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Environmental Technology Verification Report

Groundwater Sampling Technologies

Clean Environment Equipment SamplEase â Bladder Pump

Sandia National Laboratories

THE ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM

ETV JOINT VERIFICATION STATEMENT

TECHNOLOGY TYPE:	**GROUNDWATER SAMPLING TECHNOLOGIES**	
APPLICATION:	**VOC-CONTAMINATED WATER SAMPLING**	
TECHNOLOGY NAME:	**SamplEase Bladder Pump -- Model SP15T36**	
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The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification 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. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are 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 Site Characterization and Monitoring Technologies Pilot, one of 12 technology areas under ETV, is administered by EPA's National Exposure Research Laboratory. Sandia National Laboratories, a Department of Energy laboratory, is one of the verification testing organizations within the ETV Site Characterization and Monitoring Technologies Pilot. Sandia collaborated with personnel from the US Geological Survey (USGS) to conduct a verification study of groundwater sampling technologies. This verification statement provides a summary of the results from a verification test of the SamplEase bladder pump and pneumatic controller manufactured by Clean Environment Equipment.

DEMONSTRATION DESCRIPTION

In August 1999, the performance of six groundwater sampling technologies was evaluated at the US Geological Survey Hydrological Instrumentation Facility at the National Aeronautics and Space Administration (NASA) Stennis Space Center in southwestern Mississippi. Each technology was independently evaluated in order to assess its performance in the collection of volatile organic compound- (VOC) contaminated water.

The verification test design incorporated the use of a 5-inch-diameter,100-foot standpipe at the USGS facility. The standpipe, serving as an "aboveground" well, was filled with tap water spiked with various concentration levels of six target volatile organic compounds. The target compounds (1,2-dichloroethane, 1,1-dichloroethene, trichloroethene, benzene, 1,1,2-trichloroethane, and tetrachloroethene) were chosen to represent the range of VOC volatility likely to be encountered in normal sampler use. Water sampling ports along the exterior of the standpipe were used to collect reference samples at the same time that groundwater sampling technologies collected samples from the interior of the pipe. A total of seven trials were carried out at the standpipe. The trials included the collection of low (~20 µg/L) and high (~200 µg/L) concentrations of the six target VOC compounds in water at sampler depths ranging from 17 to 91 feet. A blank sampling trial and an optional "clean-through-dirty" test were also included in the test matrix. The "clean-through-dirty" test was included to investigate the potential of contaminant carryover as a sampler is lowered through a "dirty" (high VOC concentration) layer of water in order to sample an underlying "clean" (low VOC concentration) layer. The test was optional for samplers such as the SamplEase bladder pump, which is designed for permanent deployment in a single monitoring well.

The standpipe trials were supplemented with additional trials at groundwater monitoring wells in the vicinity of sites with VOC-contaminated groundwater at the NASA Stennis facility. The technologies were deployed in a number of 2-inch and 4-inch wells, along with colocated submersible electric gear pumps as reference samplers. The principal contaminant at the onsite monitoring wells was trichloroethene. The onsite monitoring provided an opportunity to observe the operation of the sampling system under typical field-use conditions.

All technology and reference samples were analyzed by two identical field-portable gas chromatograph-mass spectrometer (GC/MS) systems that were located at the test site during the verification tests. The GC/MS analytical method used was a variation of EPA Method 8260 purge-and-trap GC/MS, incorporating a headspace sampling system in lieu of a purge-and-trap unit. The overall performance of the groundwater sampling technologies was assessed by evaluating sampler precision and comparability with reference samples. Other logistical aspects of field deployment and potential applications of the technology were also considered in the evaluation.

Details of the demonstration, including an evaluation of the sampler's performance, may be found in the report entitled *Environmental Technology Verification Report: Clean Environment Equipment, SamplEase Bladder Pump,* EPA/600/R-00/078.

TECHNOLOGY DESCRIPTION

The SamplEase is a bladder pump consisting of an internal flexible Teflon bladder that is positioned within a rigid stainless steel pump body. The ends of the pump are also constructed of Teflon. The inner bladder is equipped with one-way inlet and outlet valves and passively fills with water when the pump is at depth in the well as a result of the hydrostatic pressure exerted by the surrounding water column. Following the fill cycle, compressed air or nitrogen from a cylinder or compressor at the wellhead is driven down to the pump through tubing to compress the bladder, thus driving the water sample up to the surface through a second tubing line. The pumping sequence consists of repeated fill–compress cycles, using a pneumatic controller positioned at the wellhead. The controller is used to vary the duration and frequency of the fill–compress cycles in order to deliver the desired sample flow rate at the wellhead. The bladder design offers

the advantage of minimizing sample turbulence, which can result in loss of VOCs in the sample, as well as eliminating contact of the water sample with the compressed air or nitrogen used to lift the sample to the surface.

Clean Environment Equipment offers a line of bladder pumps manufactured with various materials. The pump tested during this evaluation was the Model SP15T36, which uses polytetrafluoroethylene (Teflon) for the bladder and 316 stainless steel for the pump body, fittings, and intake screen. The pump and intake screen is 40 inches long. The pump diameter is 1.5 inches and its weight is 3.8 pounds. The pump has a maximum lift capacity of 500 feet, and flow rates are adjustable from less than 100 mL/min to over 5 L/min, depending on pump depth. The pump can draw samples from greater depths using an extended intake attached to the inlet of the pump.

The Model SC250 controller is a mechanical controller used to regulate the flow of compressed nitrogen, obtained from a cylinder at the wellhead, to the bladder pump. The controller is weatherproof and is packaged in a durable case that can be easily hand carried. The controller has overall dimensions of 10 x 9 x 7 inches and a weight of 9.8 pounds. Drive air for the bladder pump can be delivered from compressed gas cylinders or from a field-portable gasoline- or electric-powered compressor.

The bladder pump's list price is $630 and the controller lists at $1,550. An optional inlet screen is priced at $50. Teflon-lined polyethylene dual tubing is also a requirement for most VOC sampling applications and is priced at $1.30 per foot.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the SamplEase bladder pump were observed:

Precision: The precision of the sampler was determined through the collection of a series of replicate samples from 3 standpipe trials using low (~20 µg/L) and high (~200 µg/L) VOC concentrations at 17-foot and 91-foot collection depths. Each trial included 6 target VOCs for a total of 18 cases. SamplEase bladder pump precision, represented by the relative standard deviation, for all compounds at all concentrations and sampling depths evaluated in this study, ranged from 5.1 to 24.2%, with a median value of 11.7%. In 12 cases the relative standard deviation of the SamplEase bladder pump was greater than the reference, with SamplEase bladder pump precision less than or equal to reference sample precision in the other 6 cases. The F-ratio test was used to assess whether the observed precision differences were statistically significant. Test results showed that precision differences between the SamplEase bladder pump and reference samples were statistically insignificant at the 95% confidence level in 16 of 18 cases.

Comparability with a Reference: SamplEase bladder pump results from the standpipe trials were compared with results obtained from reference samples collected at the same time. Both SamplEase and reference samples were analyzed by the same analytical method using the same GC/MS system. Sampler comparability is expressed as percent difference relative to the reference data. Sampler differences for all target VOC compounds at all concentrations and sampler depths in this study ranged from −16 to 31%, with a median difference of −5%. The t-test for two sample means was used to assess whether the differences between SamplEase bladder pump and reference sample results were statistically significant. These tests showed that in 13 of 24 trials, differences were statistically indistinguishable from 0% at the 95% confidence level. In the remaining 5 cases, statistically significant negative bias was not in excess of 16%.

Versatility: Sampler versatility is the consistency with which the sampler performed over the range of target compound volatility, concentration level, and sampling depth. SamplEase bladder pump performance did not vary with changes in compound, concentration, or sampler depth. Thus, the SamplEase bladder pump is regarded as a widely versatile sampling device and applicable for sampling the types of VOCs likely to be encountered under actual field conditions.

Logistical Requirements: The sampler can be deployed and operated in the field by one person. One day of training is generally adequate to become proficient in the use of the system. The system requires a source of compressed air or nitrogen at the wellhead, such as a compressed gas cylinder or a gas- or electric-powered compressor. The SamplEase bladder pump is designed for dedicated use in a single monitoring well and is not intended for repeated deployment and retrieval in a series of wells.

Overall Evaluation: The results of this verification test show that the SamplEase bladder pump and associated pneumatic controller can be used to collect VOC-contaminated water samples that are generally statistically comparable to reference samples when analyzed with the sample method. The system is designed for use in well sampling programs that incorporate low-volume purge methodologies.

As with any technology selection, the user must determine if this technology is appropriate for the application and the project data quality objectives. For more information on this and other verified technologies, visit the ETV web site at http://www.epa.gov/etv.

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Clean Environment Equipment SamplEase Bladder Pump

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Notice

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Acknowledgments

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Abbreviations and Acronyms

BNZ	Benzene
DIFF	Difference
EPA	US Environmental Protection Agency
ETV	Environmental Technology Verification Program
GC/MS	Gas chromatograph-mass spectrometer
HIF	Hydrological Instrumentation Facility
MSL	Mean sea level
MW	Monitoring well
NASA	National Aeronautics and Space Administration
ND	Not detected
NERL	National Exposure Research Laboratory
PCE	Tetrachloroethene (perchloroethene)
PTFE	Polytetrafluoroethylene
QA	Quality assurance
QC	Quality control
REF	Reference
RPD	Relative percent difference
RSD	Relative standard deviation
SCMT	Site Characterization and Monitoring Technologies Pilot
SNL	Sandia National Laboratories
SP	Sample port
SSC	Stennis Space Center
TCE	Trichloroethene
USGS	US Geological Survey
VOC	Volatile organic compound
12DCA	1,2-dichloroethane
11DCE	1,1-dichloroethene
112TCA	1,1,2-trichloroethane

Section 1 — Introduction

Background

The U.S. Environmental Protection Agency (EPA) has created the Environmental Technology Verification Program (ETV) to facilitate the deployment of innovative or improved environmental technologies through performance verification 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. ETV seeks to achieve this goal by providing high-quality, peer-reviewed data on technology performance to those involved in the design, distribution, financing, permitting, purchase, and use of environmental technologies.

ETV works in partnership with recognized standards and testing organizations and stakeholder groups consisting of regulators, buyers, and vendor organizations, with the full participation of individual technology developers. The program evaluates the performance of innovative technologies by developing test plans that are responsive to the needs of stakeholders, conducting field or laboratory tests (as appropriate), collecting and analyzing data, and preparing peer-reviewed reports. All evaluations are conducted in accordance with rigorous quality assurance (QA) protocols to ensure that data of known and adequate quality are generated and that the results are defensible.

ETV is a voluntary program that seeks to provide objective performance information to all of the participants in the environmental marketplace and to assist them in making informed technology decisions. ETV does not rank technologies or compare their performance, label or list technologies as acceptable or unacceptable, seek to determine "best available technology," or approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research.

