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# **Environmental Technology Verification Report**

**Groundwater Sampling Technologies** 

GeoLog, Inc. Micro-Flo<sup>a</sup> Bladder Pump Model 57400





#### THE ENVIRONMENTAL TECHNOLOGY VERIFICATION **PROGRAM**







### ETV JOINT VERIFICATION STATEMENT

TECHNOLOGY TYPE: GROUND WATER SAMPLING TECHNOLOGIES

**APPLICATION:** VOC-CONTAMINATED WATER SAMPLING

Micro-Flo -- Model 57400 Bladder Pump and Model 5001 Pump Cycle Controller TECHNOLOGY NAME:

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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 Micro-Flo bladder pump and pneumatic controller manufactured by GeoLog Inc.

#### **DEMONSTRATION DESCRIPTION**

In August 1999, the performance of six ground water 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 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 ground water 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  $\mu$ g/L) and high (~200  $\mu$ g/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 Micro-Flo bladder pump, which is designed for dedicated use in a monitoring well.

The standpipe trials were supplemented with additional trials at ground water monitoring wells in the vicinity of sites with VOC-contaminated ground water at the NASA Stennis facility. The technologies were deployed in a number of 2-inch and 4-inch wells, along with collocated 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 the same field-portable gas chromatograph-mass spectrometer (GC/MS) system that was 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, with the use of a headspace sampler in lieu of a purge-and-trap unit. The overall performance of the ground water sampling technologies was assessed by comparison of technology and reference sample results with particular attention given to key performance parameters such as sampler precision and accuracy. Aspects of field deployment and potential applications of the technology were also considered.

Details of the demonstration, including an evaluation of the sampler's performance, may be found in the report entitled *Environmental Technology Verification Report: GeoLog Inc. Micro-Flo Bladder Pump*, EPA/600/R-00/075.

#### TECHNOLOGY DESCRIPTION

The Micro-Flo bladder pump consists of an internal flexible bladder that is positioned within a rigid stainless steel pump body. 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 VOC 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.

GeoLog offers bladder pumps constructed with stainless steel and Teflon or polyvinyl chloride and Teflon. The pump tested during this evaluation was the Model 57400, which is the stainless steel and Teflon version. The pump is 24 inches long with a 1.66-inch external diameter and a weight of 2.5 pounds. The volumetric capacity of the pump is 225 mL. The pump intake stainless steel screen mesh size was 0.25 mm (0.01 inch). The pump can operate at pressures up to 200 psi, which is equivalent to a lift capacity of about 460 feet.

A GeoLog Model 5001 pneumatic controller was used to control the flow of compressed nitrogen, obtained from a cylinder or compressor at the wellhead, to the bladder pump. The controller has dimensions of  $14.5 \times 10 \times 9$  inches and weighs 15 pounds. Drive air for the bladder pump can be delivered from compressed gas cylinders or from a field-portable gasoline-powered compressor.

The bladder pump tested costs \$425 and the controller is priced at \$1,295. Teflon-lined polyethylene tubing is also a requirement for most VOC sampling applications and is priced at \$2.25 to \$2.75 per foot.

#### **VERIFICATION OF PERFORMANCE**

The following performance characteristics of the Micro-Flo bladder pump were observed:

*Precision:* The precision of the sampler was determined through the collection of a series of replicate samples from 4 standpipe trials using low ( $\sim$ 20 μg/L) and high ( $\sim$ 200 μg/L) VOC concentrations at 17-foot and 91-foot collection depths. Each trial included 6 target VOCs for a total of 24 cases. Micro-Flo pump precision, represented by the relative standard deviation, for all compounds at all concentrations and sampling depths evaluated in this study, ranged from 2.7 to 26.7%, with a median value of 8.5%. In 18 cases, the relative standard deviation of the Micro-Flo bladder pump was greater than the reference, with Micro-Flo 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 precision differences were statistically significant. Test results showed that precision differences between Micro-Flo and reference samples were statistically insignificant at the 95% confidence level in all of the 24 test cases.

Comparability with a Reference: Micro-Flo bladder pump results from the standpipe trials were compared with results obtained from reference samples collected at the same time. Both Micro-Flo 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 -21 to 27%, with a median difference of -1%. The t-test for two sample means was used to assess whether the differences between Micro-Flo and reference sample results were statistically significant. These tests showed that in 17 of 24 trials, differences were statistically indistinguishable from 0% at the 95% confidence level. Statistically significant negative bias did not exceed - 21% (4 cases) and statistically significant positive bias did not exceed 27% (3 cases).

**Versatility:** Sampler versatility is the consistency with which the sampler performed with various target compounds, concentration levels, and sampling depths. Sampler performance did not significantly vary with changes in compound volatility, concentration, or sampler depth and the sampler is judged to be widely applicable to the variety of groundwater sampling situations likely to be encountered in field use.

**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-powered compressor. The bladder pumps are designed for dedicated use in a monitoring well; however, the system can also be moved from well to well.

**Overall Evaluation:** The results of this verification test show that the Micro-Flo bladder pump and associated pneumatic controller can be used to collect VOC-contaminated water samples that are statistically comparable to a reference method with regard to both precision and comparability with a reference sample. The results of a clean-through-dirty test revealed some sampler carryover of contaminants from an overlying dirty water column into an underlying clean water column. 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.

