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August 2003

Environmental Technology Verification Report

Ground Water Sampling Technologies

Geoprobe Inc.

**Pneumatic Bladder Pump,
GW1400 Series**

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Pneumatic Bladder Pump, GW1400 Series

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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY

Office of Research and Development
Washington, D.C. 20460



**ENVIRONMENTAL TECHNOLOGY VERIFICATION PROGRAM
VERIFICATION STATEMENT**

TECHNOLOGY TYPE: GROUND WATER SAMPLING TECHNOLOGIES
APPLICATION: NARROW-BORE WELL WATER SAMPLING
TECHNOLOGY NAME: GW1400 Series Pneumatic Bladder Pump
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PROGRAM DESCRIPTION

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 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.

Verification of contaminated site characterization and monitoring technologies is carried out within the Advanced Monitoring Systems (AMS) Center, one of seven ETV verification centers. Sandia National Laboratories, a Department of Energy laboratory, is one of the verification testing organizations within this ETV Center. Sandia collaborated with personnel from the US Geological Survey and Tyndall Air Force Base to conduct a verification study of ground-water sampling technologies for deployment in narrow-bore, direct-push wells at contaminated sites with potential ground-water contamination. This verification statement provides a summary of the results from a verification test of the GW1400 Series Pneumatic Bladder Pump manufactured by Geoprobe Systems Inc.

DEMONSTRATION DESCRIPTION

The performance of two ground-water sampling technologies was evaluated at the US Geological Survey Hydrological Instrumentation Facility at the NASA Stennis Space Center in southwestern Mississippi and at Tyndall Air Force Base near Panama City, Florida. Each technology was independently evaluated to assess its performance in the collection of inorganic cations, commonly encountered in ground-water, as well as volatile organic compound (VOC) contaminated ground-water.

The verification test, conducted over a one-week interval in February 2003, incorporated the use of a 5-inch diameter, 100-foot standpipe at the USGS facility. The standpipe, serving as an "above-ground" well, was filled with tap water spiked with various concentration levels of five target inorganic cations (calcium, iron, magnesium, potassium and sodium) and six volatile organic compounds. Target VOC compounds (vinyl chloride, methyl-tertiary butyl ether, cis-1,2-dichloroethene, benzene, trichloroethene and ethyl benzene) were chosen to represent the range of VOC volatility likely to be encountered in normal sampler use. Target cation concentrations were in the range of 5 to 100 mg/L and VOC concentrations were in the range of 50 to 100 µg/L. 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. Trials were carried out at two different inorganic cation concentrations, a single VOC concentration, and sampler depths ranging from 17 to 76 feet. An unspiked, tap-water, blank sampling trial was also included in the test matrix. A total of 48 cation and 24 VOC samples were collected with the sample count equally split between vendor and reference sampling methods.

The standpipe trials were supplemented with additional trials at six, 1-inch internal-diameter, direct-push-installed wells at Tyndall Air Force Base. Sampling at narrow-bore, direct-push wells provided an opportunity to observe the operation of the sampling system under typical field-use conditions. A simple reference sampler was deployed along side the vendor technology such that co-located, simultaneous samples could be collected from each well. Principal contaminants at the Tyndall monitoring wells included trichloroethene and its degradation products as well as hydrocarbon contaminants such as benzene and ethyl benzene. Ground-water VOC concentrations ranged from low µg/L to low mg/L levels. A total of 96 ground-water samples were collected, with the sample count equally split between vendor and reference methods.

All technology and reference samples were analyzed by an offsite laboratory utilizing EPA SW-846 Standard Methods 3010A (Acid Digestion of Aqueous Samples and Extracts For Total Metals by FLAA or ICP Spectrometry) and 6010B (Inductively Coupled Plasma Atomic Emission Spectrometry) for inorganic cation analysis and EPA SW-846 Standard Method 8260B (Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy) for VOC analysis. The overall performance of the ground-water sampling technologies was assessed by evaluating sampler precision and comparability with reference samples. Other logistical aspects of field deployment and potential applications of the technology were also considered in the evaluation.

Details of the demonstration, including an evaluation of the sampler's performance, may be found in the report entitled *Environmental Technology Verification Report: Geoprobe Systems, Pneumatic Bladder Pump, GW1400 Series*, EPA Report Number EPA/600/R-03/085.

TECHNOLOGY DESCRIPTION

The GW1400 Series is a narrow-diameter (23.8-inch length x 0.5-inch outside diameter) bladder pump suitable for deployment in direct-push-installed ground water wells. The pump consists of an internal, flexible and inert bladder that is positioned within a rigid stainless steel tube. The bladder's internal volume can be reduced by applying an external force via air pressure in order to collapse the bladder. The bladder is equipped with one-way inlet and outlet check 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 bladder fill cycle, a source of compressed air at the surface is used to pressurize the region between the bladder and the outer rigid tube. The bladder volume is reduced and the water within the bladder is pushed toward the surface. The pumping sequence consists of repeated fill-compress cycles that are regulated by an adjustable pneumatic controller located at the well head between a source of compressed air and the pump. The narrow-diameter sampling pump with an inert 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 with an air vacuum and further potential VOC losses.