The program now operates 12 pilots covering a broad range of environmental areas. ETV has begun with a 5-year pilot phase (1995–2000) to test a wide range of partner and procedural alternatives in various pilot areas, as well as the true market demand for and response to such a program. In these pilots, EPA utilizes the expertise of partner "verification organizations" to design efficient processes for conducting performance tests of innovative technologies. These expert partners are both public and private organizations, including federal laboratories, states, industry consortia, and private sector facilities. Verification organizations oversee and report verification activities based on testing and QA protocols developed with input from all major stakeholder/customer groups associated with the technology area. The demonstration described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Pilot. (To learn more about ETV, visit ETV's Web site at http://www.epa.gov/etv.)

The SCMT pilot is administered by EPA's National Exposure Research Laboratory (NERL). Sandia National Laboratories (SNL), one of two verification organizations associated with the SCMT pilot, conducted a verification study of groundwater sampling technologies during the summer of 1999. Groundwater sampling technologies are commonly employed at environmental sites for site screening and characterization, remediation assessment, and routine environmental monitoring. Groundwater sampling technologies generally fall into two categories: (1) active systems, including pumping systems and discrete-level grab systems; and (2) passive or diffusional systems. Both types of samplers were evaluated during this verification study.

Demonstration Overview

In August 1999, a demonstration study was conducted to verify the performance of six groundwater sampling devices: Multiprobe 100 (multi-level sampler, Burge Environmental, Tempe, AZ), Well Wizard dedicated sampling system (bladder pump, QED Environmental, Ann Arbor, MI), Micro-Flo (bladder pump, Geolog Inc., Medina, NY), Kabis sampler (discrete-level grab sampler, Sibak Industries, Solano Beach, CA), GoreSorber (diffusional sampler, W. L. Gore and Associates, Elkton, MD), and the SamplEase bladder pump (Clean Environment Equipment,

Oakland, CA). This report contains an evaluation of the SamplEase bladder pump.

It is important to point out that the scope of this technology demonstration was purposely limited to sampling device performance parameters such as precision, comparability with a reference measurement, and where applicable, deployment logistics. Several of the systems tested in this study are intended for use with low-flow sampling protocols—a relatively new approach to the collection of a representative sample from a groundwater monitoring well. This study was specifically intended to evaluate sampling device performance and did not evaluate the merits of a low-flow purge and sampling protocol. This protocol has been proposed, tested, and published elsewhere [Puls and Barcelona, 1996] and is beyond the scope of this particular investigation.

The demonstration was conducted in August of 1999 at the National Aeronautics and Space Administration (NASA) Stennis Space Center (SSC) in southwestern Mississippi. Sandia worked in cooperation with the US Geological Survey (USGS), a federal agency resident at the NASA Stennis site, and used a 100-foot standpipe testing facility associated with the USGS Hydrological Instrumentation Facility (HIF) located on the NASA site. The standpipe, serving as an "aboveground" well, was filled with water spiked with various concentration levels of six target volatile organic compounds (VOCs). Water sampling ports along the exterior of the pipe permitted the collection of reference samples at the same time that groundwater sampling technologies collected samples from the interior of the pipe.

The standpipe trials were supplemented with additional trials at a number of groundwater monitoring wells at sites with VOC-contaminated groundwater at the NASA Stennis facility. The devices were deployed in a number of 2-inch and 4-inch wells, and reference samples were collected for comparison with each sampling device. The principal contaminant at the site was trichloroethene (TCE).

All technology and reference samples were analyzed by the same field-portable gas chromatograph-mass spectrometer (GC/MS) system that was located at the test site during the verification tests. The overall performance of the groundwater sampling technologies was assessed by comparing technology and reference sample results for a number of volatile organic compounds, with particular attention given to key parameters such as sampler precision and comparability with reference sample results. Aspects of field deployment and potential applications of the technology were also considered.

A brief outline of this report is as follows: Section 2 contains a brief description of the SamplEase bladder pump and its capabilities. Section 3 outlines a short description of the test facilities and a summary of the verification test design. Section 4 includes a technical review of the data with an emphasis on assessing overall sampler performance. Appendix A contains performance data for the reference pump and Appendix B presents an assessment of quality control data associated with the analytical method used in this study.

Section 2 — Technology Description: Clean Environment Equipment SamplEase Bladder Pump

This section provides a general description and overview of the capabilities of the Clean Environment Equipment SamplEase bladder pump. The information used to prepare this section was provided by Clean Environment Equipment.

The bladder pump consists of an internal flexible polytetrafluoroethylene (Teflon) bladder that is positioned within a cylindrical pump body of Teflon and stainless steel. The ends of the pump are equipped with one-way inlet and outlet valves. The pump passively fills with water when the pump is at depth by virtue of the hydrostatic pressure. Following the fill cycle, compressed air or nitrogen from a cylinder or compressor at the wellhead is driven down to the pump through tubing and compresses the bladder, thus driving the water sample up to the surface through a second tubing line. The pumping sequence consists of repeated fill–compress cycles, using a pneumatic controller positioned at the wellhead. With the controller, the duration and frequency of the fill–compress cycles can be varied to deliver the desired flow rate at the wellhead. The bladder design offers the advantage of minimizing sample turbulence, which can result in loss of VOCs in the sample, as well as eliminating contact of the water sample with the compressed air or nitrogen used to lift the sample to the surface.

Clean Environment Equipment offers a line of bladder pumps manufactured with various materials. The pump tested during this evaluation was the SamplEase Model SP15T36. The pump is 40 inches in length when an intake screen is attached, 1.5 inches in diameter, and weighs 3.8 pounds. The pump uses Teflon for the bladder material and 316 stainless steel for the pump body, fittings, and intake screen. The pump has a maximum lift capacity of 500 feet, and flow rates are adjustable from less than 100 mL/min to over 5 L/min, depending on the pressure head.

The Model SC250 controller is a mechanical controller used to regulate the flow of compressed air or nitrogen, obtained from a cylinder at the wellhead, to the bladder pump. The controller is weatherproof and is packaged in a durable case that can be hand carried. The controller has overall dimensions of $10 \times 9 \times 7$ inches and a weight of 9.8 pounds. Drive air for the bladder pump can be delivered from compressed gas cylinders or from a field-portable gasoline- or electric-powered compressor.

The bladder pump list price is $630 and the controller list price is $1,550. An optional stainless steel pump inlet screen is priced at $50. Teflon-lined polyethylene dual tubing is also a requirement for most VOC sampling applications and is priced at $1.30 per foot.

The Clean Environment Equipment bladder pump systems are designed for dedicated well-sampling applications. The bladder pump and tubing are left in the well and the controller and drive air source are moved from well to well during typical sampling operations.

Section 3 — Demonstration Process and Design

Introduction

The principal objective of this demonstration was to conduct an independent evaluation of the capabilities of several groundwater sampling technologies for VOC-contaminated water. A number of key performance parameters were chosen to evaluate overall sampler performance. In order to ensure data integrity and authenticity of results, data quality control measures were also incorporated into the study design. The design was developed by personnel at Sandia National Laboratories with concurrence from the various technology vendors participating in the study. Technical review of the study design was also provided by EPA personnel with professional expertise in the area of groundwater sampling. A complete demonstration plan has been published [Sandia, 1999].

Site Description

The John C. Stennis Space Center in southwest Mississippi is one of ten NASA field centers in the United States. It is NASA's primary center for testing and flight-certifying rocket propulsion systems for the Space Shuttle and future generations of space vehicles. Over the years, SSC has evolved into a multiagency, multidisciplinary center for federal, state, academic and private organizations engaged in space, oceans, environmental programs and national defense. The Hydrologic Instrumentation Facility supports USGS agency-wide hydrologic data-collection activities through the identification of agency needs, development of technical specifications, and testing and evaluation.

Standpipe Facility—One of the HIF test centers is known as the Standpipe Facility. The facility was designed by Doreen Tai, an HIF chemical engineer, and is housed in a Saturn V rocket storage building at the Stennis complex. A schematic diagram of the standpipe and accessories is shown in Figure 1. The standpipe is an aboveground, 100-foot-long, 5-inch-diameter, stainless steel pipe with numerous external sampling ports along its length. Two large tanks at the top of the standpipe are used to prepare solutions that can then be drained into the standpipe. The tanks are equipped with motor-driven mixing propellers and floating lids to minimize loss of volatile compounds during mixing and transfer of solution. An external standpipe fill line at the bottom of the pipe enables the pipe to be filled from the bottom up, thereby minimizing flow turbulence and VOC losses in the prepared solutions. The external access ports allow reference samples to be taken simultaneously with the technology samples inside the pipe. As shown in Figure 1, the indoor facility has six levels of access, including the ground floor, and all levels are serviced by a freight elevator. In this demonstration, the standpipe was used in a series of controlled water sampling trials. Technology vendors sampled VOC-contaminated water solutions from the standpipe while reference samples were simultaneously taken from the external ports.

Site Hydrogeology – The second phase of this technology demonstration involved the collection of groundwater samples from six onsite wells at SSC. The site has about 200 wells that have been used for subsurface plume characterization and routine groundwater monitoring. The shallow, near-surface geology where most of the contaminant plumes are located can be summarized as follows [Foster Wheeler, 1998]: The geology generally consists of a thin veneer of clayey sediments known as Upper Clay, and found at elevations ranging from 10 to 30 feet mean sea level (MSL). These overlay a sandy unit named Upper Sand (at 5 to 15 feet above MSL). The Upper Sand is underlain by a second clayey unit named the Lower Clay and a second sandy unit called the Lower Sand (at –35 to 5 feet MSL). Below the Lower Sand, another clayey unit is present which represents an unnamed or undifferentiated Pleistocene deposit. This deposit is underlain by a thick zone of interbedded sand and clay deposits that form the Citronelle Formation (at –100 to –40 feet MSL). The VOC contamination is present in the Upper Sand and Lower Sand water bearing zones; correspondingly, most of the wells selected for use in this test were screened in these zones.