Gary J. Foley, Ph.D. Director National Exposure Research Laboratory Office of Research and Development Samuel G. Varnado Director Energy and Critical Infrastructure Center Sandia National Laboratories

**NOTICE**: EPA verifications are based on evaluations of technology performance under specific, predetermined criteria and appropriate quality assurance procedures. EPA and SNL make no expressed or implied warranties as to the performance of the technology and do not certify that a technology will always operate as verified. The end user is solely responsible for complying with any and all applicable federal, state, and local requirements. Mention of commercial product names does

# Environmental Technology Verification Report

Groundwater Sampling Technologies

GeoLog Inc.

Micro-Flo Bladder Pump Model 57400

by

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# **Notice**

The U.S. Environmental Protection Agency (EPA), through its Office of Research and Development (ORD), funded and managed, through Interagency Agreement No. DW66940927 with Sandia National Laboratories, the verification effort described herein. This report has undergone peer and administrative review and has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use of a specific product.

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## Acknowledgments

The authors acknowledge the support of all those who helped in the vendor solicitation, planning, field deployment, and analysis phases of this verification test. In particular, we recognize Steve Gardner (US EPA NERL, Las Vegas), who provided technical assistance and peer reviewed the test plan. We also acknowledge the assistance of Eugene Hays, Bill Davies, and Ed Ford (US Geological Survey) in providing access to the Standpipe Facility at the NASA Stennis Space Center as well as for their administrative and logistical support during the standpipe and groundwater monitoring trials. We also thank Ronald McGee and Jenette Gordon (NASA, Environmental Management) for their willingness to grant us access to the groundwater monitoring wells at the NASA Stennis Space Center. Thanks also to Greg New (Foster Wheeler Environmental Corporation) for his assistance in getting much of the site hydrological and well monitoring data into our hands during the planning phases of this test. Finally, we thank Craig Crume and Mika Geenfield (Field Portable Analytical) for their long hours, care, and diligence in onsite sample analysis during the field trials.

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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
REC Recovery
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
VOA Volatile organics analysis
VOC Volatile organic compound

12DCA 1,2-dichloroethane
11DCE 1,1-dichloroethane
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), SamplEase (bladder pump, Clean Environment Equipment, Oakland, CA), Well Wizard dedicated sampling system (bladder pump, QED Environmental, Ann Arbor, MI), Kabis sampler (discrete-level grab sampler, Sibak Industries, Solano Beach, CA), GoreSorber Screening Survey (diffusional sampler, W. L. Gore and Associates, Elkton, MD), and the Micro-

Flo sampler (bladder pump, Geolog, Inc., Medina, NY). This report contains an evaluation of the Micro-Flo 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 Micro-Flo 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. Section 5 presents a summary of the Micro-Flo sampling device. Appendix A contains performance data for the reference pump and Appendix B provides an assessment of quality control data associated with the analytical method used in this study.

# Section 2 — Technology Description: GeoLog Micro-Flo Bladder Pump

This section provides a general description and overview of the capabilities of the Micro-Flo bladder pump manufactured by GeoLog Inc. GeoLog Inc provided the information used to prepare this section.

The bladder pump consists of an internal flexible bladder that is positioned within a rigid pump body, such as polyvinyl chloride, Teflon, or stainless steel. The inner bladder is equipped with one-way inlet and outlet valves and passively fills with water when the pump is at depth by virtue of hydrostatic pressure. Following the fill cycle, compressed air or nitrogen from a cylinder or compressor at the wellhead is driven down through tubing to the pump 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. With the controller, the duration and frequency of the fillcompress 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.

GeoLog offers a complete line of bladder pumps and accessories for groundwater sampling applications. The bladder pump evaluated in this verification test was the Model 57400, which is constructed with stainless steel and polytetrafluoroethylene (Teflon). (GeoLog also offers a similar pump of polyvinylchloride and Teflon construction; however, this model was not evaluated in this test.) The Model 57400 pump is

24 inches in length with an external diameter of 1.66 inches, and a weight of 2.5 pounds. The pump uses Teflon for the bladder material and 316 stainless steel for the pump body, fittings, and intake screen. The pump inlet is constructed of 0.25-mm (0.01-inch) stainless steel screen mesh. The pump has a maximum lift capacity of 460 feet, and flow rates are adjustable from less than 100 mL/min to over 5 L/min, depending on pump depth and controller settings.

The Model 5001 pneumatic controller is battery operated and is used to control the flow of compressed nitrogen or air to the pump. The controller is packaged in a durable case that can be hand carried. The controller has overall dimensions of  $14.5 \times 10 \times 9$  inches and a weight of 15 pounds with battery. Drive gas for the bladder pump can be delivered at the wellhead from compressed nitrogen cylinders or from a field-portable gasoline- or electric-powered compressor.

The cost for the bladder pump tested is \$425 and the controller is priced at \$1,295. Teflon-lined polyethylene tubing is also a requirement for most VOC sampling applications and is priced at \$2.25 to \$2.75 per foot.