Pump accessories include a pneumatic controller, a source of compressed gas (typically nitrogen) or an air compressor and power source. The pump utilizes a concentric tubing configuration for air pressure connection and water transport to the surface and various tubing materials are available that can be matched to the sampling application. The nominal flow rate of the pump measured at a depth of 35 feet below the surface with a 32-foot water column above the pump was approximately 75 mL/min. Under these typical sampling conditions, the flow range of the pump is well-suited for sampling applications that incorporate low-flow sampling protocols.

Costs for the pump and accessories are as follows: pump, \$700; pneumatic controller \$1300; compressor, \$250; AC generator \$2000. Concentric tubing sets are priced as follows: HDPE (outer) /FEP-Teflon (inner), \$114 per 50-foot roll; FEP/FEP \$396 per 50-foot roll.

VERIFICATION OF PERFORMANCE

The following performance characteristics of the GW1400 Series Pneumatic Bladder Pump were observed:

Precision: The precision of the sampler was determined through the collection of a series of replicate samples from a number of standpipe trials that included known concentrations of inorganic cations and VOCs. Sampler depths ranged from 17 to 76 feet. Sampler precision, represented by the percent relative standard deviation, for all target cation compounds at all concentrations and sampling depths evaluated in this study ranged from 0.0 to 2.8 percent with a median value of 0.6 percent. Precision for VOCs at a single concentration and multiple sampler depths ranged from 0.3 to 2.8 percent with a median value of 1.3 percent. Pump precision measured in the Tyndall field trials was similar to that observed in the standpipe trials for the target cations. For VOC compounds, Tyndall monitoring-well field trials revealed considerably more variability in the replicate samples from the pump and co-located reference sampler.

Comparability with a Reference: Pneumatic bladder pump results from the standpipe trials were compared with results obtained from co-located reference port samples collected simultaneously. Both bladder pump and reference samples were analyzed at an off-site laboratory using standard EPA methods for inorganic cations and VOCs. Sampler comparability is expressed as percent difference relative to the reference data. Sampler differences for all target cations compounds at all concentrations and sampler depths in this study ranged from -14.8 to 6.5 percent with a median percent difference of -1.0. Sampler differences for all VOC compounds at all sampling depths ranged from -5.6 to 0.9 percent with a median value of -2.3 percent.

Two statistical tests, the F-ratio test and the t-test for two sample means, were used to assess whether the observed differences at the standpipe between the pneumatic bladder pump and reference port sample precision and mean pump and reference target compound concentrations were statistically significant. In general, the tests show that the observed differences between the bladder pump and reference samples with regard to both precision and accuracy can be attributed to random variation. Thus, no statistically significant bias exists between the results from the bladder pump and the reference port samples.

The percent difference values for the pump in comparison with the reference method for target cations at Tyndall monitoring wells ranged from -9.7 to 53.5 with a median value of 3.5. Comparability results for VOCs were considerably more variable with percent differences ranging from -68.7 to 571 percent with a median value of 8.4. Some of the larger percent difference values encountered are attributable to measurements of VOC concentrations near the approximate 5 µg/L method detection limit where small absolute differences between methods can result in relative large percent difference values. The controlled aspects of the standpipe tests should be considered in combination with the Tyndall field tests for a comprehensive understanding of pump performance.

Versatility: Sampler versatility is the consistency with which it performed with various target compounds, concentration levels, and sampling depths. The pneumatic bladder pump performance did not vary with changes in compounds or concentration levels. Deployment of the pump at depths in excess of 50 feet may result in flow rates that are deemed unacceptable for some sampling applications. The small surface area of the pump inlet filter can result in clogging when sampling under turbid ground water conditions. In general, the Geoprobe pneumatic bladder pump is regarded as a versatile technology and applicable for sampling the types of inorganic and VOC contaminants from narrow-diameter direct push wells.

Logistical Requirements: The sampler can be deployed and operated in the field by one person. Several hours of training are adequate to become proficient in the use of the system. The system includes a surface-located pneumatic controller and requires either a source of compressed gas or a portable air compressor and associated gasoline-powered generator or line source. The bladder pump can be used as a dedicated sampler or as a portable sampler; however, pump decontamination is required when moving from well to well.

Overall Evaluation: The results of this verification test show that the Geoprobe pneumatic bladder pump and associated accessories can be used to collect inorganic cation- and VOC-contaminated water samples from monitoring wells in such a way that sampling and analysis results are statistically comparable to reference samples. The system is specifically designed for use in narrow-bore (0.5-inch minimum internal-diameter) wells. Furthermore, the pump is compatible with sampling programs that incorporate low-volume purge methodologies.