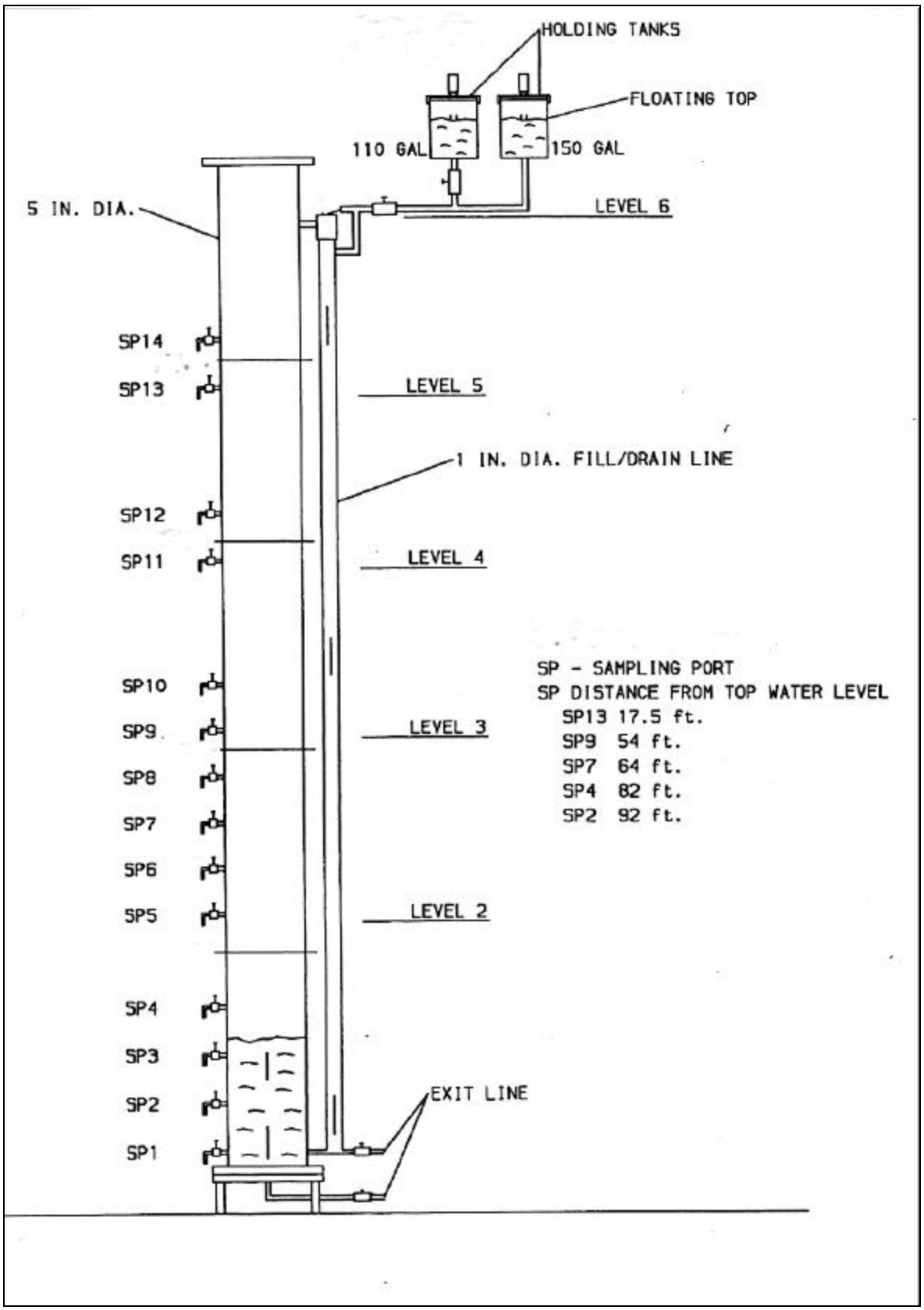

Figure 1. The standpipe at the USGS Hydrological Instrumentation Facility.

Groundwater Monitoring Wells—Construction information for the six wells selected for use in this study is given in Table 1. The wells were constructed with either 2- or 4-inch-diameter polyvinyl chloride (PVC) pipe with a 10-foot PVC screen length. All samples were collected at the midscreen level. Typical sampling depths for the wells selected for study ranged from about 15 to 85 feet from the top of the well column to the screen midpoint. The depth of the water column above the midscreen point ranged from 5 to 68 feet for the wells selected for use in this study.

Verification Test Design Summary

The verification test design consisted of two basic elements. The first was a test matrix consisting of several trials conducted under carefully controlled sampling conditions at the standpipe. These trials enabled sampler performance parameters such as precision and comparability with reference to be evaluated. The second element was an additional series of tests conducted under actual field conditions with inherently less experimental control. These trials presented an opportunity to observe the technology in actual field use in conditions very similar to those that would be encountered in routine use. Together, these two study elements provided a data set that is adequate for an overall performance assessment of these groundwater sampling devices for applications specifically involving the sampling of VOC-contaminated groundwater.

Test Design Elements

The test consisted of a variety of sampling activities carried out under relatively closely controlled experimental conditions at the standpipe, along with field sampling at selected onsite monitoring wells under less controlled conditions. Additional design element descriptions are given below. The participating technologies were split into two categories, *active samplers* and *passive samplers*, with individual sampling trials designed specifically for these two categories.

Target VOC Compounds—Six target compounds, all regulated under the EPA Clean Water Act, were selected for testing in this study. The compounds were 1,2-dichloroethane (12DCA), 1,1-dichloroethene (11DCE), trichloroethene (TCE), benzene (BNZ), tetrachloroethene (PCE), and 1,1,2-trichloroethane (112TCA). With the exception of benzene, all of these compounds are chlorinated and have regulatory limits of 5 µg/L in water as presented in the Clean Water Act. The six compounds selected encompass a range of volatility, a parameter that is likely to influence sampler performance. Target compound volatility, as represented by Henry's constants and boiling point information, is given in Table 2.

Table 1. Construction Details of Groundwater Monitoring Wells

Well No.	TOC (ft, MSL)	Total Depth (ft)	Screen Elev. (ft, MSL)		Well Diam. (in.)	Install Date	Depth to Water (ft)	Water Level (ft, MSL)	Water Depth Above Screen Midpoint (ft)
			Top	Bottom					
06-04	28.8	39.0	–1.3	–11.3	2	04/95	24.6	4.2	10.5
06-10	7.8	87.0	–55.2	–65.2	4	04/95	8.2	–0.4	59.8
06-11	15.3	150.0	–62.8	–72.8	4	05/95	15.2	0.1	67.9
06-20	7.3	75.0	–55.4	–65.4	4	12/96	7.8	–0.6	59.8
12-09	28.0	18.0	18.0	8.0	2	05/95	10.0	18.0	5.0
12-12	28.4	99.0	–11.0	–21.0	4	05/95	11.6	16.8	32.8

Notes: TOC = top of well column; water levels from most recent quarterly well-monitoring data.

Table 2. Target VOC Compounds

Compound	Henry's Constant (kg · bar/mole at 298 K)[a]	Boiling Pt. (°C)
Tetrachloroethene (PCE)	High (17.2)	121
1,1-Dichloroethene (11DCE)	High (29.4)	32
Trichloroethene (TCE)	Mid (10.0)	87
Benzene (BNZ)	Mid (6.25)	80
1,2-Dichloroethane (12DCA)	Low (1.39)	84
1,1,2-Trichloroethane (112TCA)	Low (0.91)	114

[a] Henry's constant data from NIST, 2000.

Test Concentrations—The use of the standpipe facility enabled the preparation of water mixtures containing the six target VOCs in a range of concentration levels. In four standpipe testing trials, the target compound concentration was either low (10-20 µg/L) or high (175-225 µg/L). Spike solutions of all six target compounds were prepared in methanol from neat compounds. Normally a 5-10 mL volume of the spiking solution was injected into the mixing tank, which was located at the top of the standpipe and contained about 100 gallons of tap water. This solution was covered with a floating lid to reduce volatile losses, gently mixed for 5 minutes, and then drained into the standpipe.

Standpipe Reference Samples—Preliminary studies at the standpipe revealed volatile losses of target compounds during mixing and filling. Consequently, calculated spike concentrations could not be used as reference values in this study. The standpipe has external sampling ports along its length so that reference samples could be collected simultaneously with sample collection from the interior of the pipe with devices undergoing testing. Each sampling trial consisted of the simultaneous collection of replicate test device and reference samples at a fixed concentration and sampling depth. The reference samples were collected directly into analysis vials with no intervening pumps or filters that could affect the sample. The use of multiple sequentially collected samples allowed the determination of test device and reference sampler precision. Precision in this context incorporates the variability of the technology and the reference sampler in combination with the common analytical method used on both sample types. The reference sampler precision is assumed to be the baseline with which the technology precision data can be directly compared for each of the sampling trials.

Sampler Blank—The standpipe trials included a blank test in which replicate samples were collected from a blank water mixture in the standpipe. This test was conducted to assess whether the construction materials in the various samplers could be a source of contamination of the sample for the six target compounds used in this study.

Sampler Carryover—One of the intended applications of several of the samplers involved in the study is the collection of a water sample with relatively low VOC levels at a discrete level in a well that may have overlying layers of VOC contamination at higher levels. A so-called clean-through-dirty test was incorporated to assess the degree to which the samplers were contaminated in the high-level layer that was penetrated as the sampler was lowered to a cleaner underlying layer in the well. The results of these trials are also expressed in terms of percent difference from reference samples, with recovery values significantly greater than zero indicating sampler contamination for the overlying contaminated layers in the well. Not all vendors participated in this part of the study.

Groundwater Well Reference Samples—Six onsite groundwater monitoring wells were selected for the second phase of the study. A submersible electric gear pump (Fultz, Model SP-300) was chosen as a reference sampling device for these additional field tests. Verification studies on the performance of this pump were carried out during the standpipe phase of the experiments to provide technical data substantiating its use as a reference

technology in the field. A more complete description of the sampling device along with a summary of these data is given in Appendix A. During field sampling events, the reference pump was collocated in the well with the sampling devices under test in order to obtain simultaneous reference samples from the well. Teflon tubing (¼-inch outside diameter) was used to transport the water sample from the reference pump outlet to the collection vial at the wellhead. During all sampling, the reference pump was operated at a low flow rate (100–200 mL/min).

As noted previously, the field sampling trials were not an evaluation of the low-flow purge methodology for well sampling. Consequently, water quality parameters were not monitored in the field sampling trials. A purge was used to flush the reference pump and tubing to ensure that the pump was drawing from the well column water. Whether formation water was being sampled was of secondary importance in this sampling plan.

Sampler Performance Parameters

Four performance parameters were evaluated in the assessment of each technology. They are briefly outlined in the following paragraphs.

Precision—Sampler precision was computed for the range of sampling conditions included in the test matrix by the incorporation of replicate samples from both the standpipe and the groundwater monitoring wells in the study design. The *relative standard deviation* (RSD) was used as the parameter to estimate precision. The percent relative standard deviation is defined as the sample standard deviation divided by the sample mean times 100, as shown below:

$$RSD(\%) = \frac{\sqrt{\frac{\sum (X_i - \bar{X})^2}{n-1}}}{\bar{X}} \bullet 100$$

Here, X_i is one observation in a set of n replicate samples where $\bar{X}$ is the average of all observations, and n is the number of observations in the replicate set. In the assessment of sampler precision, a statistical test was used to assess whether differences between the reference sample precision and the technology sample precision were statistically significant. Specifically, the F-ratio test compares the variance (square of the standard deviation) of the two groups to provide a quantitative assessment as to whether the observed differences between the two variances are the result of random variability or the result of a significant influential factor in either the reference or technology sample groups [Havlicek and Crain 1988a].

Comparability—The inclusion of reference samples, collected simultaneously with technology samples from the external sampling port of the standpipe, allows the computation of a comparability-to-reference parameter. The term *comparability* is to be distinguished from the term *accuracy*. Earlier investigations at the standpipe revealed that volatility losses occurred when the spike mixtures were mixed and transported during standpipe filling. As a result, the "true" concentrations of target VOCs in the standpipe were not precisely known and thus an accuracy determination is not warranted. Alternatively, a reference measurement from the external port, with its own sources of random error, is used for comparison. The term *percent difference* is used to represent sampler comparability for each of the target compounds in the sampling trials at the standpipe. Percent difference is defined as follows:

$$\%\text{DIFF} = \frac{\left(\overline{X_{\text{tech}}} - \overline{X_{\text{ref}}}\right)}{\overline{X_{\text{ref}}}} \bullet 100$$

where is $\overline{X}_{\text{tech}}$ the average reported concentration of all technology sample replicates and $\overline{X}_{\text{ref}}$ is the average reported concentration of all reference sample replicates. The t-test for two sample means was used to assess differences between the reference and technology means for each sampling trial [Havlicek and Crain, 1988b]. The t-test gives the confidence level associated with the assumption that the observed differences are the result of random effects among a single population only and that there is no significant bias between the technology and reference method.