The Micro-Flo bladder pump systems are primarily intended for dedicated well-sampling applications and a lifetime warranty is offered for dedicated pumps. In a dedicated application, the bladder pump and tubing are left in the well and the controller unit and compressed air source are moved from well to well during typical sampling operations. The pump system can also be moved from well to well; however, pump and tubing decontamination must be carried out between well deployments.

## **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. Stannis 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 agencywide 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 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 above 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.

Groundwater Monitoring Wells—Construction information for the six wells selected for use in this study is given in Table 1. The wells were

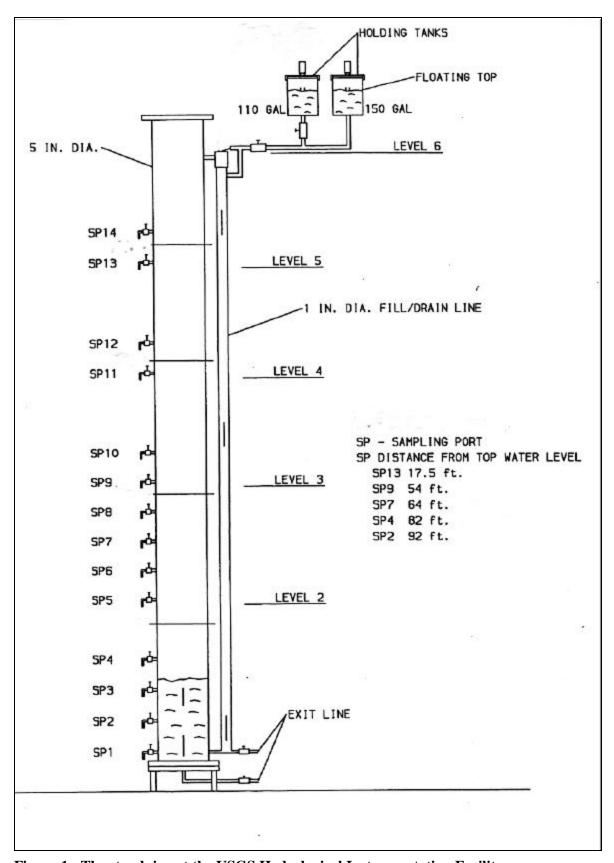


Figure 1. The standpipe at the USGS Hydrological Instrumentation Facility.

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 VOCcontaminated 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  $\mu$ g/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<br>No. | TOC<br>(ft, MSL) | Total<br>Depth |       | n Elev.<br>MSL) | Well<br>Diam. | Install<br>Date | Depth to<br>Water | Water<br>Level | Water Depth<br>Above Screen |
|-------------|------------------|----------------|-------|-----------------|---------------|-----------------|-------------------|----------------|-----------------------------|
|             |                  | (ft)           | Тор   | Bottom          | (in.)         |                 | (ft)              | (ft,MSL)       | Midpoint (ft)               |
| 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<br>(kg- bar/mole at 298 K) <sup>a</sup> | Boiling Pt.<br>(°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                 |

<sup>&</sup>lt;sup>a</sup> 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  $\mu$ g/L) or high (175-225  $\mu$ g/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 colocated in the well with the sampling devices under test in order to obtain simultaneous reference samples from the well. Teflon tubing (1/4 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:

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

Here,  $X_i$  is one observation in a set of n replicate samples where  $\overline{X}$  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 observed differences between the reference sample precision and the technology sample precision are 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 mixing and transporting the spike mixtures 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:

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

where is  $\overline{X}_{\text{tesh}}$  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 methods.

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 °C 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 °C 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.

Pre-demonstration 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 for GC/MS analysis using the headspace 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 lowconcentration (10–20 ug/L) standpipe mixture. Trials 3 and 4 were conducted at shallow and deep locations with a high-concentration (175–225 ug/L) standpipe mixture. In all trials, reference samples were collected from external sampling ports simultaneously with sample collection with the device under test.

Table 3. Sampler Verification Trials at the Standpipe

| Trial No. | Standpipe<br>Collection<br>Port | Sample<br>Collection<br>Depth (ft) | VOC Concentration<br>Level | No. of Replicates<br>per<br>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.

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 "cleanthrough-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-throughdirty" sampling trials, although some vendors chose to participate voluntarily. In this test, two mixtures, a high ( $\sim 200 \mu g/L$ ) and a low ( $\sim 20$ ug/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 lowlevel 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.

# **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.

Table 4. Sampler Verification Trials at the Groundwater Monitoring Wells

| Trial | Well    | Distance from<br>Top of Well to<br>Screen Mid-<br>point (ft) | Depth to Water<br>(ft) | Approximate TCE Conc. | No. of<br>Replicates per<br>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 colocated 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 nodetect wells and were dropped from the data set.

# **Deviations from the Verification Plan**

Under most field-testing environments, circumstances often arise that prevent a complete execution of the test plan. 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.

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 the affected 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.

## **Section 4 — Performance Evaluation for Micro-Flo 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 groundwater are discussed. Only summary data are given in this report. A complete tabulation of all test data is available from the authors via individual request.