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

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Notice

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Abbreviations and Acronyms

BNZ	Benzene
DCE	cis-1,2-Dichloroethene
DIFF	Difference
DO	Dissolved oxygen
EPA	US Environmental Protection Agency
EtBNZ	Ethyl benzene
ETV	Environmental Technology Verification Program
FEP	Fluorinated ethylene propylene
GC/MS	Gas chromatograph-mass spectrometer
HIF	Hydrological Instrumentation Facility
HDPE	High-density polyethylene
ID	Internal diameter
LCS	Laboratory calibration standard
MS	Matrix spike
MSD	Matrix spike duplicate
MTBE	Methyl tertiary-butyl ether
MW	Monitoring well
NASA	National Aeronautics and Space Administration
ND	Not detected
NERL	National Exposure Research Laboratory
OD	Outside diameter
ORP	Oxidation/reduction potential
PCE	Tetrachloroethene
PTFE	Polytetrafluoroethylene
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
QA	Quality assurance
QC	Quality control
REF	Reference
RSD	Relative standard deviation
SCMT	Site Characterization and Monitoring Pilot
SNL	Sandia National Laboratories
SP	Sample port
SSC	Stennis Space Center
TCE	Trichloroethene
USGS	US Geological Survey
VC	Vinyl chloride
VOC	Volatile organic compound

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 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.

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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,” nor approve or disapprove technologies. The program does not evaluate technologies at the bench or pilot scale and does not conduct or support research.

The ETV Program presently consists of seven ETV Verification Testing Centers covering a broad range of environmental application areas. In each of these centers, the EPA utilizes the

expertise of partner “verification organizations” to design efficient processes for conducting performance tests of innovative technologies. Verification organizations oversee and report on technology verification testing activities based on testing and QA protocols developed with input from major stakeholder/customer groups associated with the technology area. The verification test described in this report was administered by the Site Characterization and Monitoring Technologies (SCMT) Pilot within the Advanced Monitoring Systems Center and under guidance from EPA’s National Exposure Research Laboratory (NERL). More information about the ETV program is available at the ETV web site: <http://www.epa.gov/etv>.

This particular verification test was administered by Sandia National Laboratories, one of two verification organizations associated with the SCMT Pilot program. Sandia conducted an initial verification study of six different ground-water sampling technologies during the summer of 1999. Verification statements and reports from this initial verification test can be found at the ETV web site. A follow-on study that concentrated on ground-water sampling technologies specifically designed for deployment in narrow-diameter, direct-push-installed wells was subsequently planned and carried out in February of 2003. In this test two ground-water sampling technologies, a mechanically operated bladder pump and a pneumatically driven bladder pump, from Geoprobe Systems, Inc. were evaluated.

Verification Test Overview

This verification test was designed to investigate ground-water sampling devices that are specifically designed for use in narrow-diameter (less than 2-inch diameter), direct-push-installed wells. Direct-push wells are finding increased acceptance in the environmental monitoring community by virtue of the fact that well installation costs are typically much less than traditional larger diameter wells. This report outlines the testing protocol and the performance results for the Geoprobe GW1400 Series Pneumatic Bladder Pump.

This verification test was designed to evaluate critical aspects of pump performance such as precision and accuracy and, while the test did employ the use of low-flow sampling protocols, it was not intended to be an evaluation of the merits of a low-flow purge sampling protocol. This protocol and its merits have been proposed, published, and tested elsewhere [Puls et al, 1996].

The demonstration was conducted in February of 2003 and occurred in two phases. The first phase was carried out at a United States Geological Survey (USGS) facility on the grounds of the National Aeronautics and Space Administration (NASA) Stennis Space Center in southwestern Mississippi and a second phase was conducted at Tyndall Air Force Base near Panama City, Florida. A 100-foot, 5-inch diameter standpipe that is part of the USGS Hydrological Instrumentation Facility (HIF) at the NASA site was used for technology testing under relatively well-controlled conditions. The standpipe served as an “above-ground” well and was filled with water spiked with various concentration levels of target cations and volatile organic compounds (VOC). Water sampling ports along the exterior of the pipe permitted the collection of reference samples at the same time and depth that vendor sampling pumps were used to collect samples from the interior of the pipe.

The standpipe trials were supplemented with additional sampling trials at six direct-push installed ground-water monitoring wells at Tyndall Air Force Base. The contaminant mix at the

Tyndall site included both chlorinated and non-chlorinated hydrocarbons. In all sampling cases, both at the standpipe and the direct push wells, each vendor-collected sample was matched to a co-located and simultaneously collected reference sample.

All vendor pump and reference samples were analyzed by an off-site laboratory using EPA SW-846 Method 6010 for cations and Method 8260b for VOCs. Ground-water sampling technology performance was assessed by evaluating sampler precision as well as comparability with matched reference samples. Other aspects of field deployment, such as logistical requirements, and potential applications of the technology, are also considered in this evaluation.

A brief outline of this report is as follows: Section 2 contains a brief description of the Geoprobe GW1400 Series Pneumatic 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 is a technical review of the data with an emphasis on assessing overall sampler performance. Section 5 presents an update of the Geoprobe technology and provides examples of representative applications of the device in environmental characterization and monitoring settings. Appendix A includes performance data for the reference sampler and Appendix B includes an assessment of quality control data associated with the analytical methods used in this study.

Section 2 — Technology Description: Geoprobe GW1400 Series Pneumatic Bladder Pump.

This section provides descriptions of the technologies participating in the verification test. These descriptions were provided by the technology vendors, with some editing by the verification organization.