Versatility—The versatility of the sampler was evaluated by summarizing its performance over the volatility and concentration range of the target compounds as well as the range of sampling depths encountered in both the standpipe and the groundwater monitoring well trials. A sampler that is judged to be versatile operates with

acceptable precision and comparability with reference samples over the range of experimental conditions included in this study. Those samplers judged to have low versatility may not perform with acceptable precision or comparability for some of the compounds or at some of the tested sampling depths.

Field Deployment Logistics—This final category refers to the logistical requirements for deployment of the sampler under its intended scope of application. This is a more subjective category that incorporates field observations made during sampler deployment at the groundwater monitoring wells. Logistical considerations include such items as personnel qualifications and training, ancillary equipment requirements, and field portability.

Operator Influence—The sampling technician as well as the sample collection method have an influence on the overall quality of the samples taken. This is particularly true for the active samplers evaluated in this study. Such factors as the sample flow rate when filling the vial with a bladder pump, the cycle times and volume of bladder pump and others may influence overall sample quality. An evaluation of operator influence on sample quality is beyond the scope of this study. All operators were experienced in the use of their technologies and the assumption is made that these operators were operating their sampling devices under conditions that would yield the highest quality samples.

Sample Analysis

A single analytical method was used for technology and reference samples. All analyses were conducted onsite, using analytical services provided by Field Portable Analytical (Fremont, CA). The onsite instrumentation consisted of two identical field-portable gas chromatograph-mass spectrometer units (Inficon, HAPSITE, Syracuse, NY) equipped with an Inficon headspace sampling system. The analysis method used was a modified Method 8260 (purge-and-trap GC/MS) with headspace sampling replacing the purge-and-trap portion of the method [EPA, 1996]. Throughput was on the order of 4 to 6 samples per hour per instrument for a daily throughput of 60–70 samples per instrument. The Inficon field-portable GC/MS system with headspace vapor sampling accessory had previously gone through the ETV verification process. Results from this verification study showed that system accuracy and precision for VOCs in water analysis were comparable with a conventional fixed laboratory analysis using purge-and-trap sample handling combined with bench-top GC/MS analytical systems [EPA, 1998].

A brief summary of the analytical method follows: Samples were brought to the analysis location in 40-mL volatile organic analysis (VOA) vials and kept at temperatures near 4 ºC until they were prepared for instrument analysis. As a result of the relatively high sample throughput and the use of two instruments, sample holding times did not exceed 24 hours in most cases. Consequently, no sample preservatives were used in the study. Immediately prior to analysis, the chilled VOA sample vials were uncapped and immediately transferred to a 50-mL glass syringe. Half (20 mL) of the sample was then transferred to a second 40-mL VOA vial and the vial was immediately capped. A 5-µL solution containing internal standards and surrogate standards was injected through the septum cap of the vial. The vial was then placed in the headspace sampling accessory and held at 60 ºC for 15 minutes. (The original vial was again filled with the remainder of the sample, capped, and held under refrigeration as a spare.) Following the temperature equilibration time, a vapor extraction needle was inserted through the vial's septa cap and into the headspace. A pump in the GC/MS then sampled a fixed volume of headspace gas through a heated gas transfer line and in a fixed-volume gas sampling loop in the GC/MS. Under instrument control, the gas sample was then injected onto the capillary column for separation and detection. An integrated data system processed the mass detector data and output results for the six target analytes, plus internal and surrogate standards, in concentration format. The method used the internal standard method (as outlined in Method 8260) for computation of target compound concentrations. Surrogate standard results were used as measures of instrument data quality, along with other quality control measures outlined below.

Data Processing

The results from chemical analysis of both technology and reference samples were compiled into spreadsheets and the arithmetic mean and percent relative standard deviation (as defined in Section 3) were computed for each set of replicate

samples from each standpipe and monitoring well trial. All data were reported in units of micrograms per liter for the six target compounds selected. Direct trial-by-trial comparisons were then made between technology and reference sample results as outlined below. All the processed data from the verification study have been compiled into data notebooks and are available from the authors by request.

Data Quality Control

The desirability of credible data in ETV verification tests requires that a number of data quality measures be incorporated into the study design. Additional details on data quality control are provided in the following paragraphs.

Sample Management—All sampling activities were documented by SNL field technicians using chain-of-custody forms. To save sample handling time and minimize sample labeling errors in the field, redundant portions of the chain-of-custody forms and all sampling labels were printed prior to the field demonstration.

Field Logbooks—Field notes were taken by observers during the standpipe and groundwater well-sampling trials. The notes include a written chronology of sampling events, as well as written observations of the performance characteristics of the various technologies tested during the demonstration.

Predemonstration Analytical System Audit—Prior to the actual demonstration, a number of samples containing the six target compounds at various concentration levels were prepared at Sandia National Laboratories and sent via overnight mail under refrigeration temperatures to Field Portable Analytical. The samples were analyzed using the headspace GC/MS method intended for use in the final field test. Results from this preliminary audit revealed acceptable performance of the GC/MS system and its accompanying method. The written analytical method that was used during the full demonstration was also reviewed and finalized at this time.

Analytical Method—The analytical method was an adaptation of EPA Method 8260B and followed the data quality requirements outlined in the method. Included in the list of data quality measures were: (1) initial calibration criteria in terms of instrument linearity and compound recovery; (2) daily instrument calibration checks at the onset and completion of each 12-hour analysis shift; (3) blank sample instrument performance checks; (4) internal standard recovery criteria; and, (5) surrogate standard recovery criteria. A summary of the GC/MS analysis quality control data for the demonstration period is given in Appendix B.

Verification Test Plan

The preceding information, as well as that which follows, is summarized from the Groundwater Sampling Technologies Verification Test Plan [Sandia, 1999], which was prepared by SNL and accepted by all vendor participants prior to the field demonstration. The test plan includes a more lengthy description of the site, the role and responsibilities of the test participants, and a discussion of the experimental design and data analysis procedures.

Standpipe and Groundwater Well-Sampling Matrix

The sampling matrix for the standpipe sampling phase of the demonstration is given in Table 3. All standpipe and groundwater well testing was carried out sequentially, with the various participants deploying their sampling devices one at a time in either the standpipe or the groundwater monitoring wells. A randomized testing order was used for each trial. The standpipe test phase included seven trials. Trials 1 and 2 were carried out at shallow and deep locations with a low-concentration (10–20 µg/L) standpipe mixture. Trials 3 and 4 were conducted at shallow and deep locations with a high-concentration (175–225 µg/L) standpipe mixture. In all trials, reference samples were collected from external sampling ports simultaneously with sample collection with the device under test.

Trial 5 was a blank mixture measurement at the standpipe to test the cleanliness of each sampler. For this trial, the standpipe was filled with tap water and three replicates were collected by the device under test from the deep location in the pipe while three reference replicates were collected simultaneously from the adjacent exterior sampling port.

Trials 6 and 7 at the standpipe were termed “clean-through-dirty” tests and were designed to evaluate the performance of discrete-level grab samplers.

This test was optional for the other active samplers. Those sampling systems that were intended for permanent deployment in a well were not required to participate in the "clean-through-dirty" sampling trials, although some vendors chose to participate voluntarily. In this test, two mixtures, a high (~200 µg/L) and a low (~20 µg/L), were prepared in the mixing tanks. The pipe was then filled so that the high-level mixture occupied the top 1/3 of the pipe while the low-level mixture was in the bottom 2/3 of the pipe. Water samples were collected at the bottom and approximate midpoint of the pipe after the sample was lowered through the high-level mixture at the top of the pipe. Reference samples were simultaneously collected from the external sampling ports in the same manner as for the previous standpipe trials.

The onsite groundwater sampling matrix is shown in Table 4. Two of the wells originally scheduled for use were dropped from the sampling matrix because they were at no-detect levels for TCE. The groundwater sampling procedure for the bladder pump and reference sampler was as follows: Prior to insertion into the water column, the reference and bladder pumps were arranged vertically so that the reference pump was directly below the bladder pump. The two sampling devices were then lowered into the well as a pair. The inlet screen of the reference pump was at the top of the pump and the inlet screen of the bladder pump was at the bottom. With this orientation, both pumps sampled from the same location in the well. A purge volume of about 1 to 2 liters was drawn through the reference pump and bladder pump at a flow rate between 100 to 200 mL/minute. Following this purge, four replicate samples were collected with each sampling device.

Table 3. Sampler Verification Trials at the Standpipe

Trial No.	Standpipe Collection Port	Sample Collection Depth (ft)	VOC Concentration Level	No. of Replicates per Technology
1	SP14	Shallow (17)	Low (~20 µg/L)	5
2	SP3	Deep (92)	Low (~20 µg/L)	5
3	SP14	Shallow (17)	High (~200 µg/L)	5
4	SP3	Deep (92)	High (~200 µg/L)	5
5	SP3	Deep (92)	Blank	3
6	SP3	Deep (92)	Mixed (high over low)	4
7	SP12	Shallow (35)	Mixed (high over low)	4

Notes: In each trial, an equal number of reference samples were collected simultaneously with the device samples from adjacent external standpipe sampling ports. Sample collection points during trials 6 and 7 were from the low VOC concentration region after the sampler was lowered through a high VOC concentration region.

Table 4. Sampler Verification Trials at the Groundwater Monitoring Wells

Trial	Well	Distance from Top of Well to Screen Mid-point (ft)	Depth to Water (ft)	Approximate TCE Conc. (µg/L)	No. of Replicates per Technology
10	06-20MW	67.7	7.8	<5	4
11	06-11MW	83.1	15.2	500	4
13	06-04MW	35.1	24.6	500	4
14	12-09MW	15.0	10.0	20	4

Notes: Reference samples were collected using a submersible electric sampling pump that was collocated with the bladder pump in 2-inch and 4-inch wells. Well numbers 06-04 and 12-09 were 2-inch diameter wells. All other wells had 4-inch diameters. Approximate TCE concentrations are derived from NASA contractor quarterly monitoring data. Trials 12 and 15 were no-detect wells and were dropped from the data set.

Chronological Summary of Demonstration Activities

The demonstration began on Monday, August 9 and concluded on Tuesday, August 17. The first four days of the demonstration were devoted to testing those technologies designated "active samplers." Included in this group were Burge Environmental (multilevel sampler), Clean Environment Equipment (bladder pump), Geolog (bladder pump), QED Environmental (bladder pump), and Sibak Industries (discrete-level grab sampler). The second half of the demonstration interval was devoted to testing the "passive sampler" category, of which W. L. Gore (sorbent sampler) was the only participant. A short briefing was held on Monday morning for all vendor participants to familiarize them with the standpipe facility and the adjacent groundwater monitoring wells. Standpipe testing began for the active sampler category at midmorning on Monday and was completed on the following day. Two days of testing at groundwater wells followed. The passive sampler category tests were begun at the standpipe Thursday, August 12 and were completed on Monday, August 16. The passive sampler category was also deployed at a number of monitoring well sites simultaneously with standpipe testing.

