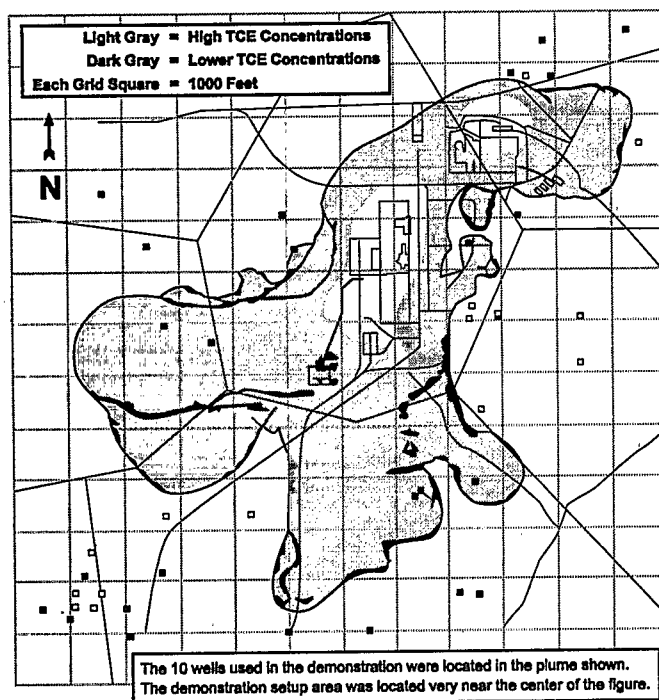
Figure 3-2. A map of the A/M area at the Savannah River Site showing the subsurface TCE plume.

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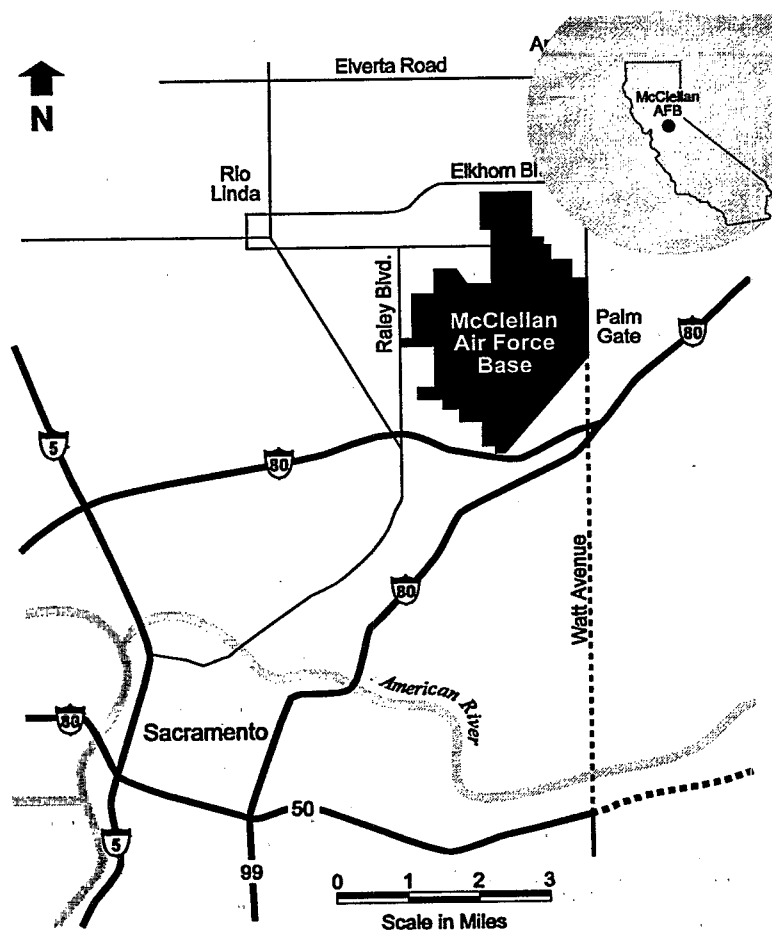
Figure 3-3. A map of Sacramento and vicinity showing the location of McClellan Air Force Base.

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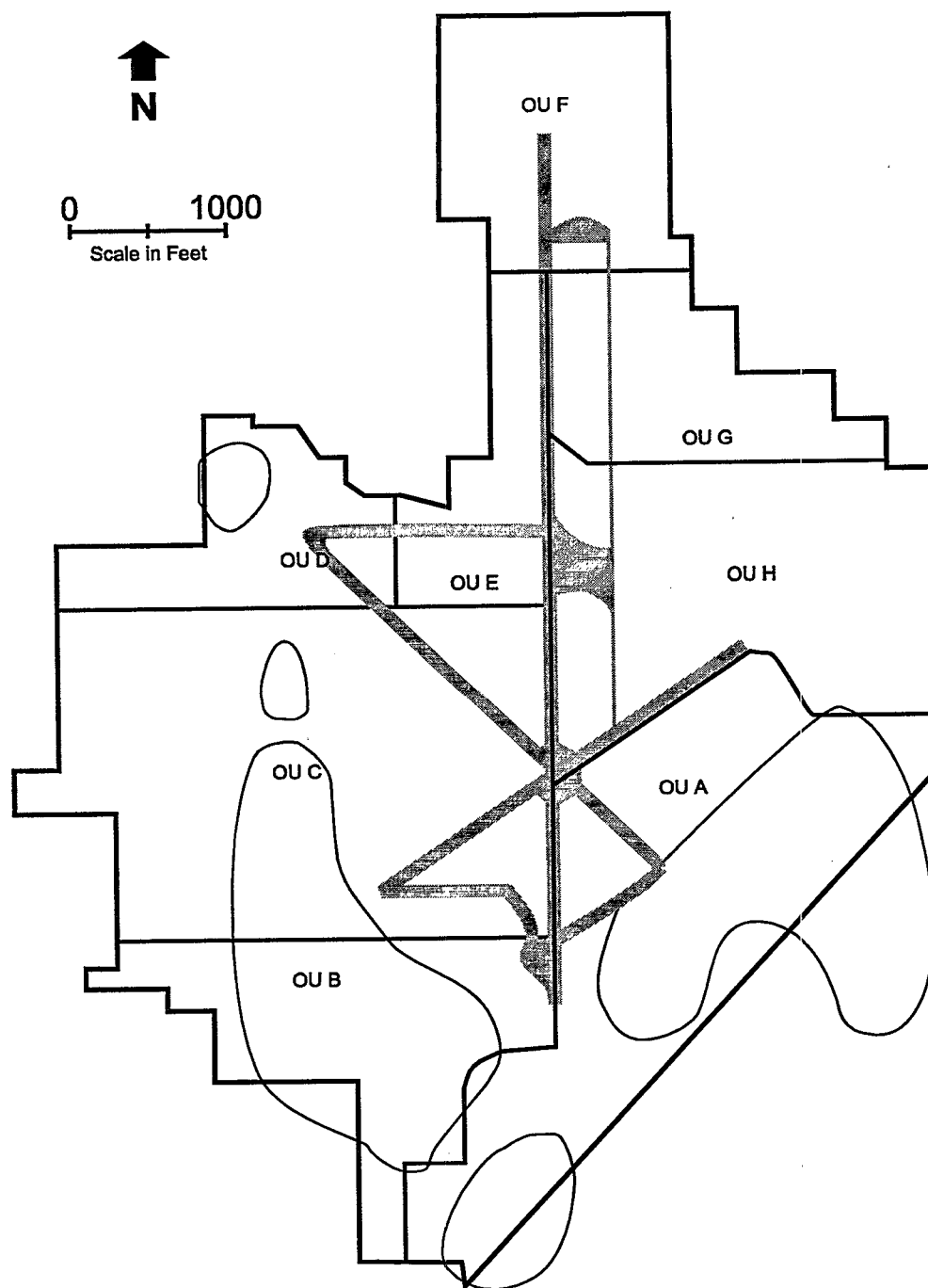
Figure 3-4. Subsurface TCE plumes at McClellan Air Force Base in the shallowest (A) aquifer layer. The circular lines enclose plume concentrations in excess of 5 μg/L TCE. OU refers to operational units. Monitoring wells used in the demonstration were primarily in OUs A and B. The demonstration setup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

Note: The description of PE samples in the following paragraphs pertains to the other four field technologies that participated in the demonstration. The narrative is included here since the laboratory data validation was based on analysis results from the PE sample set. Since the Innova 1312 is not capable of analyzing complex mixtures, a separate set of PE samples was prepared and distributed for analysis. A description of these Innova PE samples is given in the "Deviations" section at the end of this chapter.

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 of 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

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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.

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 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.

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.

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.

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.

- A different set of PE samples was prepared for the Innova 1312. The data processing algorithm used in the Innova instrument could not accommodate the complex mixtures contained in the PE mixtures distributed to the other participants. The Innova instrument was limited to the analysis of 5 compounds while the PE mixtures contained in excess of 10 chlorinated VOCs. To accommodate these special needs, 2-component PE mixtures were prepared from stock TCE and PCE methanol solutions at the SRS demonstration. The composition of these mixtures is given in Table 3-8 for SRS and Table 3-9 for MAFB.