**Sampler Precision** 

The precision for the Micro-Flo bladder pump samples and the reference samples from the first four standpipe trials is given in Table 5. These four trials consisted of low (10–20 µg/L) and high (200–500 µg/L) target compound concentrations with sample collection at shallow (17 feet) and deep (91 feet) locations in the standpipe. Relative standard deviations are tabulated by compound for a total of 24 cases. The final column in the table is the result of an F-ratio test used to determine whether the technology and reference sample precision can be regarded as statistically equivalent. 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 (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 between 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 these magnitudes under the null hypothesis. One the other hand, values of p that are less than 0.05 are indicative or larger 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%. 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 Micro-Flo sampler results are encountered for 12DCA and 112TCA at the low concentration and deep collection location and the best precision is observed for benzene at all test conditions (Table 5). Preliminary evaluation of the GC/MS headspace method performance carried out prior to the field demonstration revealed that 12DCA and 112TCA had higher analytical uncertainty than the other target compounds, and it is likely that the higher uncertainty can be attributed to the analytical method and not the sampling process.

Qualitatively, the observation can also be made that the relative standard deviations for the Micro-Flo sampler are greater for trials with low target VOC concentrations that those observed in the high concentration trials. This trend is not as evident in the reference sampler data set however. The median RSD for all compounds in all cases was 8.5% for the Micro-Flo bladder pump and 4.7% for the reference samples. From a statistical point of view, 6 of the Micro-Flo sampler RSD values were more precise than the reference values and 18 were less precise. An even or nearly even split of technology precision in the greater and less than categories would suggest equivalence between the two sampling methods. This qualitative observation suggests non-equivalence of the two methods. From a more formal statistical point of view, the results of the F-ratio test shown in the last column of Table 5 indicate that none of the tabulated F-ratios for the 24 cases had a value of p that was less than 0.05. Thus, all observed Micro-Flo bladder pump precision differences relative to the reference sampler can be explained on the basis of random variation alone without systematic bias. The overall precision of the two sampling methods is judged to be statistically equivalent.

Table 5. Precision Summary for Micro-Flo Bladder Pump and Reference Sampler

| Compound | Conc.<br>Level | Sampling<br>Depth<br>(ft) | Micro-Flo<br>Precision<br>(%RSD) | REF<br>Precision<br>(%RSD) | F-Ratio | F-Ratio<br>Test<br>p |
|----------|----------------|---------------------------|----------------------------------|----------------------------|---------|----------------------|
| 11DCE    | Low            | 17                        | 9.4                              | 4.8                        | 4.39    | 0.18                 |
|          | Low            | 91                        | 11.8                             | 4.4                        | 1.19    | 0.87                 |
|          | High           | 17                        | 2.7                              | 5.8                        | 3.00    | 0.39                 |
|          | High           | 91                        | 5.1                              | 4.6                        | 1.15    | 0.89                 |
| 12DCA    | Low            | 17                        | 10.5                             | 5.6                        | 2.84    | 0.34                 |
|          | Low            | 91                        | 17.3                             | 2.8                        | 6.00    | 0.17                 |
|          | High           | 17                        | 8.6                              | 6.2                        | 3.12    | 0.30                 |
|          | High           | 91                        | 5.6                              | 4.2                        | 1.73    | 0.61                 |
| BNZ      | Low            | 17                        | 4.6                              | 3.1                        | 8.31    | 0.06                 |
|          | Low            | 91                        | 9.6                              | 2.1                        | 1.23    | 0.85                 |
|          | High           | 17                        | 8.6                              | 4.1                        | 6.88    | 0.09                 |
|          | High           | 91                        | 5.3                              | 3.3                        | 2.41    | 0.41                 |
| TCE      | Low            | 17                        | 10.0                             | 3.1                        | 1.26    | 0.83                 |
|          | Low            | 91                        | 10.6                             | 3.0                        | 1.49    | 0.71                 |
|          | High           | 17                        | 3.6                              | 6.2                        | 3.04    | 0.39                 |
|          | High           | 91                        | 6.3                              | 4.8                        | 1.67    | 0.63                 |
| 112TCA   | Low            | 17                        | 10.4                             | 1.6                        | 2.98    | 0.32                 |
|          | Low            | 91                        | 26.7                             | 8.5                        | 7.15    | 0.08                 |
|          | High           | 17                        | 6.1                              | 8.2                        | 1.62    | 0.72                 |
|          | High           | 91                        | 5.6                              | 6.1                        | 1.15    | 0.89                 |
| PCE      | Low            | 17                        | 7.4                              | 30.8                       | 8.00    | 0.07                 |
|          | Low            | 91                        | 9.8                              | 4.1                        | 1.08    | 0.94                 |
|          | High           | 17                        | 8.3                              | 5.0                        | 2.03    | 0.51                 |
|          | High           | 91                        | 5.3                              | 5.6                        | 1.22    | 0.85                 |
| Minimum  |                |                           | 2.7                              | 1.6                        |         |                      |
| Maximum  |                |                           | 26.7                             | 30.8                       |         |                      |
| Median   |                |                           | 8.5                              | 4.7                        |         |                      |

Notes: REF = reference measurement

#### **Sampler Comparability**

The comparability of the Micro-Flo sampler with reference sampler data for standpipe trials 1 through 4 is given in Figure 2 and Table 6, and is expressed in terms of percent difference. Percent difference values were computed for each of the six target compounds in the four standpipe trials for a total of 24 cases. The difference values for the Micro-Flo pump range from -21 to 27%, with a median value of -1%. By compound, the greatest range between positive and negative differences is observed for 12DCA, 11DCE and benzene with considerably smaller difference ranges observed for the other three target VOCs. Percent difference values for 12 of the 24 results were below 0% with the other 12 values above