Sample analysis was carried out in a mobile laboratory parked near the standpipe and was carried out concurrently with field testing. With the exception of the first day of sample analysis, all technology and matched-reference samples were analyzed on the same instrument and usually on the same day. This approach was taken to minimize the possible influence of instrument variability on the analysis results.

The demonstration technical team recorded observations during operation of the devices at the standpipe and monitoring well trials with regard to their logistical requirements and ease of use. These observations also were used to document any performance anomalies as well as the technical skills required for operation.

Deviations from the Verification Plan

Under most field-testing environments, circumstances often arise that prevent a complete execution of the test plan, and this test was no exception. A list of the deviations from the test plan that are judged to be important are summarized, along with an assessment of the resulting impact on the field test data set.

Lost/Dropped Samples—Out of over 800 samples, 1 was dropped and lost in the field and 3 were not analyzed either because they were overlooked or lost in handling by the field technicians or analysts. Because 4 or 5 replicates were collected in each sampling trial, the loss of a few samples does not affect the overall study results.

QC-Flagged Data—Several samples on the first day of GC/MS operation were reported with low internal standard recovery as a result of gas transfer line problems. A close examination of the data revealed that these results are comparable with replicate sample results that passed quality control (QC) criteria. Consequently, these data were used in the final analysis. A note indicating the use of flagged data is included in the appropriate data tables. No flagged data were encountered with regard to SamplEase bladder pump and associated reference samples in this study.

Samples Below Quantitation Limit of GC/MS—One of the wells sampled produced reference and vendor samples that were at or below the practical quantitation limit of the GC/MS system. These data were manually reprocessed by the analyst to obtain a concentration estimate. Where this occurs, these data are flagged and appropriate notice is given in the analysis section of this report.

Blank GW Monitoring Wells—Six groundwater monitoring wells were selected for study, based on preliminary assessment of observed TCE concentration levels using either historical data or data from previous onsite well screening activities. In three trials, well TCE concentration levels were below the limits of detection, despite evidence to the contrary from preliminary screening. Sampler contamination during preliminary screening carried out prior to the field test was determined to be the cause of erroneously high readings. One of the "blank" wells was kept in the data set to assess sampler blank performance in the field. The other wells were dropped from the list of trials. The impact on the overall data set is not important, since the objective parameters of performance such as sampler precision and comparability with reference are derived from the standpipe data.

Open Fill Valve at Standpipe—A fill valve was inadvertently left open while the SamplEase pump was being used to collect low-concentration samples from the deep location during trial 2. This open valve resulted in the collection of SamplEase and reference samples with differing VOC compositions. This procedural anomaly was discovered subsequent to the test during data analyses and thus could not be remedied. These suspect data were deleted from the data set. The remaining data provide an adequate sample size for evaluating SamplEase bladder pump performance, although evaluation at low VOC concentration and deep collection depth was not possible.

Section 4 — Performance Evaluation for SamplEase Bladder Pump

Introduction

This section briefly discusses the results of test data analysis and summarizes sampler performance. Sampler precision, comparability with reference sample data, and overall versatility of the sampler for collection of VOC-contaminated water are discussed. Only summary data are given in this report. A complete tabulation of all test data are available from the authors via individual request.

Sampler Precision

The precision for both SamplEase and reference samples from the first four standpipe trials is given in Table 5. The results are listed by the six compounds for 3 test conditions (low concentration at shallow sampling depth, high concentration at shallow sampling depth, and so on), for a total of 18 cases.[1] Included in the table are the standard deviations of the SamplEase bladder pump and reference method. The final column in the table is the result of an F-ratio test used to determine whether the technology and reference precision can be regarded as statistically different. The *p* value tabulated in the final column of the table is an estimate of the probability of encountering the observed difference in precision, if the assumption is made that the two groups of measurements (technology and reference) are equivalent. In statistical terms, this is the null hypothesis and the accompanying assumption is that only random influences are present and no systematic bias is present in the two sets of measurements. Values of *p* that are close to 1 reflect small differences in precision with a corresponding high probability of encountering differences of this magnitude under the null hypothesis. On the other hand, values of *p* that are less than 0.05 are indicative of larger precision differences that may warrant a rejection of the null hypothesis. Differences of such magnitude cannot be satisfactorily explained by random variation alone in the two sets of data being compared. If the assumption is made that the two data sets are from the same population, and only random effects are occurring, the probability of observing a difference in two precision values corresponding to a 0.05 value of *p* is 5%. In other words, such a difference would be highly unlikely. For values of *p* less than 0.05, it is more likely that some systematic bias exists between the two sets of data.

The greatest imprecision in the SamplEase bladder pump results are encountered for 12DCA and 112TCA at the high VOC concentrations and the shallow collection depth (Table 5). Preliminary evaluations of GC/MS performance carried out prior to the field demonstration revealed that these two compounds had higher analytical uncertainty than the other target compounds, so this effect can be attributed to the analytical method and not the sampling process. The median RSD for all compounds in all trials was 11.7% for the SamplEase bladder pump and 10.7% for the reference samples. In 12 of the 18 cases shown in the table, the SamplEase pump precision was worse than the reference sample precision with the remaining cases having precision better than or equal to the reference sample precision. An even or nearly even split of technology precision in the greater-than and less-than categories would suggest equivalence between the two sampling methods. Qualitatively, the indications are that the SamplEase bladder pump is less precise than the reference method. On a more formal statistical basis, the F-ratio test results shown in the last column of Table 5 reveal that 2 of 18 cases had a value of *p* that was less than 0.05. Thus, differences in precision between SamplEase pump samples and reference samples are statistically insignificant in 16 of the 18 cases. Overall, the conclusion can be made that the SamplEase and reference sample sets are comparable in terms of precision.

[1] Six cases from the low concentration, deep sampling point were deleted from the standpipe trial data set. The data were rejected because of an obvious mismatch between SamplEase and reference samples caused by an open valve at the base of the standpipe. The SamplEase and reference samples were from different mixtures and were not comparable. This experiment procedural error was not noted until after the field trials were completed and thus could not be remedied.

Table 5. Precision Summary for SamplEase Bladder Pump and Reference Sampler

Compound	Conc. Level	Depth (ft)	SamplEase Precision (%RSD)	REF Precision (%RSD)	F-Ratio	F-Ratio Test *p*
11DCE	Low	17	6.6	15.2	4.62	0.08
	Low	91	No data	No data	No data	No data
	High	17	12.1	12.4	1.61	0.32
	High	91	10.4	8.0	1.40	0.38
12DCA	Low	17	18.2	13.4	1.59	0.33
	Low	91	No data	No data	No data	No data
	High	17	17.8	12.1	3.66	0.12
	High	91	11.6	6.2	2.76	0.17
BNZ	Low	17	5.1	9.9	3.32	0.14
	Low	91	No data	No data	No data	No data
	High	17	16.4	11.5	3.04	0.15
	High	91	11.7	6.7	2.60	0.19
TCE	Low	17	7.4	12.4	2.94	0.16
	Low	91	No data	No data	No data	No data
	High	17	13.2	5.8	6.82	**0.04**
	High	91	7.9	4.6	2.32	0.22
112TCA	Low	17	12.7	12.9	1.27	0.41
	Low	91	No data	No data	No data	No data
	High	17	24.2	5.9	24.72	**<0.01**
	High	91	6.9	6.5	1.11	0.46
PCE	Low	17	8.4	14.4	3.45	0.13
	Low	91	No data	No data	No data	No data
	High	17	12.2	5.7	5.03	0.07
	High	91	7.7	4.1	2.48	0.20
Minimum			5.1	4.1		
Maximum			24.2	15.2		
Median			11.7	10.7		

Notes: Values of *p* less than 0.05 are shown in bold. REF = Reference. See text for explanation regarding missing values.

Sampler Comparability

The comparability of the SamplEase bladder pump with reference data for the standpipe trials is given in Figure 2 and Table 6. Percent difference values were computed for each of the six target compounds in the three valid standpipe trials for a total of 18 cases. The percent difference values for the SamplEase bladder pump range from –16 to 31%, with a median value of –4.5%. Average difference values for 8 of the 18 cases were above 0%, with the other 10 cases below 0%. An even or nearly even split of percent difference values in the greater than zero and less than zero categories would be indicative of equivalence between the two sampling methods. In this case the split is nearly even giving qualitative evidence of comparability. On a more formal statistical basis, t-test results show that all but 5 of the 18 cases have *p* values greater than 0.05. This indicates that in many cases, random variation among a single population can account for the observed differences between the SamplEase bladder pump samples and the reference samples. Thus, the presence of any significant SamplEase bladder pump bias can be ruled out relative to the reference method.

The SamplEase bladder pump data reveal that no statistically significant negative differences in excess of –16% (PCE, high concentration, deep sampling) are observed. Although positive differences of greater magnitude are observed, they are judged with less concern since loss of VOCs in the sampling process is expected to be the primary factor influencing sampler performance.

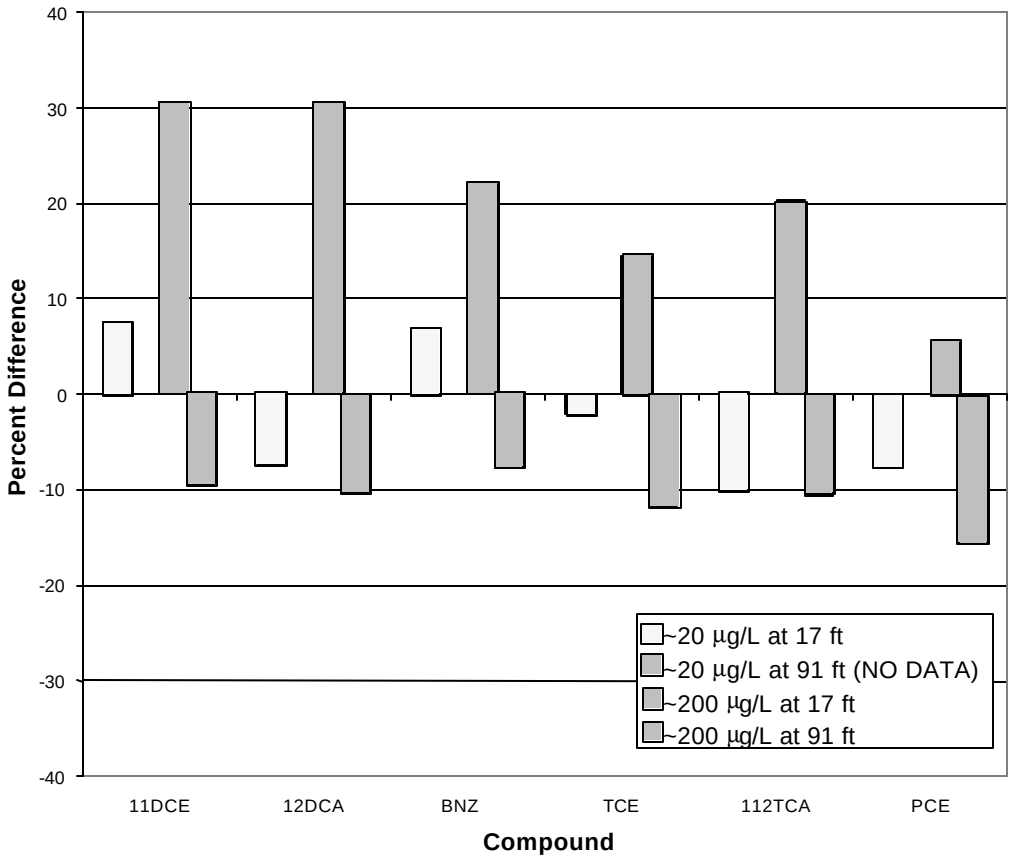

Figure 2. SamplEase bladder pump sample comparability with reference samples from the standpipe trials.