Background

Geoprobe Systems began development and design of direct-push probing machines and the affiliated tooling in the late 1980s. The initial application for the direct push machines and tools was for collection of soil gas samples. Because of the effectiveness and efficiency of the direct push method, it was soon applied to soil sampling and ground water sampling for environmental investigations. More recently, Geoprobe Systems has developed the equipment and methods to install small diameter monitoring wells for use in environmental water quality investigations. Because of the small diameter of the direct-push installed temporary ground water sampling tools and monitoring wells, smaller diameter sampling pumps are needed. Additionally, research has found that low-flow sampling rates are usually required to obtain representative water quality samples [EPA, 1996a]. This is especially true for volatile organic compounds that are sensitive to pressure and temperature changes and inorganic analytes, such as iron and chromium, that may be affected by elevated levels of turbidity in the sampled ground water.

Non-dedicated or temporary, small-diameter ground water sampling tools, that are installed by direct-push methods are often used for site assessments and investigations in many geo-environmental projects [Thorton et al, 1997]. In these instances, the temporary sampling devices are installed, samples are collected, and the sampling devices are removed for decontamination and multiple re-use. Such temporary installations provide an efficient and cost effective method for site characterization. Additionally, permanent small-diameter wells installed by direct push methods are substantially growing in use and gaining wider regulatory acceptance for water quality monitoring applications [McCall, 2002]. Traditionally, these small-diameter tools and wells were sampled with peristaltic pumps, inertial pumps (or check

valves), and mini-bailers. Each of these sampling methods has significant limitations and often may not provide representative samples [EPA, 1996a]. Because of the need for a cost-effective, small-diameter ground water sampling device that can provide high quality, representative samples from these direct-push tools and wells, Geoprobe Systems has developed a pneumatically operated bladder pump. Bladder pumps have been found acceptable for sampling of all environmental parameters [ASTM, 2001].

Design

The Geoprobe GW1400 Series Pneumatic Bladder Pump, shown schematically in Figure 1, incorporates a FEP (fluorinated ethylene polymer) Teflon™ bladder within a rigid tube with check valves positioned on the upper and lower ends of the bladder. Concentric tubing is used to connect the pump to a controller and gas supply at the surface. The outer tubing material is either high-density polyethylene (HDPE) or polypropylene and the inner tubing material is FEP Teflon. The outer-tube is used to supply down-hole gas pressure and the inner-tube is the sample return line. The bladder is alternately compressed and expanded by application of cyclic pressure to the exterior surface of the bladder. No contact occurs between the pressurizing gas and the water being sampled. During the positive pressure stroke of the pump, water inside the bladder is pushed out of the bladder through the upper check valve and up the sample line to the surface. During the pressure release stroke, well water that is under hydrostatic pressure enters the pump inlet through the lower check valve and fills the bladder. If the pump is near the static water level, there may be insufficient hydrostatic pressure to fill the bladder. Under these conditions, vacuum may be applied to the exterior of the bladder to actively open it and reduce the bladder fill time. The pneumatic controller located at the surface includes a vacuum assist option for this sampling condition. The pump controller is pneumatically operated and thus no electrical supply or batteries are required for its operation.

The pumps are available in two sizes. The smaller pump dimensions are 0.50 inches outside diameter (OD) x 23.8 inches long. The pump can be used

in nominal 1/2-inch PVC or larger casing as well as in direct-push drive rods. The larger pump is 0.75 inches OD x 20 inches long and can be used in

nominal 3/4-inch PVC or larger casing. Only the narrow-diameter version of this pump underwent ETV testing.