0%. An even or nearly even split of percent difference values in the greater than zero and less than zero categories qualitatively suggests equivalence between the two sampling methods. On a more formal statistical basis, t-test results show that 17 of the 24 cases have p values that are greater than 0.05. Of the other seven cases, with values of p less than 0.05, three have a positive bias and the other four have a statistically significant negative bias. Thus, in most test cases statistical equivalence between the two methods is indicated. The Micro-Flo bladder pump comparability data reveal that no statistically significant negative differences greater than – 21% (11DCE, low concentration, shallow sampling) are observed.

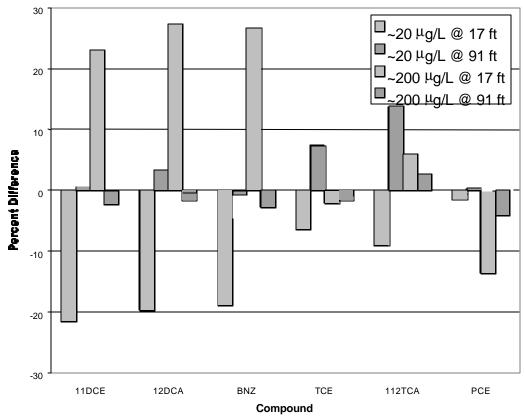


Figure 2. Micro-Flo bladder pump comparability with reference samples from the standpipe trials.

# Blank and Clean-Through-Dirty Test Results

The analytical results from the blank trial at the standpipe were all reported as non-detectable for all target compounds for both the Micro-Flo and the reference samples. These results indicate that a new pump does not measurably contaminate a clean sample of water.

The Micro-Flo bladder pump is primarily intended for application as a dedicated sampling system. It can be used, however, as a portable system provided that appropriate decontamination procedures are used between well deployments. The results of the clean-through-dirty test at the standpipe are shown in Table 7. The sampler was lowered through a layer of relatively high (~200  $\mu$ g/L) target VOC concentration at the top of the standpipe for sample collection at depths of 35 and 91 feet in water with lower (approximately 15 to 50  $\mu$ g/L) VOC concentrations. The tabulated

results are shown in terms of percent difference relative to the reference samples collected simultaneously with the Micro-Flo sampler. Note that the tabulated difference levels for this trial are not normalized with the percent difference levels shown in Table 6. Positive difference levels are indicative of sampler carryover from the overlying dirty layer. Difference levels for the Micro-Flo sampler for all compounds at both depths vary from -5 to 65% with the most pronounced carryover effects seen at the deepest sampling level. Most values are greater than zero, suggesting that the sampler entrained contaminants from the overlying dirty layer and/or was inadequately purged prior to sample collection. This carryover phenomenon may be of concern when the sampler is deployed at a multiscreened well with high concentration levels of contaminants overlying lower concentration contaminant levels at the desired sampling depth.

Table 6. Comparability of Micro-Flo Bladder Pump and Reference Sampler Data from Standpipe Trials

| Compound | Conc.<br>Level <sup>a</sup> | Depth<br>(ft) | Micro-Flo<br>Difference<br>(%) | t-Test <sup>b</sup><br>p |
|----------|-----------------------------|---------------|--------------------------------|--------------------------|
| 11DCE    | Low                         | 17            | -21                            | 0.02                     |
|          | Low                         | 91            | 1                              | 0.91                     |
|          | High                        | 17            | 23                             | <0.01                    |
|          | High                        | 91            | -2                             | 0.47                     |
| 12DCA    | Low                         | 17            | -20                            | 0.03                     |
|          | Low                         | 91            | 3                              | 0.71                     |
|          | High                        | 17            | 27                             | <0.01                    |
|          | High                        | 91            | 0                              | 0.90                     |
| BNZ      | Low                         | 17            | -19                            | <0.01                    |
|          | Low                         | 91            | -1                             | 0.88                     |
|          | High                        | 17            | 27                             | <0.01                    |
|          | High                        | 91            | -3                             | 0.34                     |
| TCE      | Low                         | 17            | -6                             | 0.35                     |
|          | Low                         | 91            | 7                              | 0.29                     |
|          | High                        | 17            | -2                             | 0.51                     |
|          | High                        | 91            | -1                             | 0.79                     |
| 112TCA   | Low                         | 17            | -9                             | 0.10                     |
|          | Low                         | 91            | 14                             | 0.09                     |
|          | High                        | 17            | 6                              | 0.21                     |
|          | High                        | 91            | 3                              | 0.49                     |
| PCE      | Low                         | 17            | 0                              | 0.96                     |
|          | Low                         | 91            | 0                              | 0.97                     |
|          | High                        | 17            | -14                            | <0.01                    |
|          | High                        | 91            | -4                             | 0.27                     |
| Minimum  |                             |               | -21                            |                          |
| Maximum  |                             |               | 27                             |                          |
| Median   |                             |               | -1                             |                          |

<sup>&</sup>lt;sup>a</sup> The low-level concentration was in the range of 10 to 20  $\mu$ g/L for all 6 target compounds. The high-level concentration was in the range of 175 to 250  $\mu$ g/L.