Table 3-8. Innova PE Sample Composition and Count for SRS Demonstration

Sample Conc. Range	PE Mixture and Composition (µg/L)		Replicates
Very low	Mix SVL1	10 (trichloroethene and tetrachloroethene)	6
Low	Mix SL1	50 (trichloroethene and tetrachloroethene)	3
	Mix SL2	100 (trichloroethene and tetrachloroethene)	3
Mid	Mix SM1	200 (trichloroethene and tetrachloroethene)	3
	Mix SM2	256 trichloroethene 245 tetrachloroethene	4
High	Mix SH1	400 (trichloroethene and tetrachloroethene)	3
	Mix SH2	693 trichloroethene 713 tetrachloroethene	4
Very high	Mix SVH	1278 trichloroethene 1223 tetrachloroethene	4

Table 3-9. Innova PE Sample Composition and Count for MAFB Demonstration

Sample Conc. Range	PE Mixture and Composition (µg/L)		Replicates
Very low	Mix MVL1	9 trichloroethene 11 tetrachloroethene	5
Low	Mix ML1	42 trichloroethene 47 tetrachloroethene	4
	Mix ML2	80 trichloroethene 89 tetrachloroethene	4
Mid	Mix MM1	169 trichloroethene 188 tetrachloroethene	4
	Mix MM2	319 trichloroethene 355 tetrachloroethene	4
High	Mix MH1	758 trichloroethene 845 tetrachloroethene 401 1,1-dichloroethene 392 benzene	4
Very high	Mix MVH1	1434 trichloroethene 1598 tetrachloroethene 761 1,1-dichloroethene 741 benzene	4

- Eight blank water samples were also included in the sample set at each site and were submitted blind. A total of 38 and 37 PE and blank samples were prepared and submitted to the Innova team at the SRS and MAFB sites, respectively.

- The groundwater samples submitted to the Innova team for analysis were the same as those submitted to the other demonstration participants.

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.

DCL Laboratory Control Standard Recoveries
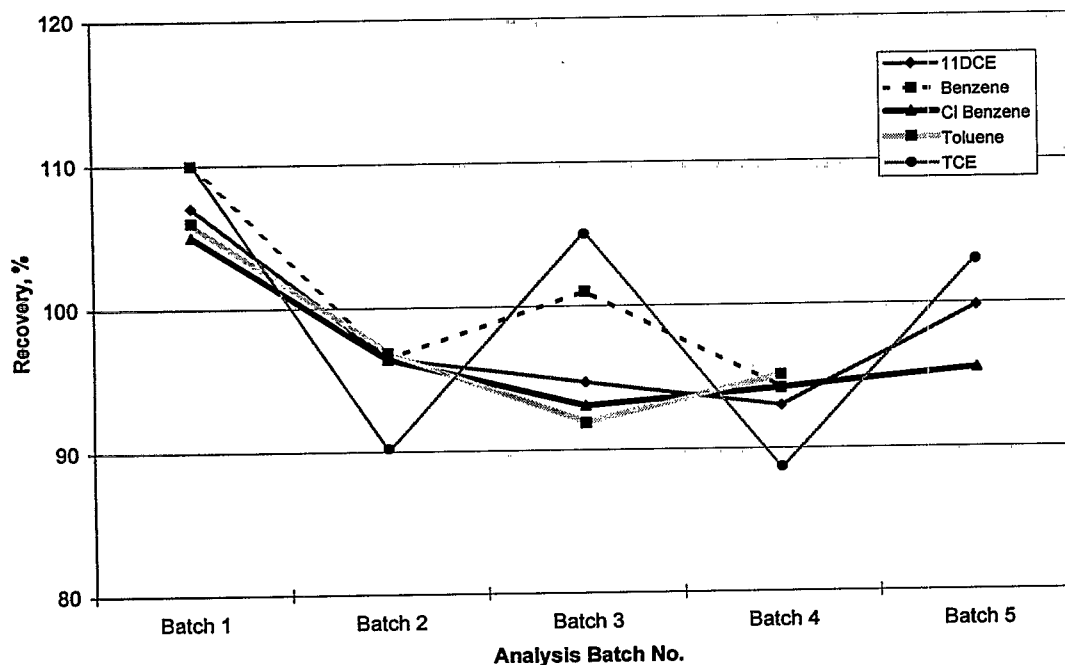**Savannah River Data Set**

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

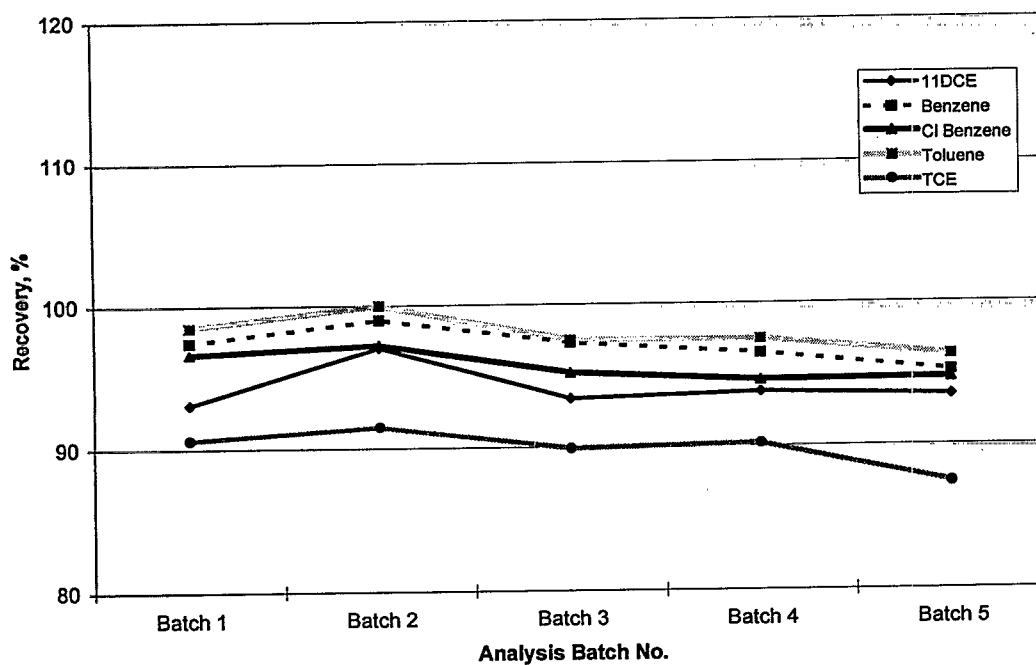**DCL Laboratory Control Standard Recoveries**
McClellan Data Set

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

Surrogate Standard

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

Summary of Analytical and QC Deviations

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

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

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

Other Data Quality Indicators

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

PE Sample Precision

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

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

PE Sample Accuracy

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

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

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

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

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

DataChem PE Sample Precision
Site: Savannah River Mix 1
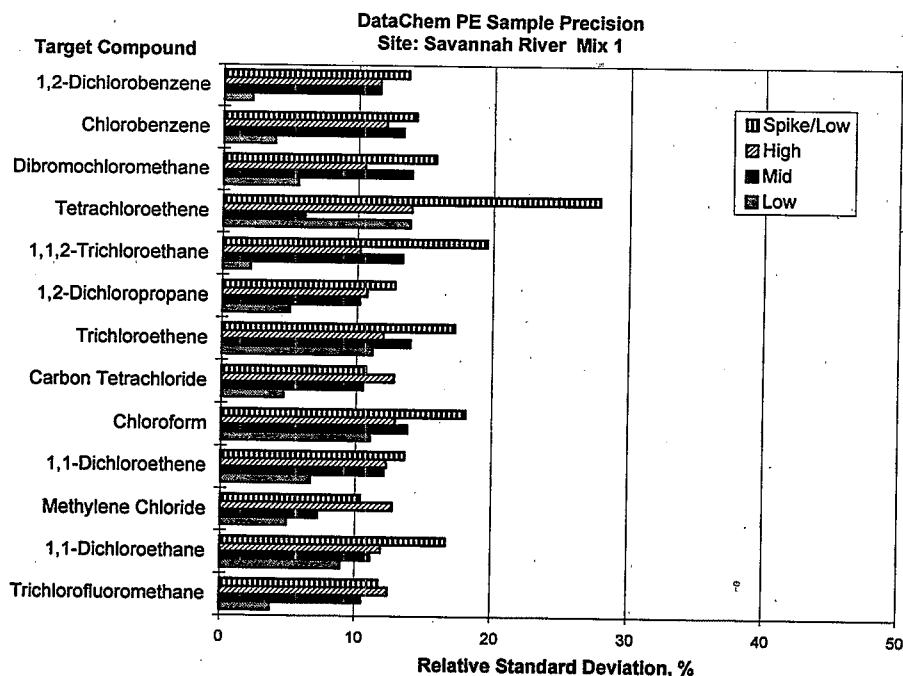
Figure 4-3. Laboratory precision on SRS PE samples containing mix 1. Trichloroethene was spiked into the spike/low samples.