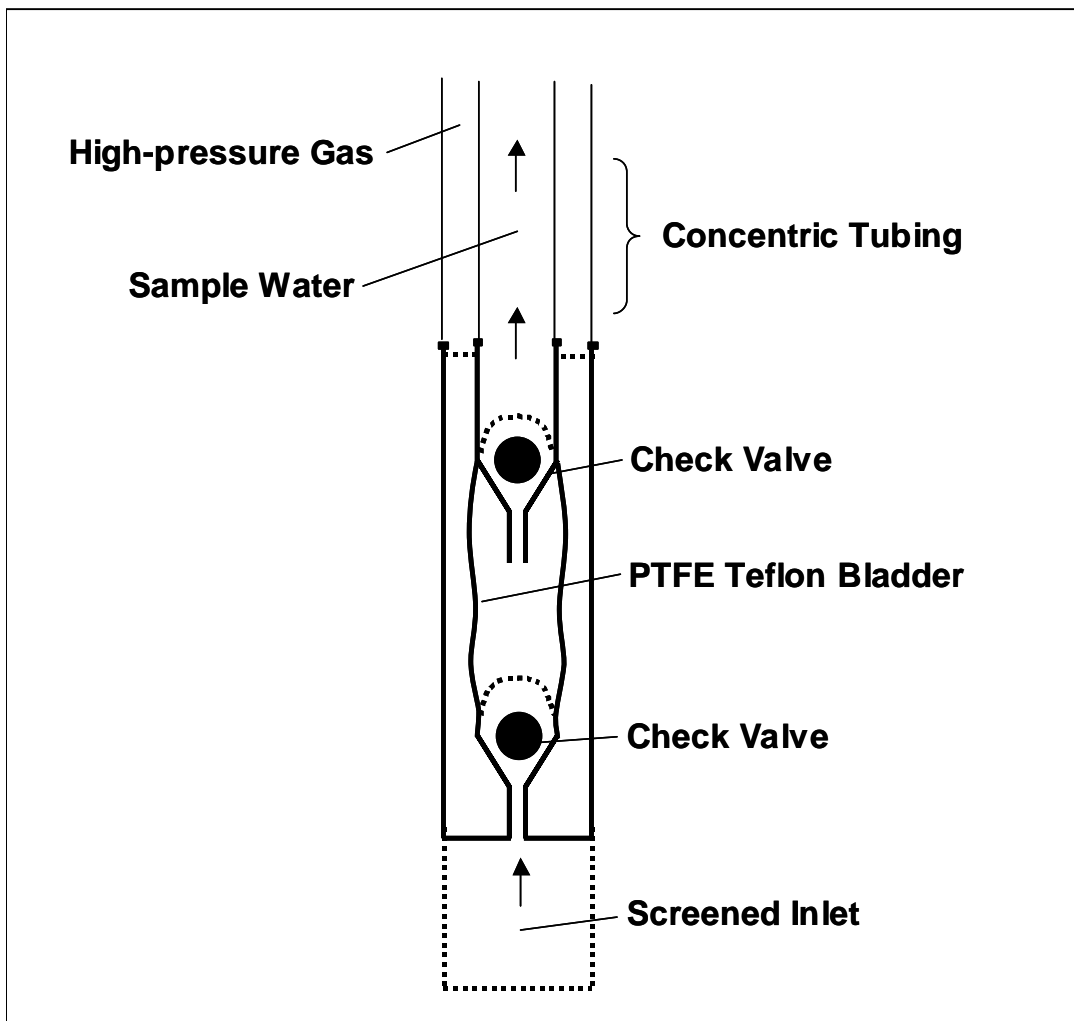


Figure 1. Schematic cross-sectional diagram of the GW1400 Series pneumatic bladder pump. (Drawing is not to scale).

The pump may be equipped with a sintered stainless steel inlet filter to minimize pump clogging and sample turbidity. The flow rate that can be achieved by either pump is a function of: the depth the pump is submerged below the static water level; the distance from ground surface to the static water level; and the maximum pressure of the supply gas. Under optimum flow conditions the 0.5-inch OD pump provides flow rates between 100 to 120 mL/min whereas the 0.75-inch OD pump yields flow rates from 300 to 500 mL/min under optimal conditions. These flow rates are well within those specified by the low flow sampling method [EPA, 1996a]. The 0.5-inch pump has been operated in wells with a static

water level between 95 and 120 feet below grade. Under these difficult conditions flow rates of 20 to 30 mL/min were obtained.

The chemically inert character of Teflon™ for many environmental contaminants is well documented and known by the regulators and regulated community. However, at least two studies [Parker and Ranney, 1997], [Parker and Ranney, 1998] found that Kynar™ (PVDF) tubing may be less sorptive than FEP Teflon™ for several of the halogenated VOCs, and particularly the chlorinated hydrocarbons. As Kynar™ tubing is more rigid than FEP it may prove to be a better material, both mechanically and for chemical

inertness, for use as the inner tube component of the pneumatic bladder pump. Also, if the pneumatic bladder pump is to be used as a portable sampling device during site characterization with temporary ground water sampling tools, it may be preferable to use less expensive materials for the concentric tubing. The inner tube could be made of polypropylene, which is much less expensive than FEP or Kynar™. Polypropylene is almost as chemically inert as FEP, making it an attractive substitute when the tube will be used once and discarded, as for portable applications.

The pump body, check balls and all other metal components of the pneumatic bladder pump are fabricated from 304 stainless steel. This material is resistant to corrosion under most groundwater geochemical conditions [EPA, 1991; Driscoll, 1986] and is recommended for use in the construction and fabrication of well screens and groundwater sampling tools [Parker and Ranney, 1997; Parker and Ranney, 1998] especially when organic contaminants are the primary analytes of interest.

Field Operation

The gas source for the bladder pumps can either be a portable air compressor or a compressed-gas cylinder. A compressor also requires a power source such as a gasoline-powered portable generator. Minimum compressor capacity for pump operation is 1.5 cubic feet per minute flow rate per 20 feet of tube. The pump is assembled and attached to the concentric tubing set and lowered to the desired depth in the well. The following steps outline the field operation procedure:

- The concentric tubing from the pump is attached to the pump head. For dedicated installations, the pump head is fitted on to the well casing.
- The air supply hose from the pneumatic pump controller is attached to the pump head.
- The controller is attached to the gas supply with the quick connect hose.
- Inlet gas pressure is adjusted to optimal operating range, typically 60 to 90 psig.
- The pump controller is turned on.

- The pump “on time” and “off time” cycles are adjusted to optimize pump flow to the desired rate.
 - On time controls how long the gas pressure valve is open to supply pressure to the exterior of the bladder. A longer interval increases maximum pressure but results in slower pump cycle.
 - Off time controls how long the gas pressure is left off. A longer interval gives the bladder more time to open and fill with water but also results in slower pump cycle.
- The vacuum assist option may be operated if the pump is positioned near the static water level and pump recharge is slow. Vacuum assist will speed up bladder filling and thereby decrease the ‘off time’ duration.
- The sample return line may be attached to an inline flow cell to monitor ground water quality parameters (e.g. pH, DO, ORP, etc.) if desired.
- Water from the sample return line is collected in containers for the analyses of interest.