<sup>&</sup>lt;sup>b</sup> The t-test was used to compare the percent difference of the Micro-Flo bladder pump results relative to the reference sampler results for each compound in each trial. The p value gives a quantitative measure in probabilistic terms of the likelihood that the difference is attributable to random effects alone. Values less than 0.05 are shown in bold and suggest a sampler bias. See text for further details.

Table 7. Clean-through-dirty Test Results for the Micro-Flo Bladder Pump

| Compound | Sampling<br>Depth<br>(ft) | Micro-Flo<br>Average<br>Concentration<br>(■g/L) | Micro-Flo<br>Precision<br>(%RSD) | Reference Average Concentration (=g/L) | Reference<br>Precision<br>(%RSD) | Micro-Flo<br>Percent<br>Difference |
|----------|---------------------------|---|----------------------------------|--|----------------------------------|------------------------------------|
| 11DCE    | 35                        | 40.4  | 9.3                              | 41.0                                   | 7.6                              | <b>–1</b>                          |
|          | 91                        | 25.1  | 29.0                             | 16.2                                   | 8.1                              | 55                                 |
| 12DCA    | 35                        | 52.0  | 12.2                             | 51.8                                   | 5.3                              | 0                                  |
|          | 91                        | 29.7  | 30.6                             | 18.4                                   | 2.4                              | 61                                 |
| BNZ      | 35                        | 39.6  | 8.9                              | 38.8                                   | 6.1                              | 2                                  |
|          | 91                        | 23.0  | 32.7                             | 13.9                                   | 9.0                              | 65                                 |
| TCE      | 35                        | 45.0  | 6.2                              | 43.5                                   | 2.8                              | 3                                  |
|          | 91                        | 24.8  | 26.7                             | 16.3                                   | 9.5                              | 52                                 |
| 112TCA   | 35                        | 63.7  | 10.2                             | 65.5                                   | 9.7                              | -3                                 |
|          | 91                        | 30.9  | 32.0                             | 24.1                                   | 2.7                              | 29                                 |
| PCE      | 35                        | 41.9  | 6.0                              | 44.0                                   | 4.1                              | -5                                 |
|          | 91                        | 26.7  | 27.8                             | 17.5                                   | 8.5                              | 53                                 |

#### **Monitoring Well Results**

Micro-Flo bladder pump results from groundwater sampling at four wells are shown in Table 8 alongside reference data from the same wells. Four replicate samples were taken with the Micro-Flo bladder pump and the reference sampler (a submersible electric gear pump). Relative standard deviations of both Micro-Flo and the reference samples are given in the table along with the mean percent differences between the two sets of data. Micro-Flo sampler precision in the field was generally similar to that observed at the standpipe. Micro-Flo sampler percent differences compared to the reference sampler for the highconcentration wells do not exceed 14%. Micro-Flo sampler and reference sampler difference for the low-concentration well (well number 12-09)

are very high and may suggest, in light of the good performance of the Micro-Flo sampler at the standpipe, that the co-located Micro-Flo 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.

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

Table 8. Micro-Flo and Reference Pump Results from Groundwater Monitoring Wells

| Well<br>Number | Micro-Flo Average TCE Concentration (=g/L) | Micro-Flo<br>Precision<br>(%RSD) | Reference Average TCE Concentration (=g/L) | Reference<br>Precision<br>(%RSD) | Micro-Flo<br>Percent<br>Difference |
|----------------|--|----------------------------------|--|----------------------------------|------------------------------------|
| 06-11MW        | 506  | 7.6                              | 505  | 8.4                              | 0                                  |
| 06-04MW        | 499  | 16.7                             | 438  | 4.2                              | 14                                 |
| 12-09MW        | 9.2  | 49.5                             | 18.1                                       | 33.6                             | -49                                |
| 06-20MW        | ND (<5)                                    | -                                | ND (<5)                                    | -                                |                                    |

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#### **Sampler Versatility**

The precision and comparability performance parameters presented for the Micro-Flo bladder pump indicate that the device can collect water samples contaminated with VOCs that cover a range of volatility and solubility (as noted previously in Section 3), concentration, and sampling depth with performance characteristics generally equivalent to a reference method. Thus, the sampler is judged to have wide versatility in site groundwater characterization and monitoring applications.

#### **Deployment Logistics**

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

- One person can 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 equipment is self-contained and requires no external power to operate. The pump control module is compact and lightweight and is battery powered.
- The pump requires a source of compressed air or nitrogen. This is supplied by either a compressed gas bottle or a gasoline- or electric-powered compressor. These accessories are heavy and bulky and reduce

- the overall portability of the system.
- The pump is designed for dedicated use in single monitoring wells; however, it can also be moved from well to well provided that decontamination is carried out between deployments. The controller and air source are designed to be moved from wellhead to wellhead during routine sampling operations.
- The pump is essentially maintenance free with few moving parts. GeoLog Inc. offers a lifetime pump warranty for dedicated well installations.
- The pump and controller are designed for compatibility with low-flow sampling and low volume purge sampling protocols.