DataChem PE Sample Precision
Site: Savannah River Mix 2
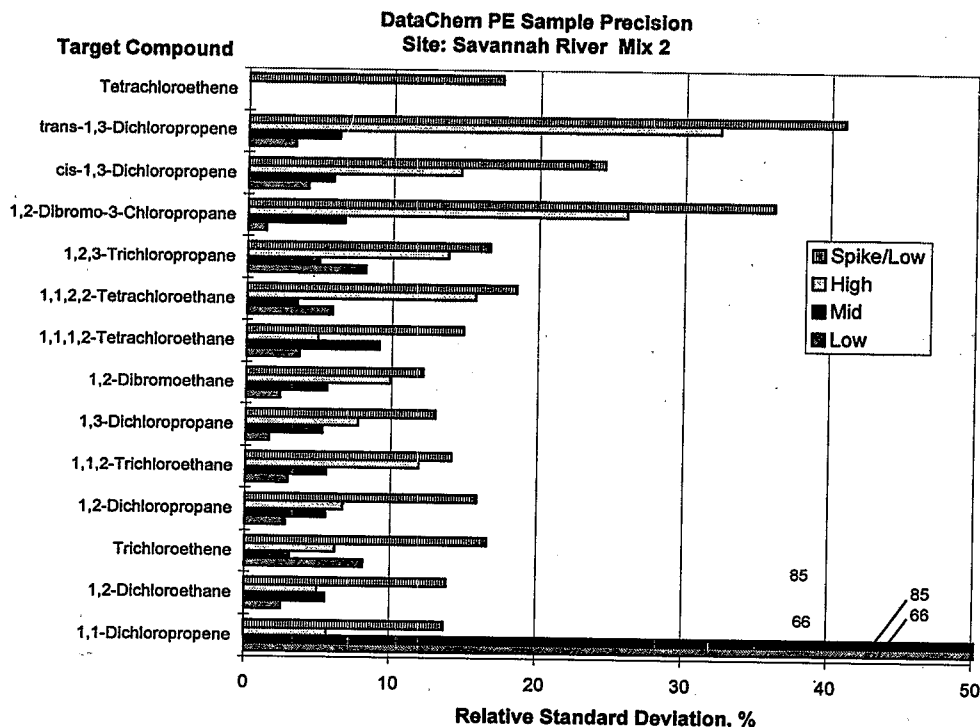
Figure 4-4. Laboratory precision on SRS PE samples containing mix 2. Tetrachloroethene was spiked into the mix 2 samples. Trichloroethene and tetrachloroethene were spiked into the spike/low samples.

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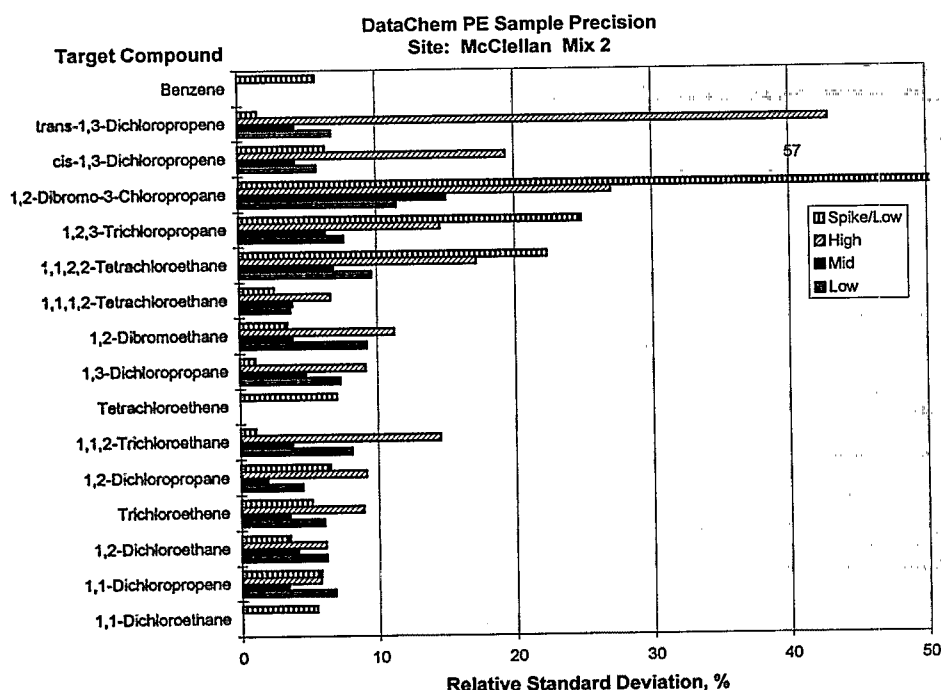
Figure 4-5. Laboratory precision on MAFB PE samples containing mix 2. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.

DataChem PE Sample Precision
Site: McClellan Mix 3
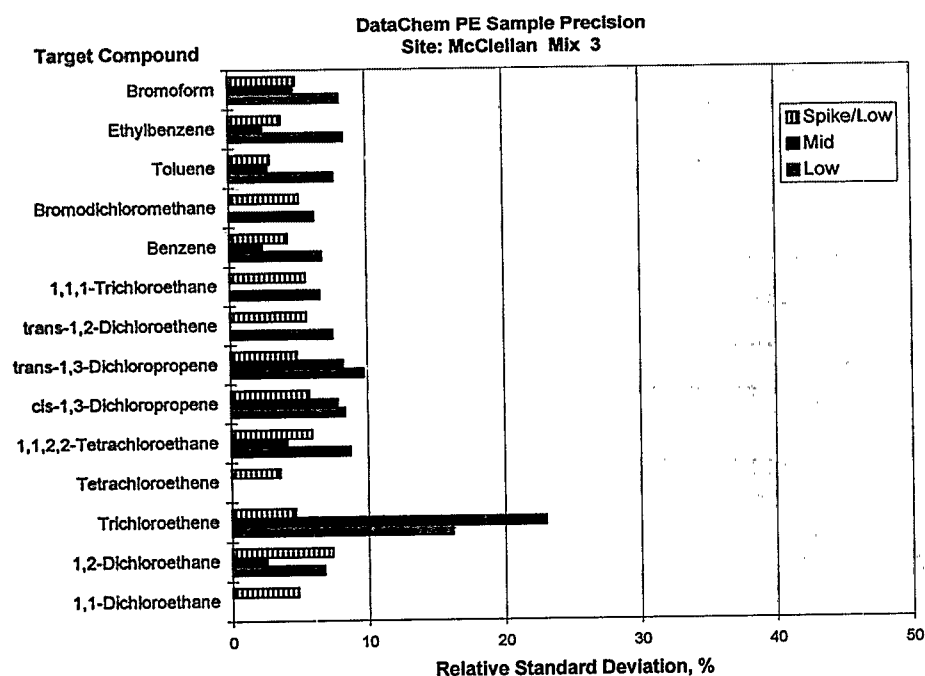
Figure 4-6. Laboratory precision on MAFB PE samples containing mix 3. Trichloroethene, tetrachloroethene, 1,1-dichloroethane, and benzene were spiked into the spike/low samples.
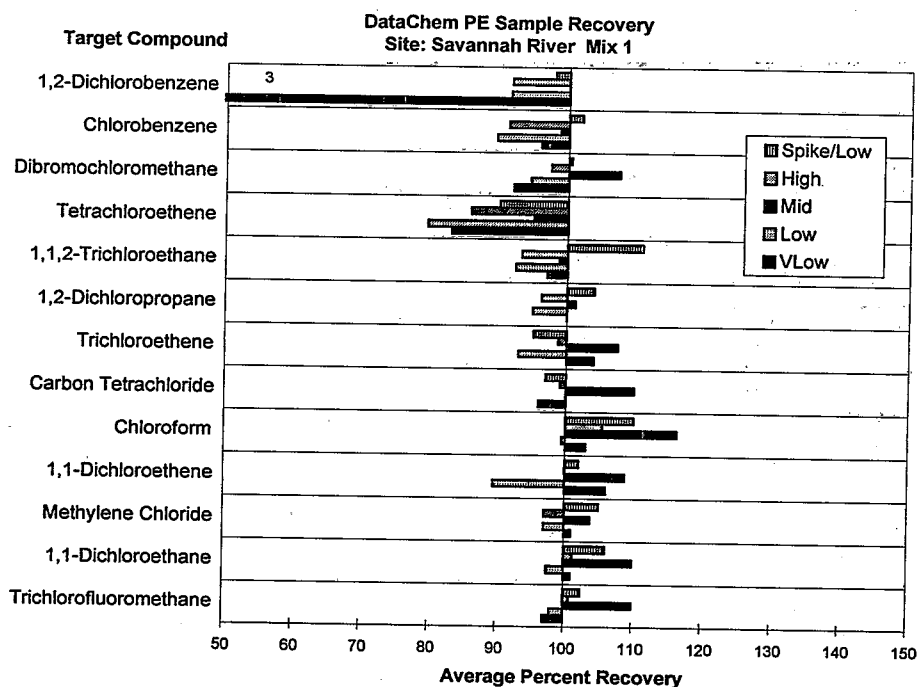
Figure 4-7. Laboratory mean recoveries for SRS PE samples containing mix 1. Trichloroethane was spiked into the spike/low samples.
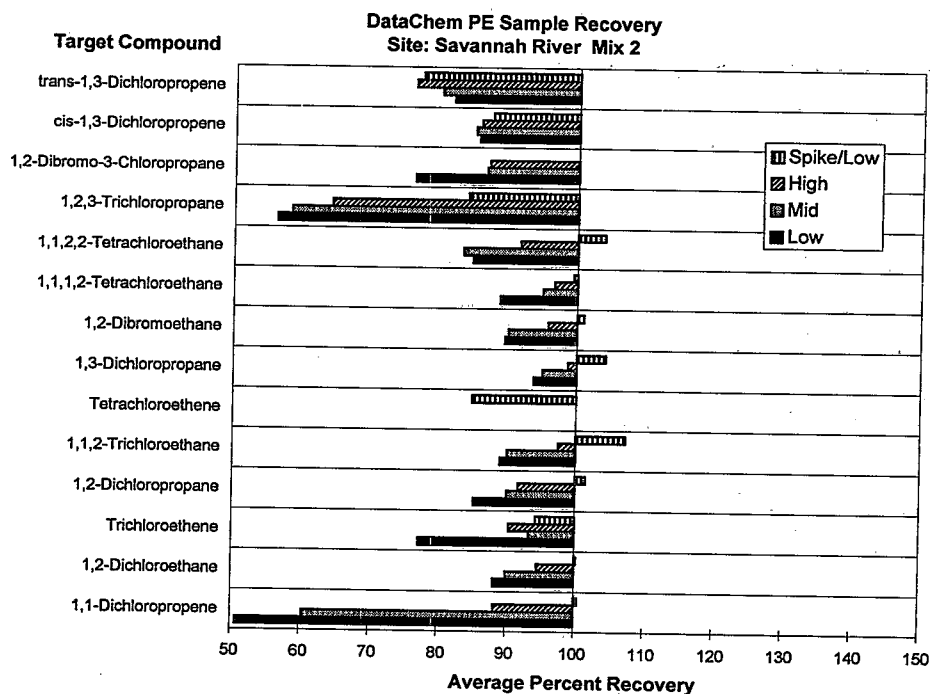
Figure 4-8. Laboratory mean recoveries for SRS PE samples containing mix 2. Trichloroethane and tetrachloroethene were spiked into the spike/low samples.