Blank and Clean-Through-Dirty Test Results

The results from the standpipe trials using blank solutions show that both the SamplEase and reference samples had non-detectable levels of all six target compounds. These results indicate that a new or decontaminated pump does not measurably contaminate a clean sample of water.

The SamplEase bladder pump is designed for permanent deployment in a single well and is not recommended for movement from well to well. Consequently, the vendor chose not to participate in the clean-through-dirty tests.

Monitoring Well Results

SamplEase bladder pump results from groundwater monitoring samples collected at four wells are shown in Table 7 alongside reference sample data from the same wells. Four replicate samples were taken with the SamplEase bladder pump and the reference sampler (a submersible electric gear pump). Relative standard deviations of both SamplEase and the reference samples are given in the table along with the mean percent difference between the two sets of data. The observed relative standard deviations indicate that SamplEase precision in the field was generally similar to that observed at the standpipe. SamplEase bladder pump differences compared to reference samples for the high-concentration wells are both less than 8%. SamplEase bladder pump differences for the low-concentration well (number 12-09) are very high and may suggest, in light of the good performance of the SamplEase bladder pump at the standpipe, that the co-located SamplEase and reference samplers were not collecting a homogeneous mixture from the well. The difference may be further accentuated by the fact that the concentration levels were near the GC/MS headspace method detection limit, resulting in relatively imprecise measurements.

Table 6. Comparability of SamplEase Bladder Pump and Reference Sample Data from Standpipe Trials

Compound	Conc. Level[a]	Depth (ft)	SamplEase Difference (%)	t-Test[b] (*p*)
11DCE	Low	17	7	0.35
	Low	91	No data[c]	No data
	High	17	31	**<0.01**
	High	91	–9	0.12
12DCA	Low	17	–7	0.47
	Low	91	No data	No data
	High	17	31	**0.03**
	High	91	–10	0.09
BNZ	Low	17	7	0.21
	Low	91	No data	No data
	High	17	22	0.07
	High	91	–8	0.21
TCE	Low	17	–2	0.77
	Low	91	No data	No data
	High	17	15	0.08
	High	91	–12	**0.01**
112TCA	Low	17	–10	0.23
	Low	91	No data	No data
	High	17	20	0.16
	High	91	–10	**0.03**
PCE	Low	17	–8	0.32
	Low	91	No data	No data
	High	17	5	0.41
	High	91	–16	**<0.01**
Minimum			-16	
Maximum			31	
Median			-4.5	

[a] The low-level concentration was in the range of 10 to 20 µg/L for all 6 target compounds. The high-level concentration was in the range of 175 to 250 µg/L.

[b] The t-test was used to compare the mean percent difference of the SamplEase bladder pump samples relative to the reference samples for each compound in each trial. Small values of *p* (<0.05) shown in bold are suggestive of sampler bias. See text for further details.

[c] During data analysis following the test, it was discovered that a fill valve was inadvertently left open during a portion of SamplEase pump testing. As a result, SamplEase and reference samples were different. The data from this trial were dropped from the data set used in the analysis.

Table 7. SamplEase and Reference Sampler Results from Groundwater Monitoring Wells

Well Number	Well Number	SamplEase Average TCE Concentration (µg/L)	SamplEase Precision (%RSD)	Reference Average TCE Concentration (µg/L)	Reference Precision (%RSD)	SamplEase Difference (%)
06-11MW	06-11	485	4.6	479	4.6	1
06-04MW	06-04	682	12.1	633	4.5	8
12-09MW	12-09	11.9	46.1	21.2	20.3	–44
06-20MW	06-20	ND (<5)	--	ND (<5)	--	--

Note: ND = not detected.

Both the SamplEase and the reference pump samples were non-detectable for the well with no TCE. These results indicate that the SamplEase bladder pump is not a potential source of contamination in low-level sampling operations.

Sampler Versatility

The performance parameters for the SamplEase bladder pump discussed previously indicate that the device can collect water samples contaminated with VOCs of varying volatility, concentration, and sampling depths with acceptable performance. In almost all test cases, SamplEase bladder pump samples were not statistically different from reference samples with regard to precision. In comparison with reference samples, most SamplEase results were within ±20% difference. Based on these considerations, the SamplEase bladder pump is judged to have wide versatility in site groundwater characterization and monitoring applications.

Deployment Logistics

The following observations were made during testing of the SamplEase bladder pump at both the standpipe and groundwater monitoring wells.

- Only one person is needed to operate the pump and controller. Training requirements are minimal, with a day of training required for a technician to become proficient in routine field use of the equipment.
- The pump and controller are both compact and require no external power to operate. The pump control module is contained in a small lightweight weatherproof enclosure.
- The pump requires a source of compressed air or nitrogen supplied by either a compressed gas bottle or a gasoline- or electric-powered compressor. These accessories are heavy and required additional effort to transport and operate at the wellhead.
- The pump is designed for dedicated use in monitoring wells. The controller and air source are designed to be moved from wellhead to wellhead during routine sampling operations. The bladder pump itself is not well suited for moving from well to well during routine well monitoring operations since this movement requires that the pump be decontaminated and that new tubing (or decontaminated tubing) be used with each new deployment.
- The pump is essentially maintenance free, with few moving parts. Pump failure is usually remedied by complete replacement as opposed to a more costly repair option. Clean Environment Equipment offers a 10-year warranty for pumps that are equipped with intake screens.
- The pump can be used with the EPA low-flow, low-volume-purge sampling protocol.

Performance Summary

SamplEase bladder pump performance is summarized in Table 8. Evaluation categories include precision, comparability with a reference, versatility, and logistical requirements. Cost and physical characteristics of the equipment are also included. The results of this verification test show that the SamplEase bladder pump and associated pneumatic controller can be used to collect VOC-contaminated water samples that are generally statistically comparable to a reference method with regard to both precision and comparability. The SamplEase bladder pump system is well suited for use in well-sampling programs that incorporate low flow sampling and low-volume purge sampling protocols. The pumps are optimized for dedicated placement in monitoring wells that are included in a routine monitoring program.

Table 8. Performance Summary for SamplEase Bladder Pump

Performance Parameter	Summary
Precision	For 6 target compounds at low (20 µg/L) and high (200 µg/L) concentrations and at 17-foot and 91-foot sampling depths: Relative standard deviation range: 5.1 to 24.2% (reference: 4.1 to 15.2%) Median relative standard deviation: 11.7% (reference: 10.7%) In 16 of 18 standpipe test cases, SamplEase pump precision was statistically comparable to the reference sampler precision (See note in "Other" category)
Comparability with Reference Samples	For 6 target compounds at low (20 µg/L) and high (200 µg/L) concentrations and at 17-foot and 91-foot sampling depths: Percent difference range: –16 to 31% Median percent difference: –5% In 13 of 18 standpipe test cases, SamplEase pump differences relative to reference samples were statistically indistinguishable from 0%. (See note in "Other" category)
Sampler versatility	The SamplEase pump demonstrated consistent performance across the tested range of compound volatility and sampler depth, and is judged to be widely versatile.
Logistical requirements	System can be operated by one person with a day of training. System requires a source of compressed air or nitrogen at the wellhead.
Completeness	System was successfully used to collect all of the samples prescribed in the test plan.
Purchase cost	Model SP15T36 pump: $630 Inlet screen: $50 Model SC250 pneumatic controller: $1,550 Teflon-lined poly tubing costs: $1.30 per foot
Size and weight	Model T1220M pump: 1.5-inch dia. × 40-inch length (with intake screen), 3.8 pounds Model SC250 controller: 10 × 9 × 7 inches, 9.8 pounds
Other	System is designed for low-volume purge applications. Pumps are optimized for dedicated placement in wells. Comparison at low VOC concentration and deep collection depth could not be done as a result of missing reference data caused by an experimental procedural error that was not attributable Clean Environment Engineering personnel.

Note: Target compounds were 1,1-dichloroethene, 1,2-dichloroethane, benzene, trichloroethene, 1,1,2-trichloroethane, and tetrachloroethene.

Section 5 — SamplEase Bladder Pump Technology Update and Representative Applications

Note: The vendor chose not to submit any material for this section.

Section 6 — References

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Appendix A — Reference Pump Performance

Introduction

In addition to the sampling at the standpipe, the verification test design included the collection of vendor samples from onsite groundwater monitoring wells. During monitoring well sampling, a reference pump was collocated in the well with the vendor sampler. Both vendor and reference samples were collected simultaneously to enable a comparison of the results. This appendix summarizes the reference sampler chosen and outlines its performance and acceptability as a reference sampling technique.

System Description

The reference pump selected for use in this verification study was a submersible electric gear pump (positive displacement, low-speed pump, Fultz, Model SP-300, Lewistown, PA). Pump construction materials are stainless steel and polytetrafluoroethylene (PFTE), and pump dimensions are 7.5 inches in length by 1.75 inches in diameter. This pump is a positive displacement device. Water is introduced into the pump through a 60-mesh inlet screen into a stainless steel cavity. Two PFTE gears inside the cavity push the water to the surface through 100 feet of ¼-inch outside diameter PFTE tubing. An electronic controller is used to regulate the flow rate of the pump. Nominal sample collection flow rates were in the range of 100–200 mL/min.

Performance Evaluation Method

The gear pump was tested during the standpipe trials in the same manner as the other vendor pumps. Water samples were collected from the interior of the standpipe in four separate trials with both low (~20 µg/L) and high (~200 µg/L) target concentrations at low (17 feet) and high (91 feet) sampling depths (see Section 3 for additional details). Reference samples were collected from external sampling ports simultaneously with the pump samples. In each trial, five replicate pump samples and five replicate port samples were collected. Following collection, all samples were analyzed using the same onsite GC/MS system.

Pump Precision

A summary of pump precision is given in Table A-1. The percent relative standard deviation results for each of the six target compounds in the four standpipe trials (low concentration—shallow, low concentration—deep, and so on) for the gear pump and the external sampling port are given in columns 4 and 5, respectively. The relative standard deviation range for the pump was 3.2 to 16.3%, with a median value of 7.6%. The port precision data ranged from 2.8 to 16.2%, with a median value of 10.1%. The final column in the table gives the value of p associated with the F-ratio test (see Section 3 for a description of this test). Values of p less than 0.05 may indicate that significant, nonrandom differences exist between the two estimates of precision.

Out of 24 trials, only 2 show values of p less than 0.05. These data indicate that pump precision was not statistically different from the precision obtained from the reference samples taken directly from the standpipe external ports.