If the pump is used as a portable sampling device it should be decontaminated and re-assembled according to the manufacturers instructions before use at the next well or sampling location.

Advantages and Limitations

A brief summary of the advantages and limitations of the pneumatic bladder pump is provided below. The features of the pneumatic bladder pump are discussed relative to other pump designs commonly used for environmental water quality sampling activities.

Advantages

- The narrow-diameter pump design makes it possible to obtain high quality samples from small-diameter direct-push-installed wells or temporary ground water sampling tools during initial site characterization activities.
- The pump is small, lightweight, and portable.
- The pump can be operated without an electrical power supply.

- The pump can be operated with either an air compressor or compressed gas cylinders.
- Pump flow rate can be adjusted to provide the desired flow to meet the stringent low flow sampling criteria. For the 1/2-inch pump, flows can be varied from less than 30 to over 100 mL/min depending on field conditions.
- The ability to conduct low-flow sampling minimizes the amount of pre-sample purge water generated, thereby reducing waste handling and disposal costs.
- Since there are a limited number of moving parts and no electrical motor or electrical components in the pump, generation of down-hole heat is essentially eliminated. Excess heat generated by motor driven pumps can raise the temperature of the water being sampled potentially altering the water quality and resulting in loss of volatile constituents.
- The pump can be operated either as a dedicated or a portable pump.
- Simple construction makes field service and repair easy.
- Bladders may be replaced in the field.
- Maintenance requirements are minimal.
- Inert construction materials such as FEP Teflon™ bladders and tubing and the stainless steel outer body make this pump acceptable for essentially all environmental water-sampling requirements.
- For portable sampling activities, low-cost polypropylene or HDPE tubing may be

substituted for the more expensive FEP Teflon™ components.

Limitations

- These small pumps are not designed to provide high flow rates (e.g. several gallons per minute) but usually are operated at flows of tens to a few hundred milliliters per minute.
- In wells with a deeper static water level (e.g. 50+ ft) it will be difficult, at best, to achieve the higher flow rates.
- Operation of the pneumatic bladder pump requires a pump controller, compressor and power supply or compressed gas cylinder. This increases the initial purchase cost and significantly adds to the level of effort required for field mobilization.
- A moisture trap (or bowl) must be used on the compressor to prevent build up of moisture in the supply line and around the bladder. Build up of moisture around the bladder can significantly reduce operating efficiency.
- Fines can plug the small pore size in the sintered stainless steel filter.

Additional information on potential applications of the system for environmental characterization and monitoring can be found in Section 5—Technology Updates and Application.

Section 3 — Demonstration Process and Design

Introduction

The principal objective of this verification test was to conduct an independent evaluation of the capabilities of two Geoprobe ground-water sampling technologies designed for deployment in narrow-diameter, direct-push-installed wells. A number of key performance parameters were chosen to evaluate overall sampler performance. In order to insure 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 and Battelle Memorial Institute with concurrence from the technology vendor participating in the study. Technical review of the study design was also provided by EPA personnel with professional expertise in the area of ground-water sampling. A complete verification test plan has previously been published [Sandia, 2003].

Site Descriptions

Verification testing was conducted at the United States Geological Survey (USGS) Hydrological Instrumentation Facility in Southwestern Mississippi and at Tyndall Air Force Base near Panama City, Florida. The following paragraphs briefly describe these two testing sites.

Standpipe Facility – The USGS is one of the resident agencies at the NASA-Stennis complex in southwestern Mississippi and maintains and operates a number of testing facilities as a part of its Hydrologic Instrumentation Facility (HIF). This facility supports USGS agency-wide hydrologic data-collection activities through the identification of agency needs, development of technical specifications, and instrument testing and evaluation. The USGS Standpipe was used during the first phase of this two-phase study. The standpipe was designed by Doreen Tai, a USGS chemical engineer, and is housed in a former Saturn V rocket hangar at the Stennis complex. A schematic diagram of the standpipe and related accessories is shown in Figure 2. The standpipe is an above-ground, 100-foot long, 5-inch diameter, stainless steel pipe with numerous external

sampling ports along its length. Two large mixing tanks with tap-water feeds are positioned at the top of the standpipe and are used to prepare spiked solutions which 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 solution mixing and transfer. 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. External access ports equipped with needle valves allow reference samples to be taken from the standpipe simultaneously with the collection of technology samples inside the pipe. As shown in Figure 2, the indoor facility has six levels of access, including the ground floor, and a freight elevator services all levels. In this verification test, the standpipe was used in a series of controlled, water-sampling trials. The technology vendor deployed pumps in the standpipe and sampled water spiked with inorganic cations and volatile organic compounds while reference samples were simultaneously collected at the external ports.