DataChem PE Sample Recovery
Site: McClellan Mix 2

Target Compound

Benzene
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
1,2-Dibromo-3-Chloropropane
1,2,3-Trichloropropane
1,1,2,2-Tetrachloroethane
1,1,1,2-Tetrachloroethane
1,2-Dibromoethane
1,3-Dichloropropane
Tetrachloroethene
1,1,2-Trichloroethane
1,2-Dichloropropane
Trichloroethene
1,2-Dichloroethane
1,1-Dichloropropene
1,1-Dichloroethane

Legend: Spike/Low, High, Mid, Low

Average Percent Recovery (x-axis: 50 60 70 80 90 100 110 120 130 140 150)

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.

DataChem PE Sample Recovery
Site: McClellan Mix 3

Target Compound

Bromoform
Ethylbenzene
Toluene
Bromodichloromethane
Benzene
1,1,1-Trichloroethane
trans-1,2-Dichloroethene
trans-1,3-Dichloropropene
cis-1,3-Dichloropropene
1,1,2,2-Tetrachloroethane
Tetrachloroethene
Trichloroethene
1,2-Dichloroethane
1,1-Dichloroethane

Legend: Spike/Low, Mid, Low, VLow

Average Percent Recovery (x-axis: 50 60 70 80 90 100 110 120 130 140 150)

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.

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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%.
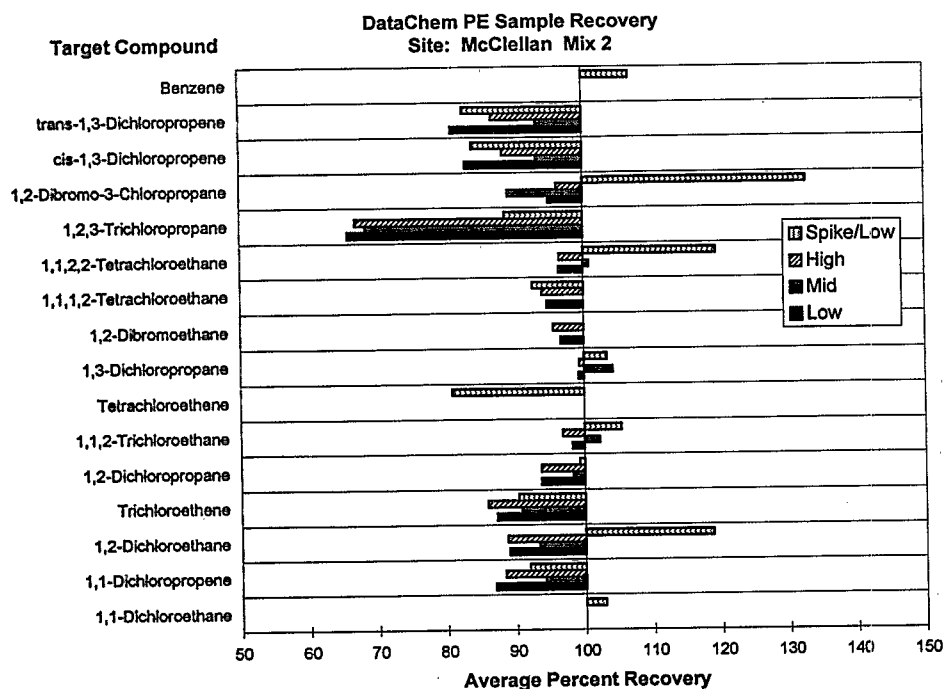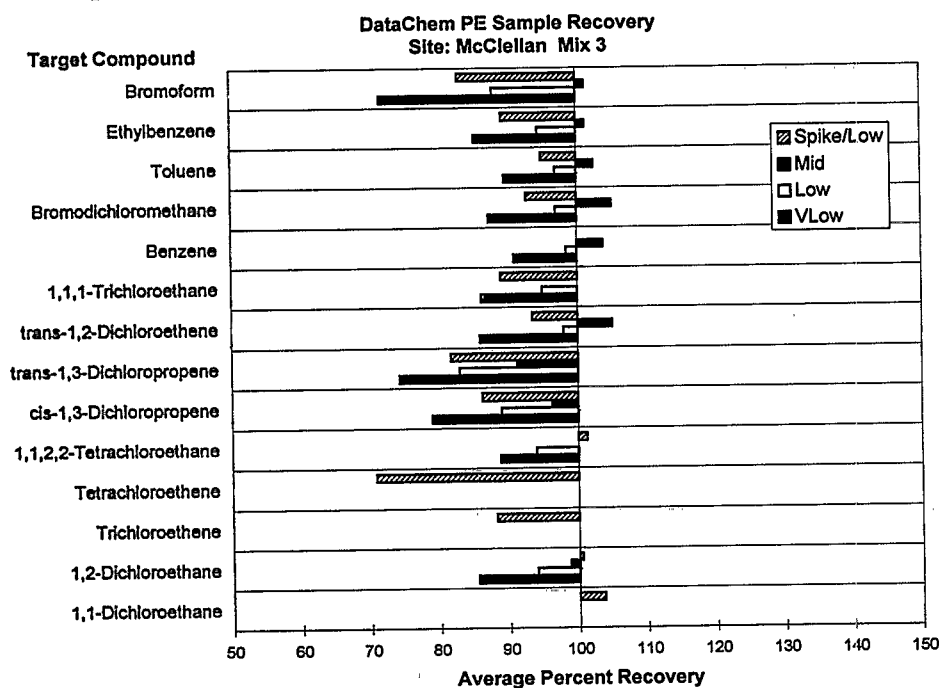
Table 4-5. Summary of SRS Groundwater Analysis Precision

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

Type 1312 Calibrated and Reported Compounds

The 1312 was calibrated primarily for TCE and PCE in this demonstration, and PE mixtures containing only these two compounds were provided to the Innova team for analysis. In selected groundwater samples, other compounds were reported when the appropriate bandpass filters and calibration data for the instrument were available in the field. Table 5-1 lists the compounds for which the 1312 reported results in either PE or groundwater samples.

Table 5-1. Type 1312 Calibrated and Reported Compounds

Compounds Reported at SRS
Trichloroethene
Tetrachloroethene
1,1,1-Trichloroethane
Compounds Reported at MAFB
Trichloroethene
Tetrachloroethene
Carbon tetrachloride
cis-1,2-Dichloroethene
Chloroform

Preanalysis Sample Information

As noted in Chapter 2, successful use of the Type 1312 requires that the composition of the sample be known so that spectral interferences can be accounted for. Consequently, both PE and groundwater samples were accompanied by information on the chain-of-custody forms indicating the contaminants that were present in the sample. For groundwater samples, the most recent quarterly monitoring results from each sampled well (given in Chapter 3) were used for information on sample composition.

Sample Completion

All but one of the 141 PE and groundwater samples submitted for analysis to the Innova team were completed at both demonstration sites. A PE sample from the very low category at the SRS was lost by the Innova team during handling.

Blank Sample Results

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

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

SRS Blank Samples		MAFB Blank Samples	
Compound	False Positive	Compound	False Positives
Trichloroethene	1 of 8 (13%)	Trichloroethene	1 of 8 (13%)
Tetrachloroethene	0 of 8	Tetrachloroethene	0 of 8

Performance at Instrument Detection Limit

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

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

SRS PE Mix 1 10 μg/L (TCE and PCE)		MAFB PE Mix 3 9 μg/L TCE and 11 μg/L PCE	
Compound	False Negative	Compound	False Negative
Trichloroethene (2)	0 of 6	Trichloroethene (2)	1 of 4 (25%)
Tetrachloroethene (2)	3 of 6 (50%)	Tetrachloroethene (2)	1 of 4 (25%)

Note: Vendor-provided detection limits (in μg/L) are shown in parentheses after each compound.

PE Sample Precision

Precision results from each of the replicate sample sets provided from seven PE mixtures at the SRS and six mixtures at MAFB are shown in Figures 5-1 and 5-2, respectively. The figures show the relative standard deviation for TCE and PCE at the concentration levels used in the study. (The composition and concentrations of each of these mixtures are given in Table 3-8 for SRS and Table 3-9 for MAFB.) Note that precision and accuracy were not determined for the "very low" concentration level. The data are also presented in tabular form in Table 5-4.