Table A-1. Precision of Gear Pump and Reference Samples in Standpipe Trials

Compound	Conc. Level	Depth (ft)	Gear Pump Precision (%RSD)	Port Precision (%RSD)	F-Ratio	F-Ratio *p*
11DCE	Low	17	15.7	14.2	1.11	0.46
	Low	91	3.5	14.4	14.7	**0.01**
	High	17	4.0	8.6	4.81	0.08
	High	91	7.6	9.7	1.28	0.41
12DCA	Low	17	15.4	12.5	2.35	0.21
	Low	91	3.2	13.2	14.1	**0.01**
	High	17	5.1	9.0	3.18	0.14
	High	91	6.0	10.4	2.38	0.21
BNZ	Low	17	8.1	11.8	1.71	0.31
	Low	91	7.6	12.9	2.30	0.22
	High	17	3.7	8.4	5.02	0.07
	High	91	6.1	9.4	1.83	0.29
TCE	Low	17	16.3	10.5	2.41	0.21
	Low	91	5.9	12.1	3.12	0.15
	High	17	6.4	2.9	4.82	0.08
	High	91	9.6	8.6	1.55	0.34
112TCA	Low	17	9.4	16.2	3.38	0.13
	Low	91	8.4	15.0	2.81	0.17
	High	17	7.6	3.5	4.76	0.08
	High	91	11.0	6.5	3.43	0.13
PCE	Low	17	12.9	9.6	1.36	0.39
	Low	91	9.0	11.7	1.50	0.35
	High	17	4.5	2.8	2.28	0.22
	High	91	12.7	8.8	2.38	0.21
Minimum			3.2	2.8		
Maximum			16.3	16.2		
Median			7.6	10.1		

Pump Comparability with Reference Samples

Gear pump comparability is expressed as the percent difference relative to the reference sample concentration by subtracting the average reference value from the average gear pump value, dividing the result by the average reference value, and multiplying by 100. The percent differences for each of the 24 trials are given in Table A-2. They range from −13 to 24% with a median value of 7%. A t-test for two sample means was used to evaluate the statistical significance of the differences between the gear pump and reference samples. The tabulated values of *p* give a quantitative measure of the significant of the observed difference in probabilistic terms. Values of *p* less than 0.05 suggest that a statistically significant bias may exist for the trial. With five exceptions, all values of *p* are greater than 0.05, indicating that overall, the differences between the two sampling methods are statistically indistinguishable.

Table A-2. Comparability of the Gear Pump with the Reference Samples in Standpipe Trials

Compound	Conc Level[a]	Depth (ft)	Difference (%)	t-Test[b] *p*
11DCE	Low	17	–4	0.64
	Low	91	7	0.31
	High	17	–3	0.54
	High	91	13	**0.05**
12DCA	Low	17	24	**0.05**
	Low	91	10	0.13
	High	17	–2	0.71
	High	91	12	0.06
BNZ	Low	17	11	0.13
	Low	91	13	0.11
	High	17	0	0.98
	High	91	14	**0.03**
TCE	Low	17	0	0.99
	Low	91	16	**0.04**
	High	17	0	0.95
	High	91	11	0.10
112TCA	Low	17	–6	0.51
	Low	91	7	0.41
	High	17	1	0.77
	High	91	10	0.15
PCE	Low	17	–13	0.08
	Low	91	6	0.37
	High	17	–6	**0.03**
	High	91	6	0.42
Minimum			-13	
Maximum			24	
Median			7	

[a] The low-level concentration was in the range of 10 to 20 µg/L for all 6 target compounds. The high-level concentration was in the range of 175 to 250 µg/L.

[b] The t-test was used to compare differences between SamplEase pump and reference samples for each compound in each trial. Small values of *p* (<0.05) are shown in bold and are suggestive of a statistically significant difference. See text for further details.

The percent recovery data for the gear pump are also shown graphically by target compound in Figure A-1 for each of the four standpipe trials. Fifteen of the 24 percent difference values are in the positive percent difference range, suggesting that many of the samples collected with the gear pump contained higher concentrations than those samples collected from the corresponding external sampling port. An exhaustive evaluation of the data was not performed to characterize this phenomenon; however, it is possible that this was a result of bias in the analytical method, since one would not expect sample losses to be significant in the reference sampling procedure.

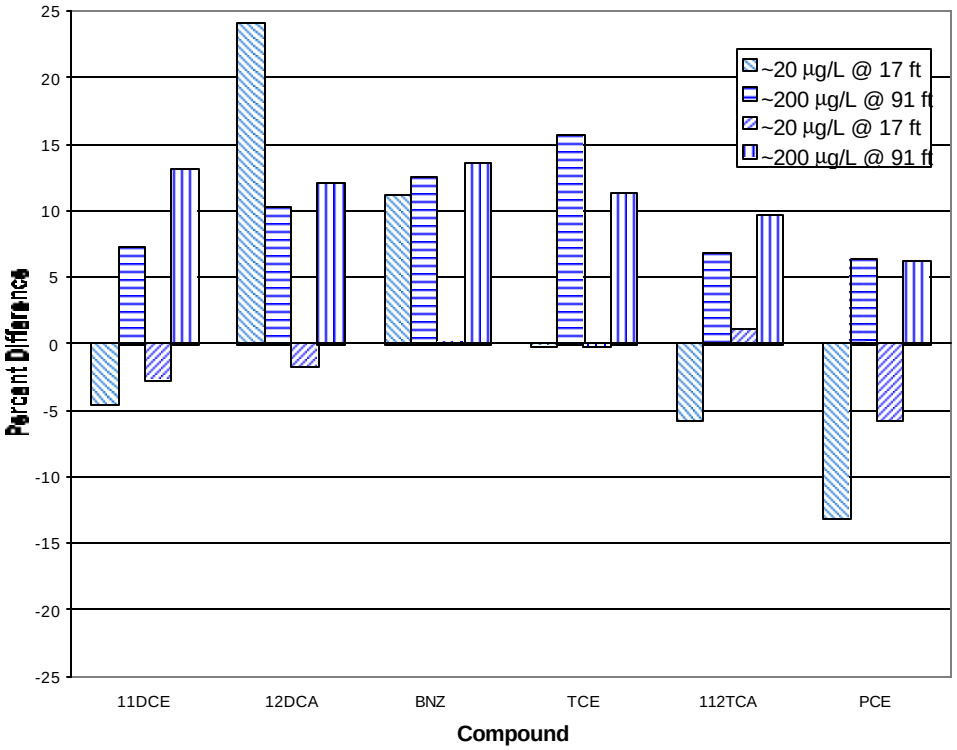

Figure A-1. Percent recoveries of the reference pump by compound for the four standpipe trials.

Reference Pump Performance Summary

The test data for the reference pump reveal considerable variability for PCE and 12DCA. However, the variability and comparability for TCE, the only compound encountered in the field trials, are acceptable. The mean relative standard deviation for TCE at concentration levels ranging from 20 to 200µg/L was 9.6 and the mean percent difference for TCE in the same concentration range was 7%. The data presented for TCE show that the pump is equivalent to the reference sampling method in terms of both precision and accuracy and is acceptable for use as a reference standard.

Appendix B — Quality Summary for Analytical Method

Introduction

An onsite GC/MS-headspace method was chosen for analysis of all samples in this study. Two identical GC/MS systems were operated by Field Portable Analytical (Folsom, CA) using a modified EPA Method 8260 (for a summary of the method, see Section 3). Data quality measures were incorporated into all onsite analyses consistent with the guidelines in Method 8260. This appendix summarizes those data quality measures, thereby demonstrating the adequacy of the method for this verification study.

Data Quality Measures

A number of data quality measures were used to verify acceptable instrument performance and the adequacy of the final analytical results throughout the course of the study. These measures are summarized in Table B-1. All data quality measures in this table were followed, with the exception of duplicates. Duplicates were not routinely run since all of the samples from the field were in batches of replicates. Earlier predemonstration studies indicated that the field replicates were the same in composition so that they could be treated as analysis duplicates.

Table B-1. Onsite GC/MS-Headspace Method Quality Control Measures

Quality Control Check	Minimum Frequency	Acceptance Criteria	Corrective Action
MS tune check w/ bromofluorobenzene (BFB)	Every 12 hours	Ion abundance criteria as described in EPA Method TO-14	1) Reanalyze BFB 2) Adjust tune until BFB meets criteria
5-Point (Minimum) calibration	Beginning of each day	%RSD ≤ 30%	Rerun levels that do not meet criteria
Continuing calibration check (CCC)	Beginning of each day	± 25% difference of the expected concentration for the CCC compounds	1) Repeat analysis 2) Prepare and run new standard from stock 3) Recalibrate
End calibration checks	End of each day	± 25% RPD of the beginning CCC	1) Repeat analysis 2) If end check is out, flag data for that day
Duplicates	10% of the samples	Relative percent difference ≤ 30%	1) Analyze a third aliquot 2) Flag reported data
Method blanks	After beginning of day CCC	Concentrations for all calibrated compounds < practical quantification level	Rerun blanks until criteria are met

Data Quality Examples

The following data are examples of system performance throughout the course of the study. In the interest of brevity, all quality control data are not shown in this appendix. A complete tabulation of all quality control data is included in the GW SAMPLING DATA NOTEBOOK and is available for viewing through a request to the ETV Site Characterization and Monitoring Technologies Pilot Manager.

Method Blank Check

Method blanks were run at the beginning of each 12-hour analysis session. Concentration levels of the six target compounds were reported as ND <5 µg/L for all method blank samples.

Continuing Calibration Check

The method criterion for the continuing calibration checks run at the beginning and end of each analysis cycle was a value within 25% of the expected value. The results of the TCE continuing calibration checks for both of the GC/MS instruments used in the study are shown in Figures B-1 and B-2. Similarly, the results of the PCE continuing calibration check for both instruments are shown in Figures B-3 and B-4. All check compound recoveries fall within the predefined control interval of 70 to 130%. The control interval is specified in EPA Method SW-846, from which this method is adapted. The relative percent differences between the pre- and post-analysis batch calibration check samples are shown in Figure B-5. In two cases, the relative percent difference falls outside the 25% window. Data from these days were not rejected, however, since the ±30% criteria for the calibration check was met.

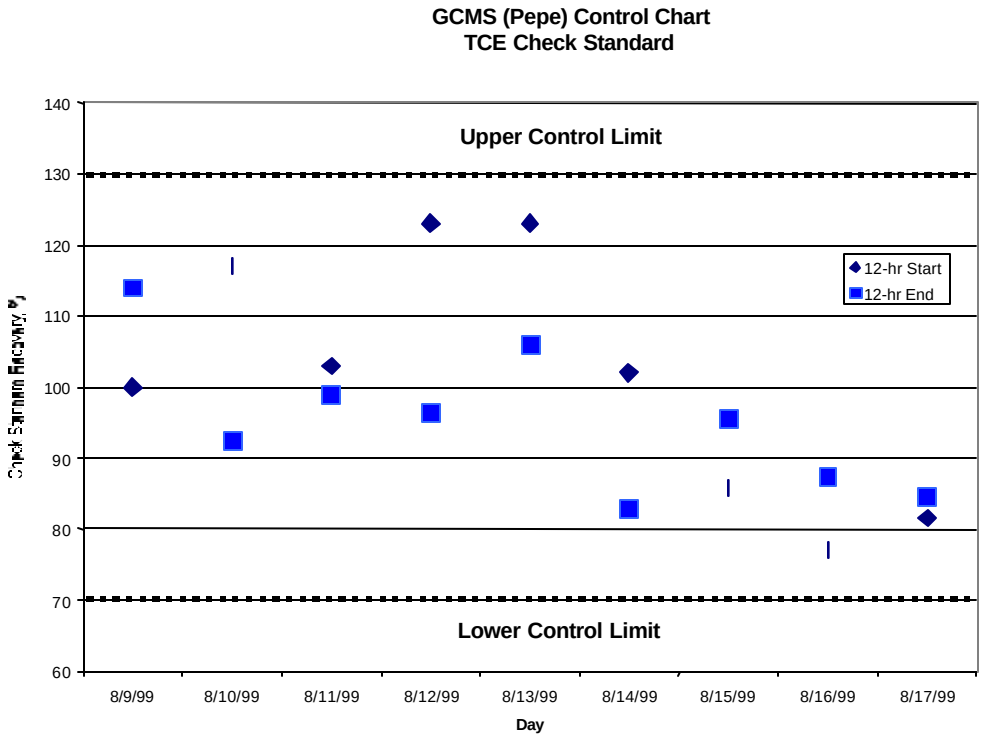

Figure B-1. Calibration check control chart for TCE on GC/MS #1.