Direct-Push Ground-water Monitoring Wells- The second phase of this technology demonstration involved the collection of ground-water samples with the vendor pumps from a set of direct-push wells at Tyndall Air Force Base near Panama City, Florida. The Tyndall facility has a number of co-located, direct-push and conventional wells and was part of a nationwide study, sponsored by the Department of Defense Environmental Technologies Certification Program to examine the comparability of direct-push and conventional drilled wells. Numerous conventional and direct-push wells have been installed into relatively shallow contaminated ground-water zones at Tyndall. Contaminants include those arising from hydrocarbon fuel leakage from various aviation fuel storage tanks as well as various chlorinated solvents and their degradation byproducts associated with aircraft maintenance activities at the base.

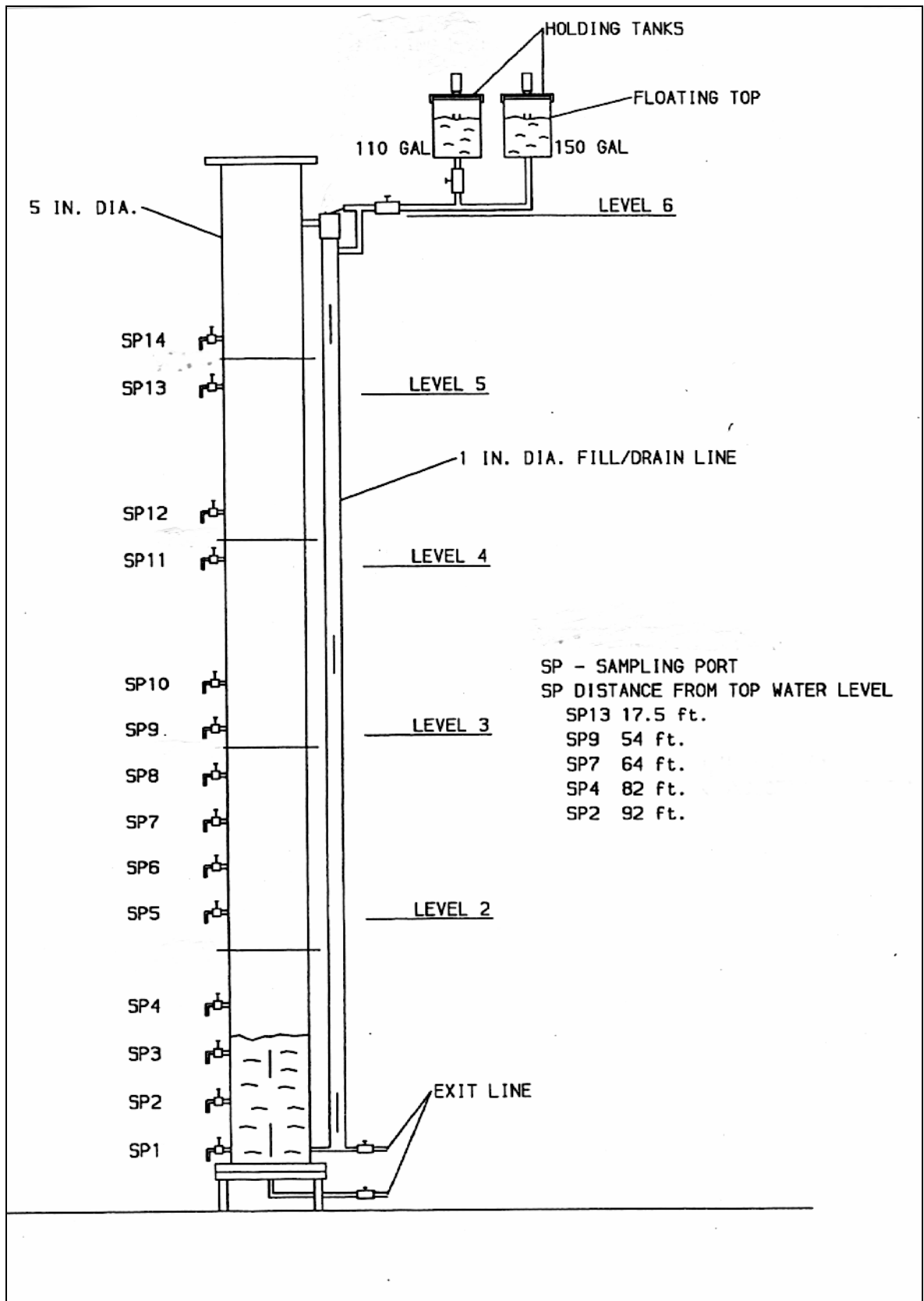


Figure 2. The Standpipe at the USGS Hydrological Instrumentation Facility.

Verification Test Design Summary

The verification test design consisted of two basic elements. The first was a test matrix, consisting of several standpipe trials conducted under relatively well-controlled sampling conditions. These trials enabled sampler performance parameters such as precision and comparability to reference samples to be evaluated. The second element incorporated 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. In an effort to represent pump performance in applications likely to be encountered in typical field use, the suite of contaminants investigated in this study included both non-volatile, inorganic cations as well as a series of volatile organic compounds that covered a range of volatility.

Test Design

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. In both phases of testing, simultaneous, co-located reference samples were collected to enable direct comparison of vendor and reference sample results.