Table 5-4. Precision for TCE and PCE at Both Sites

Compound	Site	Relative Standard Deviation (%)						
		Low 1	Low 2	Mid 1	Mid 2	High 1	High 2	Very High1
Trichloroethene	SRS	22	18	13	7	19	9	22
	MAFB	16	17	20	14	4		8
Tetrachloroethene	SRS	46	21	11	8	8	10	7
	MAFB	38	22	13	22	16		5

Note: Blank cells indicate that no data were reported.
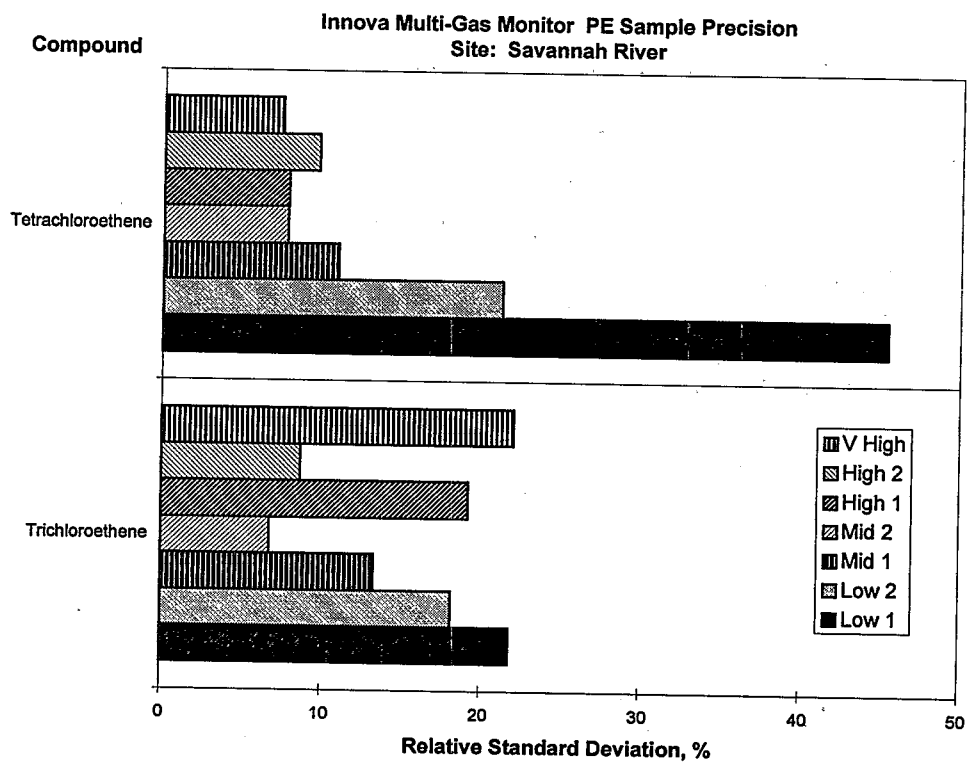
Figure 5-1. Type 1312 PE sample precision at the SRS.
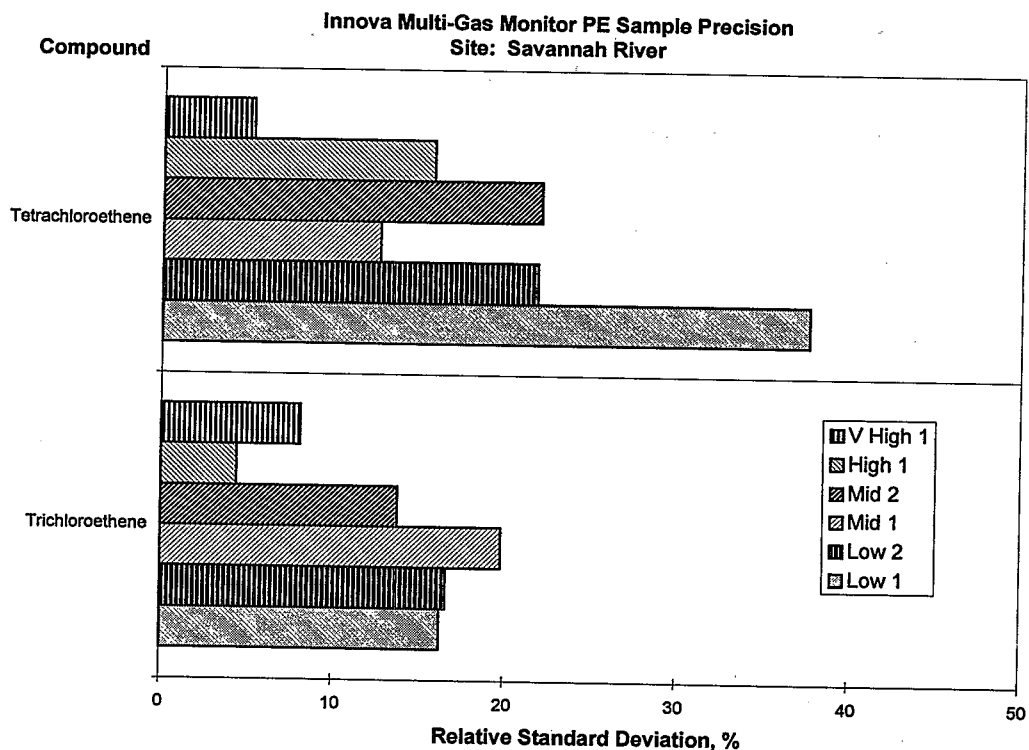
Figure 5-2. Type 1312 PE sample precision at MAFB.

Overall instrument precision is summarized in Table 5-5 for PE mixtures used at each site. 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 5-5. Summary of PE Sample Precision and Percent Difference Statistics for the SRS and MAFB

Parameter	Percentile	SRS	MAFB	Combined Sites
RSD, %	50th	12	16	15
	95th	30	29	34
	Number in pool	14	12	26
Absolute percent difference	50th	36	9	29
	95th	48	22	47
	Number in pool	14	12	26

PE Sample Accuracy

The accuracy of the Type 1312 in analyzing PE samples was determined by comparing the average value from each of the replicate sample sets with the known concentration of the PE mixture (Tables 3-8 and 3-9 for SRS and MAFB, respectively). These comparisons are shown as percent recoveries[1] in Figures 5-3 and 5-4 for the SRS and MAFB, respectively. To assist in assessing the sign of the difference, the percent recovery data are plotted as either a positive or negative difference from the 100% recovery line. The percent recovery values are also expressed as absolute percent difference (APD) values[2] and are shown in Table 5-6. (For example, a 90% recovery is equivalent to a −10% difference; a 120% recovery is equivalent to a +20% difference.) Table 5-5 contains a summary of overall 1312 absolute percent differences relative to the true or reference value of the PE mixtures, along with the precision summary. These summaries are from pooled TCE and PCE data from each site. The median and 95th percentiles of the absolute values of these pooled values were computed and are reported under the absolute percent difference category in Table 5-5.

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

Target Compound	Site	Absolute Percent Difference						
		Low 1	Low 2	Mid 1	Mid 2	High 1	High 2	Very High1
Trichloroethene	SRS	39	39	34	35	35	38	48
	MAFB	20	15	4	11	5		10
Tetrachloroethene	SRS	42	34	25	33	34	36	48
	MAFB	24	21	8	2	3		7

Note: Blank cells indicate that no data were reported.

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[1] Percent recovery is the Type 1312 value divided by the true value, multiplied by 100.
[2] 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%.

Innova - Mult-Gas Monitor PE Sample Recovery
Site: Savannah River
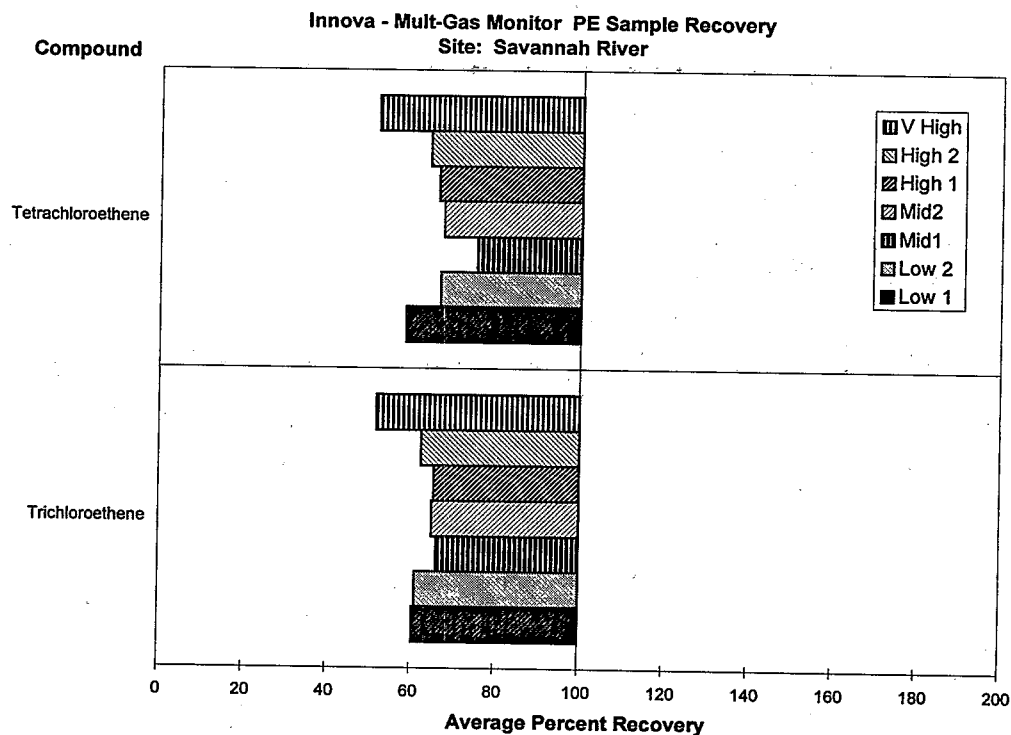
Figure 5-3. Type 1312 PE sample recovery at the SRS.