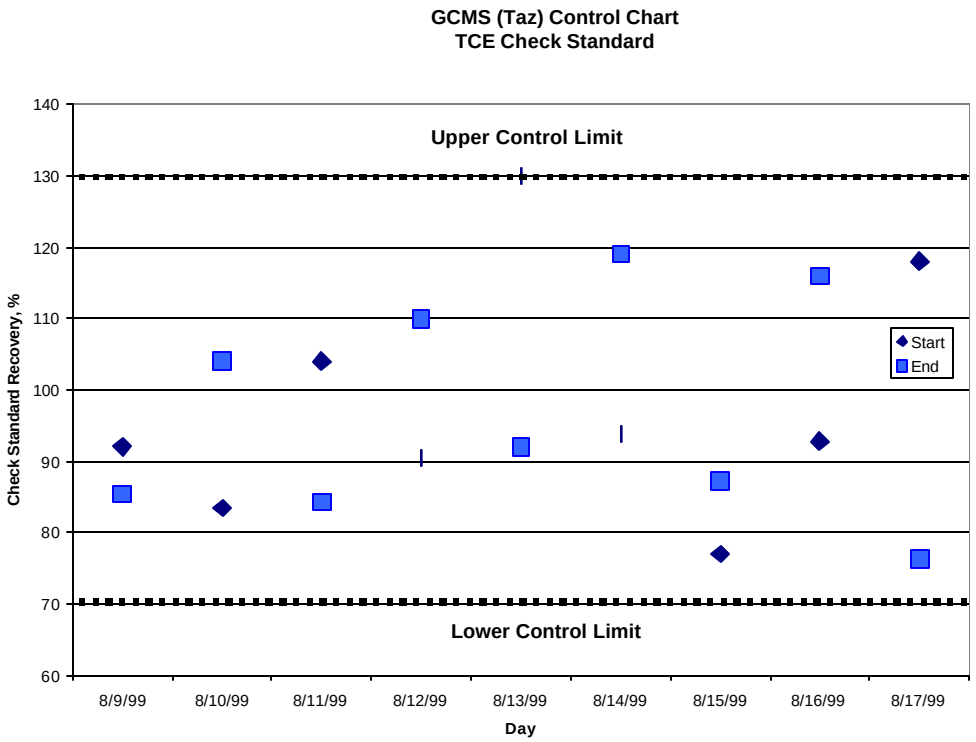

Figure B-2. Calibration check control chart for TCE on GC/MS #2.

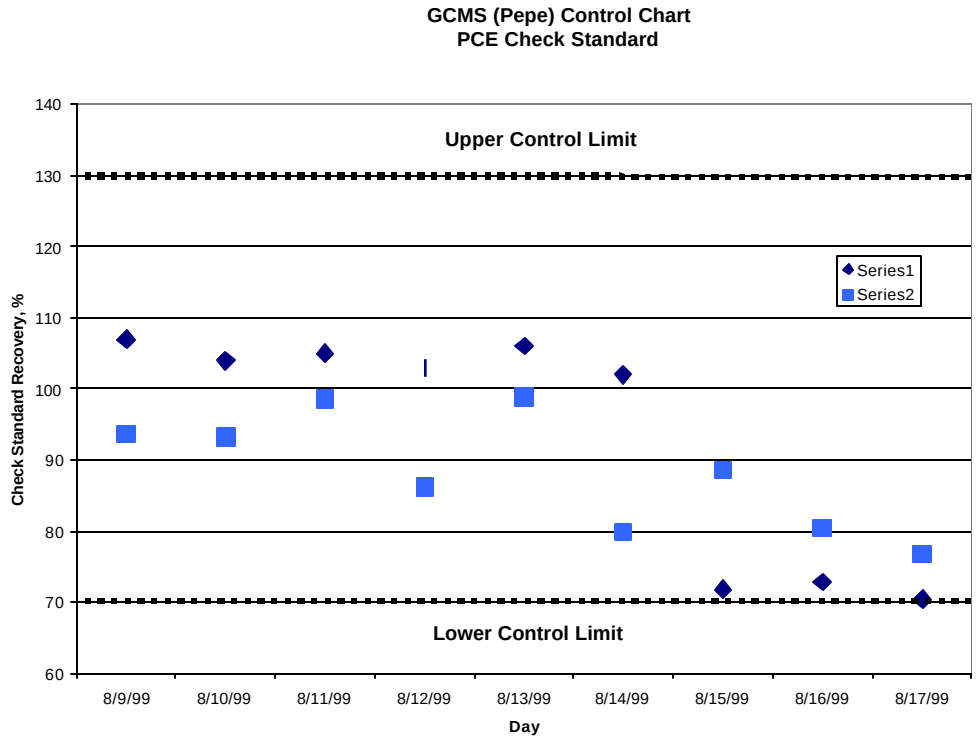

Figure B-3. Calibration check control chart for PCE on GC/MS #1.

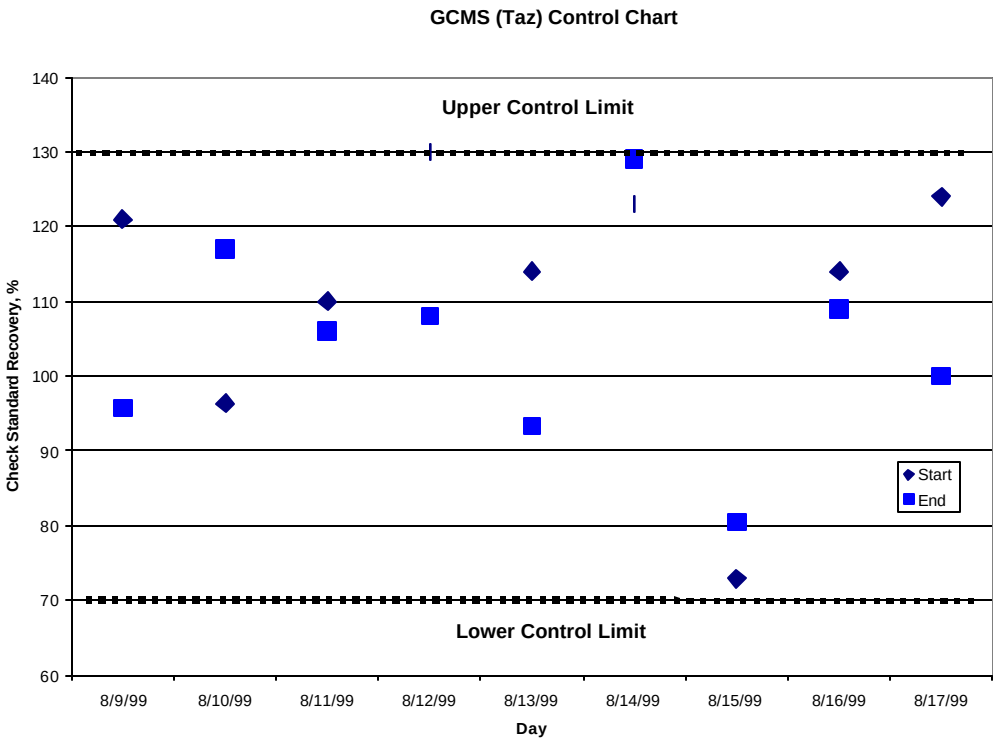

Figure B-4. Calibration check control chart for PCE on GC/MS #2.

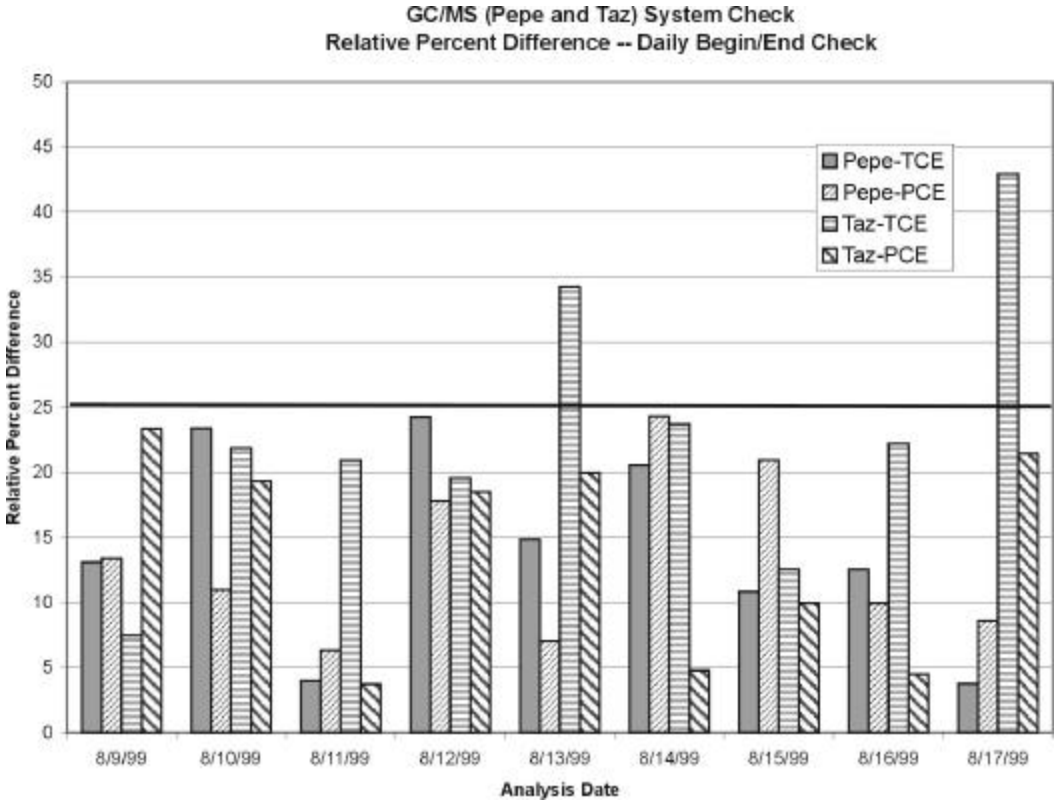

Figure B-5. GC/MS system check relative percent differences.