#### **Performance Summary**

Micro-Flo bladder pump performance is summarized in Table 9. Performance categories include precision, comparability, versatility, and logistical requirements. Cost and physical characteristics are also included.

The results of this verification test show that the Micro-Flo bladder pump and associated pneumatic controller can be used to collect VOC-contaminated water samples that are generally comparable to a reference method with regard to both precision and comparability with reference data. The pumps are optimized for dedicated placement in monitoring wells that are included in a routine monitoring program.

Table 9. Performance Summary for Micro-Flo Bladder Pump

| Performance<br>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: 2.7 to 26.7% (reference: 1.6 to 30.8%)  |  |  |
|                                      | Median relative standard deviation: 8.5% (reference: 4.7%)   |  |  |
|                                      | In all 24 standpipe test cases, Micro-Flo pump precision was statistically comparable to reference sampler precision.  |  |  |
| Comparability with reference samples | For 6 target compounds at low (20 $\mu$ g/L) and high (200 $\mu$ g/L) concentrations and at 17-foot and 91-foot sampling depths:                               |  |  |
|                                      | Percent difference range: -21 to 27%   |  |  |
|                                      | Median percent difference: -1%   |  |  |
|                                      | In 17of 24 standpipe test cases, Micro-Flo pump difference values relative to reference samples were statistically indistinguishable from 0%.                  |  |  |
| Sampler versatility                  | The Micro-Flo 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.  |  |  |
|                                      | One day of training is required to operate the system.   |  |  |
|                                      | System requires a source of compressed nitrogen at the wellhead.   |  |  |
| Purchase cost                        | Model 57400 pump cost: \$425   |  |  |
|                                      | Model 5001 pneumatic controller cost: \$1,295  |  |  |
|                                      | Tubing costs: \$2.25 to \$2.75 per foot  |  |  |
| Size and weight                      | Model 57400 pump: 1.66-inch dia. × 24-inch length, 2.5 pounds  |  |  |
|                                      | Model 5001 controller: $14.5 \times 10 \times 9$ inches, 15 pounds (with battery)  |  |  |
| Other                                | System is designed for low-volume purge and sampling applications.   |  |  |
|                                      | Pump is optimized for dedicated placement in wells.  |  |  |
|                                      | Clean-through-dirty tests indicate that sampler may carry over contamination from an overlying dirty water column into cleaner underlying water.               |  |  |

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

# Section 5 — Micro-Flo Bladder Pump Technology Update and Representative Applications

Note: The following comments were provided by the vendor and were edited only for editorial consistency with the rest of the report.

One of the biggest benefits associated with using a dedicated bladder pump and following a low-flow, minimal-drawdown sampling protocol is the reduction in turbidity in the collected samples. It is common during the purging cycle of the sampling process to monitor water quality parameters such as pH, temperature, conductivity, dissolved oxygen, and oxygen reduction potential. The inclusion of turbidity measurements in the sampling protocol can result in significant additional instrumentation costs for a water quality monitoring system.

Many studies have shown how a sampling program that utilizes a dedicated bladder pump significantly reduces turbidity in the collected samples. The reduction is largely attributable to the permanent location of the pump within the monitoring well. Agitation of the water column, commonly encountered following installation and sample collection with portable pumps and bailers, is not observed with the use of dedicated pumps.

Although this study has focused on VOC sample acquisition, other field studies have shown that reduced turbidity in the collected samples eliminates the need to use groundwater filter capsules in the field to remove metals while acquiring and bottling the field sample. This can result in further sampling cost reductions for facilities that have a large number of wells in a quarterly long-term monitoring program. This cost reduction coupled with capital cost savings associated with instruments measuring turbidity, as well as the operational cost savings resulting from reduced purge water volumes, makes lowflow sampling protocols with a dedicated bladder pump a viable option.

#### **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 Teflon gears inside the cavity push the water to the surface through 100 feet of ½ inch outside diameter Teflon 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 ( $\sim$ 20 µg/L) and high ( $\sim$ 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.<br>Level | Depth<br>(ft) | Gear<br>Pump<br>Precision<br>(%RSD) | Port<br>Precision<br>(%RSD) | F-Ratio | F-Ratio<br><i>p</i> |
|----------|----------------|---------------|-------------------------------------|-----------------------------|---------|---------------------|
| 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 14% 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.

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

| Compound | Conc.              | Depth | Difference | t-Test <sup>b</sup> |
|----------|--------------------|-------|------------|---------------------|
|          | Level <sup>a</sup> | (ft)  | (%)<br>-4  |                     |
| 11DCE    | Low                | 17    |            | <u>р</u><br>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   |                    |       | 6.5        |                     |

 $<sup>^</sup>a$  The low-level concentration was in the range of 10 to 20  $\mu g/L$  for all 6 target compounds. The high-level concentration was in the range of 175 to 250  $\mu g/L$ .

<sup>&</sup>lt;sup>b</sup> The t-test was used to compare differences between the gear 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.