Innova Mult-Gas Monitor PE Sample Recovery
Site: McClellan
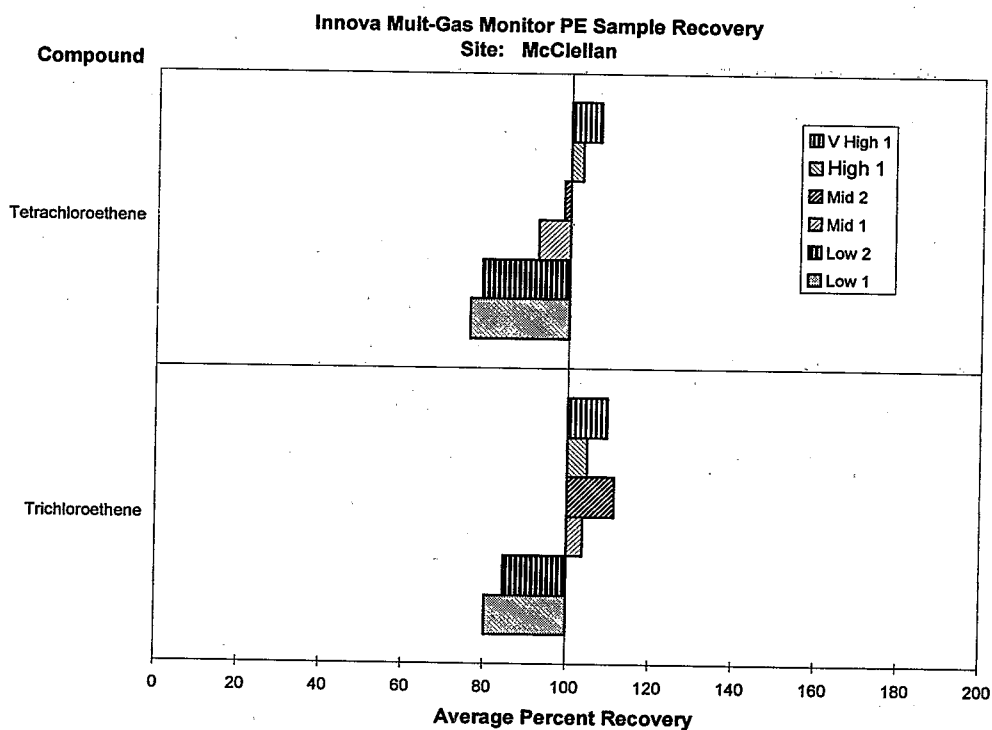
Figure 5-4. Type 1312 PE sample recovery at MAFB.

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Comparison with Laboratory Results

At each demonstration site, a total of 33 samples collected from 10 wells were provided to the participants and to the reference laboratory. Replicate sample sets were composed of either 3 or 4 samples from each well. Average laboratory results from each replicate set were used as the reference values for comparison with technology results. A side-by-side comparison of laboratory and Type 1312 results for all groundwater samples is given in Table 5-7 for the SRS and Table 5-8 for MAFB. The RSD values and their statistical summaries are included in the table. Well designation (very low, low, mid, high, and very high) is based on TCE concentration levels; however, other compounds were present in the groundwater samples at concentration levels noted in the tables.

The average percent difference between average Type 1312 and laboratory results for TCE and PCE at SRS and TCE only at MAFB is shown in Figures 5-5 and 5-6, 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 5-5 includes only TCE and PCE. Two well samples at the SRS were also contaminated with 1,1-dichloroethene, chloroform, and carbon tetrachloride, as noted in Table 5-7. The groundwater samples at MAFB were more complex, as indicated by the additional compounds shown in Table 5-8. As noted previously, the Type 1312 was configured for analysis of only a few compounds, principally TCE and PCE, and thus was unable to detect the other compounds in the samples.

Table 5-7. Type 1312 and Reference Laboratory Results for SRS Groundwater Samples

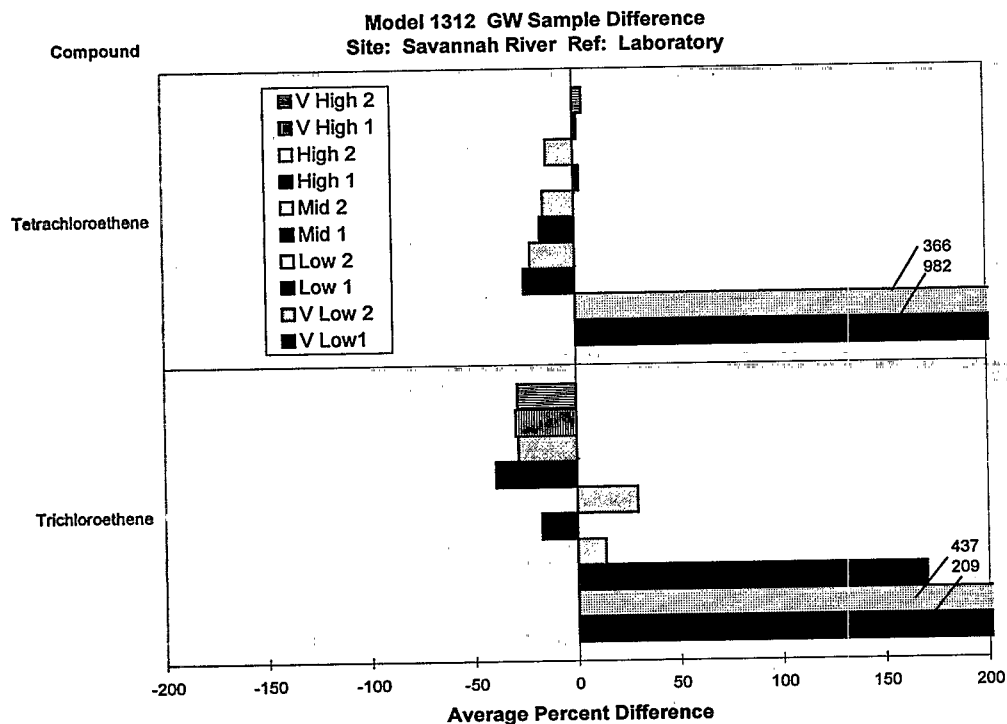| Sample Description	Well Number	Compound	Replicates	Lab. Avg. (µg/L)	Lab. RSD (%)	Type 1312[a] Avg. (µg/L)	Type 1312[a] RSD (%)
Very low 1	MSB 33B	Trichloroethene Tetrachloroethene	3	9.0 3.5	11 14	28 37	50 87
Very low 2	MSB 33C	Trichloroethene	3	2.4	34	13	41
Low 1	MSB 18B	Trichloroethene Tetrachloroethene	3	11 27	5 6	29 20	13 63
Low 2	MSB 37B	Trichloroethene Tetrachloroethene Chloroform Carbon tetrachloride	4	27 22 1.3 1.0	7 9 0 15	31 17 NR NR	12 23 NR NR
Mid 1	MSB 4D	Trichloroethene Tetrachloroethene	4	150 87	9 12	124 73	7 6
Mid 2	MSB 64C	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	3	35 240 12	7 4 8	45 203 NR	16 16 NR
High 1	MSB 4B	Trichloroethene Tetrachloroethene	3	747 33	1 2	453 34	53 18
High 2	MSB 70C	Trichloroethene Tetrachloroethene 1,1-Dichloroethene	4	1875 520 32	12 8 8	1345 451 NR	13 21 NR
Very high 1	MSB 14A	Trichloroethene Tetrachloroethene	3	1367 800	8 6	961 816	5 4
Very high 2	MSB 8C	Trichloroethene Tetrachloroethene	3	4933 3668	6 6	3519 3835	15 5
Range					0 – 34		4 – 87
Median					8		16
95th Percentile					15		65

[a] NR = not reported.

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Table 5-8. Type 1312 and Reference Laboratory Results for MAFB Groundwater Samples

Sample Description	Well Number	Replicates	Compound	Lab. Avg. (µg/L)	Lab. RSD (%)	Type 1312[a] Avg. (µg/L)	Type 1312[a] RSD (%)
Very low 1	EW-86	3	Trichloroethene	4.6	5	13	22
			1,1-Dichloroethene	7.7	9	NR	NR
Very low 2	MW-349	3	Trichloroethene	13	0	34	27
			Tetrachloroethene	2.0	6	149	32
			Chloroform	9.0	1	NR	NR
			1,1-Dichloroethene	3.8	3	NR	NR
			Carbon tetrachloride	137	4	NR	NR
Low 1	MW-331	4	1,1-Dichloroethene	2.5	7	NR	NR
			1,1-Dichloroethane	15	0	NR	NR
			Carbon tetrachloride	7.5	2	9.8	3
			Chloroform	4.8	2	57	97
			Trichloroethene	16	4	40	5
Low 2	MW-351	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	NR	NR
Mid 1	EW-87	4	1,1-Dichloroethene	180	12	NR	NR
			1,1-Dichloroethane	3.0	9	NR	NR
			cis-1,2-Dichloroethene	3.3	13	NR	NR
			1,1,1-Trichloroethane	6.8	12	NR	NR
			Trichloroethene	114	11	146	12
			Tetrachloroethene	1.2	14	17	5
Mid 2	MW-341	3	cis-1,2-Dichloroethene	15	4	NR	NR
			Chloroform	3.5	5	130	23
			Trichloroethene	280	4	244	8
High 1	MW-209	3	cis-1,2-Dichloroethene	38	4	NR	NR
			Chloroform	6.9	21	64	21
			Trichloroethene	238	2	262	8
High 2	MW-330	4	trans-1,2-Dichloroethene	7.7	4	NR	NR
			cis-1,2-Dichloroethene	66	5	NR	NR
			Chloroform	42	5	NR	NR
			1,2-Dibromochloropropane	6.1	6	NR	NR
			Trichloroethene	380	5	NR	NR
Very high 1	MW-334	3	1,1-Dichloroethene	690	3	NR	NR
			cis-1,2-dichloroethene	237	7	NR	NR
			Chloroform	397	5	NR	NR
			Benzene	283	5	NR	NR
			Trichloroethene	10,667	5	13,864	4
			Carbon tetrachloride	350	5	NR	NR
Very high 2	MW-369	3	cis-1,2-Dichloroethene	207	10	NR	NR
			Chloroform	63	6	NR	NR
			Carbon tetrachloride	51	5	NR	NR
			Trichloroethene	6167	8	6443	11
Range					0 – 21		3 – 97
Median					5		12
95th Percentile					13		55

[a] NR = not reported.

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Figure 5-5. Type 1312 groundwater results at the SRS relative to laboratory results.
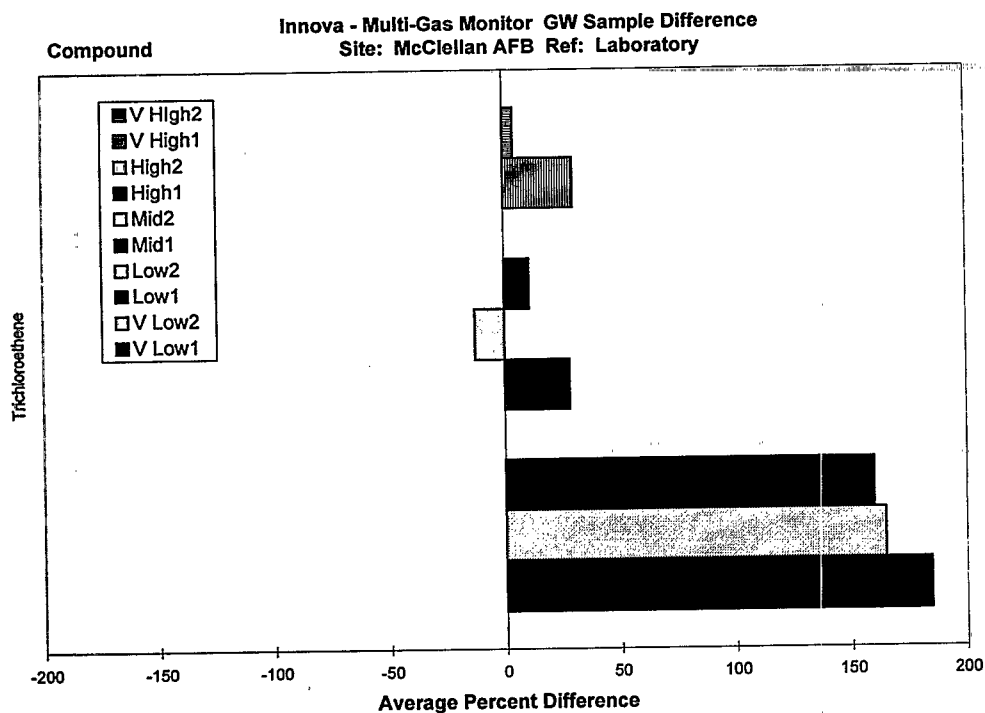
Figure 5-6. Type 1312 groundwater results at MAFB relative to laboratory results.

The median and 95th percentiles of the distribution of absolute percent differences between 1312 and laboratory results for all groundwater samples are given in Table 5-9.

Table 5-9. Type 1312 Absolute Percent Difference Summary for Pooled Groundwater Results

Percentile	SRS	MAFB	Combined Sites
50th	26	156	29
95th	493	4922	2236
Number of samples in pool	19	14	33

To assess the degree of linear correlation between some of the 1312 and laboratory groundwater data pairs shown in Tables 5-7 and 5-8, correlation coefficients (r) were computed. The correlation analysis was carried out for all TCE and PCE data pairs with laboratory values less than or equal to 300 µg/L. Only a few data pairs exist above this concentration level and including them in these analyses would result in spuriously high r values (Havlicek and Crain, 1988). The computed correlation coefficients are shown in Table 5-10.

Table 5-10. Correlation Coefficients for Reference Laboratory and Type 1312 Groundwater Analyses

Data Set	Correlation Coefficient	Number of Data Pairs
SRS Laboratory (1 through 300 µg/L)	0.984	12
MAFB Laboratory (1 through 300 µg/L)	0.892	8

Sample Throughput

The throughput rate for the Type 1312 was in the range of one to two water samples per hour. Two identical instruments were used at the MAFB site; however, these sample rates assume operation with one instrument.

Performance Summary

Table 5-11 contains a summary of instrument performance parameters and operational features of the 1312 that were verified in this demonstration. For groundwater samples, the precision results for the reference laboratory are given alongside the Type 1312 performance results to facilitate comparison of the two methodologies.

Table 5-11. Type 1312 Performance Summary

Instrument Feature/Parameter	Performance Summary
Blank sample	False positives detected at low (<15%) rates for TCE.
Detection limit sample	False negatives reported at low rates ($\leq$25%) for TCE and higher (<50%) rates for PCE at concentration levels of approximately 10 µg/L.
PE sample precision	TCE, RSD range: 4 to 22% PCE, RSD range: 5 to 46% TCE and PCE combined, Type 1312 median RSD: 15%; 95th percentile RSD: 34% TCE and PCE combined, reference laboratory median RSD: 9%; 95th percentile RSD: 18%
PE sample accuracy	TCE, APD range: 4 to 48% PCE, APD range: 2 to 48% TCE and PCE combined, Type 1312 median APD: 29%; 95th percentile APD: 47% TCE and PCE combined, reference laboratory median APD: 10%; 95th percentile APD: 25%
Type 1312 comparison with laboratory results for groundwater samples	Type 1312 median RSD: 15% Laboratory median RSD: 6% Type 1312 95th percentile RSD: 73% Laboratory 95th percentile RSD: 14% Type 1312: laboratory median APD: 29%; 95th percentile APD: >2000% Type 1312: laboratory correlation: SRS ($\leq$300 µg/L) r = 0.984 MAFB ($\leq$300 µg/L) r = 0.892
Analytical versatility	PE samples: calibrated for TCE and PCE; up to three components can be detected if sample composition is known. GW samples: calibrated for TCE and PCE; also reported results for carbon tetrachloride, chloroform, and *cis*-1,2-dichloroethene when possible. Reported results for 29 of 31 detects of TCE and PCE in all GW samples reported by the laboratory.
Sample throughput	1–2 samples per hour
Support requirements	110-V ac power or 12-V dc-to-ac with inverter
Operator requirements	Sample processing: minimally trained technician Data processing and review: B.S. chemist or equivalent
Total system weight, including accessories	30 pounds
Portability	Transportable – best suited for use in vehicle at the wellhead
Total system cost	$28,000 - $35,000 (depending upon options selected)
Shipping requirements	Air freight, luggage check, carry-on

Chapter 6
Field Observations and Cost Summary

Introduction

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

Method Summary

The 1312 employs a static (equilibrium) headspace method with no temperature control. It uses photoacoustic infrared analysis of the headspace vapors at preselected wavelengths to measure selected chlorinated VOCs in water. Compounds are quantified by using a classical least-squares matrix analysis at multiple wavelengths to account for spectral overlaps when more than one chlorinated VOC is encountered in the sample. The method requires that the composition of the sample be known so that spectral interferences from other chlorinated compounds can be avoided by selecting the appropriate bandpass filter in the instrument.

Equipment

The 1312, shown in Figure 6-1, has dimensions of 7 inches × 16 inches × 11 inches and weighs 20 pounds without accessories. A magnetic stir plate accessory has dimensions of 4 inches × 5 inches × 5 inches and weighs 6 pounds. A glass, 2-L flask with a dual-inlet cap and Teflon tubing for connection to the instrument is also employed. The system did not include a printer. It can be powered from line ac or from a 12-V dc auto battery. The system was powered with 110 V ac from a portable generator at the SRS demonstration and by line ac from the local power grid at McClellan. The equipment was transported as air freight to both demonstration sites. The system could also be checked as baggage in a shipping case.