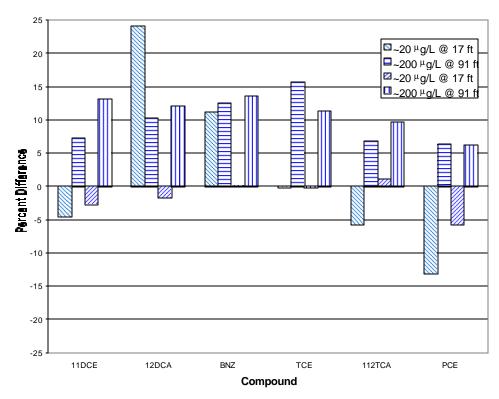


Figure A-1. Percent recoveries of the reference pump by compound for the four standpipe trials.

#### **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  $200~\mu g/L$  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<br>Check                        | Minimum<br>Frequency       | Acceptance<br>Criteria   | Corrective<br>Action  |
|---|----------------------------|--|---|
| MS tune check w/<br>bromofluorobenzene<br>(BFB) | Every 12 hours             | Ion abundance criteria<br>as described in EPA<br>Method TO-14                    | Reanalyze BFB     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<br>the expected<br>concentration<br>for the CCC<br>compounds | Repeat analysis     Prepare and run     new standard     from stock     Recalibrate |
| End calibration checks                          | End of each day            | ± 25% RPD of the beginning CCC   | Repeat analysis     If end check is     out, flag data     for that day             |
| Duplicates                                      | 10% of the samples         | Relative percent difference ≤ 30%  | Analyze a third aliquot     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  $\pm 30\%$  criteria for the calibration check was met.

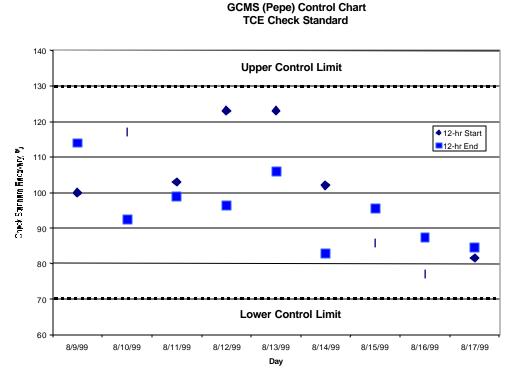


Figure B-1. Calibration check control chart for TCE on GC/MS #1.

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#### GCMS (Taz) Control Chart TCE Check Standard

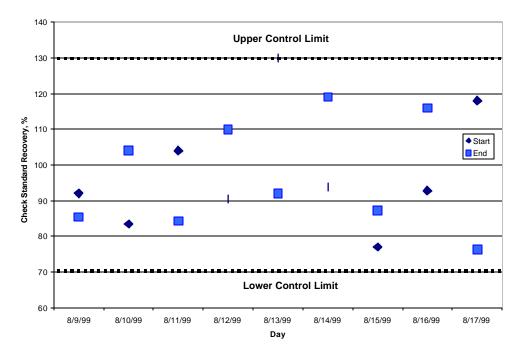
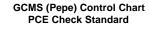


Figure B-2. Calibration check control chart for TCE on GC/MS #2.



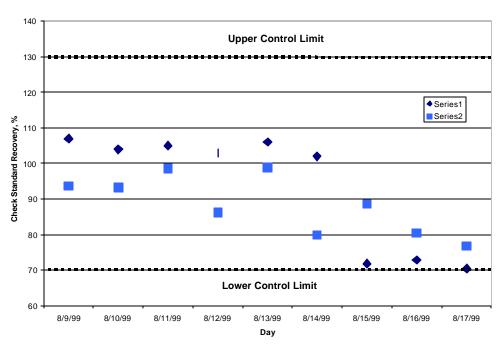


Figure B-3. Calibration check control chart for PCE on GC/MS #1.

#### GCMS (Taz) Control Chart

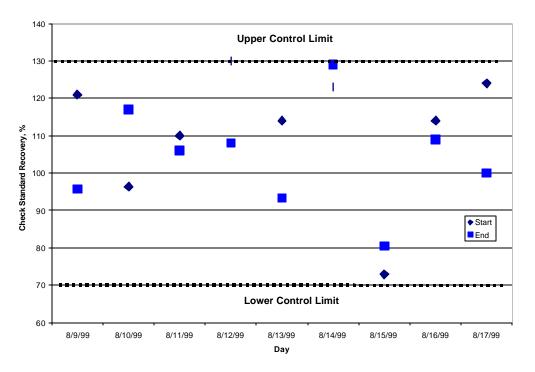


Figure B-4. Calibration check control chart for PCE on GC/MS #2.

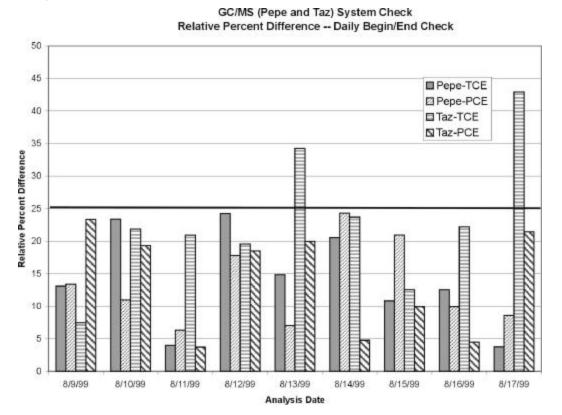


Figure B-5. GC/MS system check relative percent differences.

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