Sample Preparation and Handling

At the request of the Innova team, PE and groundwater samples were provided in 1-L amber bottles with zero headspace. Sample preparation was begun by pouring the entire contents of the cold 1-L sample into the 2-L flask. This flask, containing a magnetic stir bar, was immediately sealed with a cap equipped with two inlets and microvalves in the closed position. The flask was placed on a motor-driven stir plate and was stirred at moderate speed under ambient temperature conditions. After 30 minutes, Teflon tubing leads from the two inlets on the cap were connected to the inlet and outlet ports on the rear of the 1312 instrument and the microvalves near the cap were opened. An air pump inside the instrument circulated headspace vapors through the analysis cell for 20 to 30 seconds prior to a 1½ minute measurement period. The analysis cycle consisted of ten consecutive
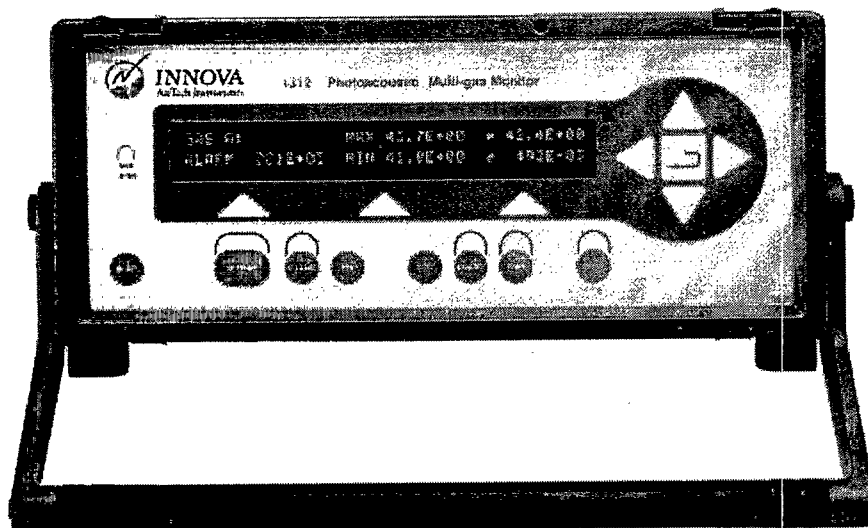
Figure 6-1. The Innova Type 1312 Multi-gas Monitor.

measurements of the headspace vapor. An average value from the ten measurements was used to compute the results for each sample. The entire measurement period, including equilibration time, lasted for about 45 minutes. The Innova team chose to use a 60-minute equilibration time at MAFB. Consequently, the total analysis time at that site was 75 minutes. The analysis result is displayed in units of parts per million volume on a display panel. This result is then converted to micrograms per liter (ppb) in water through the use of a calibration curve. The instrument also measures the temperature of the gas in the cell and the water vapor content in the sample. These data are used in the data processing algorithm to correct for water vapor spectral interferences. Following each analysis, the gas analysis cell in the instrument was flushed with ambient air and the headspace flask was rinsed with distilled water before refilling it with another sample.

Consumables
The only consumable used in operating the instrument is a fine-particle air inlet filter that needs replacement once a month.

Historical Use
The 1312 has been used extensively for chlorinated VOC measurements in soil gas and air at various environmental sites, including extensive testing and routine operation at SRS. This is the first demonstration of the 1312 for analysis of volatile organics in water using this headspace technique.

Equipment Cost
The 1312 has a price range of $28,000 to $35,000, depending upon the number of instrument options selected. Instrument costs are summarized in Table 6-1. For the purposes of comparison, reference laboratory costs were $95 per sample in addition to overnight shipping costs of approximately $30 per batch of 12 samples. Sample throughput for the 1312 was on the order of 1 to 2 samples per hour.

Table 6-1. Type 1312 Cost Summary

Instrument/Accessory	Cost
Instrument (1312)	$28,000 to 35,000
Instrument accessories (flasks, stir motor, tubing)	$300 to $500
Sample handling accessories (syringes, vials, standards)	None required
Maintenance costs	$100/year

Operators and Training

One operator is required for system operation. For wellhead monitoring operations where operator and the instrument would follow a well-sampling team, one operator is probably sufficient since only one or two samples would be provided per hour. Sample preparation and instrument operation could be carried out by a field technician with several hours of training.

Data Processing and Output

The instrument, as configured for the demonstration, reported analytical results in units of parts per million volume for up to five calibrated compounds. Results were read from the instrument display and manually recorded by the instrument operator. The results were converted to units of micrograms per liter in water by reference to a series of calibration curves produced during instrument calibration at the manufacturer's facility in Denmark before the demonstration. Thus, considerable operator involvement in the data analysis and reporting process was required. The instrument is capable of communication with a laptop computer and in fact can be operated from a computer using Innova software developed for the instrument. However, these features were not employed at this demonstration.

Compounds Detected

The instrument was calibrated for the following five compounds prior to the demonstration: TCE, PCE, chloroform, carbon tetrachloride, and cis-1,2-dichloroethene. As noted in Chapter 2, the method utilizes an infrared spectrophotometric method with many potential spectral interferences in multicomponent mixtures. The instrument is only capable of analyzing five or fewer compounds simultaneously and prior knowledge of the composition of the sample is required to avoid spectral interferences and possible erroneous readings.

Initial and Daily Calibration

The instrument was calibrated at the factory before the demonstration by injecting known amounts of the target compounds into 1 L of water and recording the resulting concentration in the headspace. The analyses were repeated at three or four points over the desired calibration range. Linear regression was used to determine the relationship between water concentration ($\mu g/L$) and headspace vapor concentration (ppmv). Three sets of calibration curves were prepared for each of the five target analytes over the entire working range of the instrument in the following concentration categories: low, 0 to 500 $\mu g/L$; medium, 500 to 1000 $\mu g/L$; and high, 1000 $\mu g/L$ and up.

The instrument's calibration is reported to be highly stable over a period of a year or more. Consequently, daily calibration checks are not specified in the field method.

QC Procedures and Corrective Actions
No QC checks were included in the field method.

Sample Throughput
Maximum throughput is about one sample per 45 minutes. Typical throughput is between one and two samples per hour.

Problems Observed During Audit
Data from PE samples of known composition reported initially at the SRS site showed a consistent negative bias. Further investigation into this discrepancy revealed that data were being reported in units of microliters per liter in water instead of micrograms per liter in water. Liquid density values for the target compounds were obtained by the Innova team and the data were converted to the appropriate units. No temperature control of the sample was done at either site. The temperature of the sample was inferred from a dewpoint measurement that was made with each sample. At the SRS, the temperature of the sample was typically below that used during calibration of the instrument. This temperature effect would translate to a negative bias in the reported results since equilibrium headspace concentrations increase with temperature. Sample temperatures at MAFB were in closer agreement with those used during calibration, resulting in less bias in the reported results.

Data Availability and Changes
Data from the 1312 were obtained at the end of each demonstration day in hard copy. Data were provided in spreadsheet format at the conclusion of each demonstration week. Several typographical errors were corrected at the final data review; however, with the exception of the density correction factor noted above, no substantive data changes were made. The instrument operators also reported instances where specific interferents might influence reported TCE and PCE results in groundwater samples. Such information would be useful in data interpretation by the final user if previous information on groundwater composition is available.

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

Based on its performance in this demonstration, the Innova Type 1312 Multi-gas Monitor is best suited for monitoring applications where the contaminant content of the samples is known. For example, the instrument could be used in a routine quarterly monitoring program to analyze TCE in groundwater samples. The instrument is not well suited for characterization or screening applications where the contaminants at the site are not known since interferences from unknown contaminants in the samples could cause considerable error in the reported results.

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.

During the testing of PE samples at the SRS, we encountered some low recoveries that we suspected were caused by temperature. Our instrumentation allows us to read out the dewpoint, which was 58 to 70 °F at SRS and 75 to 80 °F during the calibration in the laboratory. For that reason we were more concerned about temperature at MAFB and therefore allowed the samples to equilibrate for a longer time before analysis. At MAFB we obtained dewpoints of 70 to 85 °F, which were closer to those observed during the calibration, and noted analysis recoveries closer to 100%.

We are currently working on procedures that will be less dependent on sample temperature, including thermostatting and temperature compensation algorithms. We are also working on a system for permanent on-line monitoring of chlorinated organic solvents using the same technology. The first installations are already in place in England.

Chapter 8
Previous Deployments

The following documents report on previous use of the 1312 Multi-gas Monitor.

L. C. Waters, R. A. Jenkins, R. W. Counts, and L. Hernandez, "A Photoacoustic Infrared Method for the Detection of Selected Chlorinated Volatile Organic Chemicals (VOC) in Water: Method OSO30," in DOE Methods for Evaluating Environmental and Waste Management Samples, pp. OSO30-1 to OSO30-15, DOE/EM-0089T; U.S. Department of Energy, Washington, DC, 1994.

J. E. Sollid, "Soil Pore-Gas Sampling by Photoacoustic Radiometry," paper presented at the Air and Waste Management Association/Society of Photo-optical Instrumentation Engineers (AWMA/SPIE) Conference on Optical Sensing for Environmental and Process Monitoring, Air and Waste Management Association, Pittsburgh, PA, 1994.

K. Gunn, Z. Guo, and B. A. Tichenor, "Tracer Gas Measurement of Indoor-Outdoor Air Exchange Rates," paper presented at the EPA/Air and Waste Management Association Specialty Conference on Measurements of Toxic and Related Air Pollutants, Air and Waste Management Association, Pittsburgh, PA, 1994.

W. Buttner, P. Wagner, A. Husain, S. Pfeifenrot, K. Dooly, and S. Barrie, "*In-situ* Sampling of Aqueous-Phase Contamination of Chlorinated Solvents," paper presented at the Air and Waste Management Association Specialty Conference on Field Analytical Methods for Hazardous Wastes and Toxic Chemicals, Air and Waste Management Association, Pittsburgh, PA, 1997.

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EPA, 1996a, "A Guidance Manual for the Preparation of Site Characterization and Monitoring Technology Demonstration Plans," Office of Research and Development, National Exposure Research Laboratory, Las Vegas, NV. [Available at the ETV Web Site (www.epa.gov/etv) in pdf format.]

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Havlicek, L. L., and R. D. Crain, 1988, *Practical Statistics for the Physical Sciences*, pp. 80–93. American Chemical Society, Washington, DC.

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