Target Inorganic Compounds - Five inorganic cations were selected for use in the study to assess pump performance for non-volatile species. The cations selected were calcium, iron, magnesium, potassium and sodium. These cations are ubiquitous in most ground-water samples and thereby provide pump performance assessment under conditions of typical use.

Target VOC Compounds - Six target volatile organic compounds with varying degrees of volatility were selected for use in this study. The compounds were benzene (BNZ), ethyl benzene (EtBNZ) methyl-tertiary-butyl ether (MTBE), trichloroethene (TCE), cis-1,2-dichloroethene (DCE), and vinyl chloride (VC). With the exception of MTBE, all of these compounds have regulatory limits dictated by the Safe Drinking Water Act that range from 0.002 mg/L for vinyl chloride to 0.7 mg/L for ethyl benzene. While MTBE is presently not regulated, concern lies in the fact that it is found in ground-water that has been contaminated from leaking hydrocarbon fuel storage tanks containing MTBE as a fuel additive. The six compounds selected also span a range of volatility and solubility; parameters that are likely to influence sampler performance. Target compound volatility and other relevant physical data are given in Table 1.

Table 1. Target VOC Compounds

Compound	Volatility (Henry's Constant, Atm/Moles x Liter ⁻¹)	Boiling Pt. (°C)
Methyl tertiary-butyl ether	0.6	55
Benzene	5.6	80.1
cis-1,2-Dichloroethene	7.8	60.3
Ethyl Benzene	8.3	136
Trichloroethene	9.1	86.7
Vinyl Chloride	22	13.9

Test Concentrations - The use of the standpipe facility enabled the preparation of water mixtures containing the target inorganic cations at two concentration levels and VOCs at one concentration level. Spiked solutions of both inorganic and VOC compounds were prepared by diluting special-order stock solutions. The

inorganic certified stock solution was prepared by Accustandard (New Haven, CT) at a concentration level of 5000 µg/mL for each component in 10 percent nitric acid. The custom VOC certified stock solution was also prepared by Accustandard in methanol at a nominal concentration level of 2000 µg/mL for each mixture component. The

VOC solutions were stored in sealed 20-mL glass ampoules that were refrigerated until use. An appropriate volume of either the inorganic or VOC stock mixture was injected into the mixing tank which was pre-filled with tap water. The solution was then gently mixed for 5 minutes prior to draining into the standpipe. Preliminary studies have shown the loss of some of the VOC compounds during mixing and standpipe filling. Consequently spike concentrations were not used as a reference values in this study. Alternatively, the study design included the collection of simultaneous and co-located reference samples from standpipe external sampling ports for a direct comparison with vendor-collected samples.

Sampler Blank - The standpipe trials included a blank test, where replicate samples were collected from a blank water mixture in the standpipe. This test was conducted to assess whether the materials of construction in the various samplers were a possible source of contamination of the sample for the six target VOC compounds and five target cations used in this study.

Deep Water Sampling - In all but one test, the standpipe was completely filled and sampling was performed at water depths of 17 and 35 feet. In one test, the pipe was filled to the half-way point (approximately 50 feet below the standpipe top) and samples were drawn from a depth of 76 feet relative to the top of the standpipe in order to evaluate the lift capacity of the pump under water column head conditions near the upper limit of the useful range of the pump.

Standpipe Port Samples - The standpipe included external sampling ports along its length such that reference samples could be collected simultaneously, and at the same depth, with the collection of vendor technology samples from the interior of the standpipe. Each sampling trial consisted of the simultaneous collection of paired technology and port samples. The reference samples were collected directly into analysis vials with no intervening pumps, filters or other devices that could potentially affect the sample. The use of multiple sequentially collected samples at each sampling location allowed the determination of sampler and reference sample precision. The resulting precision data reflects the overall uncertainty in the measurement and includes variability of the technology and the reference sample in combination with the common

analytical method. The reference sample precision is used as a baseline against which the vendor technology precision can be directly compared for each of the sampling trials.

Ground-water Well Reference Samples - Use of six onsite monitoring wells in the second phase of the study posed a technical challenge for the collection of reference data with which to compare the technology data. A simple tube sampler with a check valve positioned at the tube inlet was chosen as the reference method. The configuration of this sampler enabled the collection of simultaneous co-located samples from the direct push wells chosen for study in this investigation. Verification studies on the performance of this tube sampler were carried out during the standpipe phase of the experiments to provide technical data substantiating its use as a reference method in the field. A more complete description of the tube sampler and how it was deployed is given in Appendix A. Performance data on the sampler obtained during the standpipe trials are also included in this Appendix.

Low-Flow Sampling Protocol - In all field-sampling trials, a low-flow sampling protocol [Puls and Barcelona, 1996] was used during sampling events and water quality parameters were continuously monitored until stability was achieved in the field sampling trials. In three of the six wells selected for study, the water quality parameters were simultaneously monitored on both the reference and the vendor sampling systems to insure that comparable results were obtained with both sampling methods. For the other three wells, water quality parameters were only measured on the reference sampling line. In all cases, sample collection procedures were not initiated until stability of the critical water parameters was achieved.

Sampler Performance Parameters

Four performance parameters were evaluated in the assessment of this 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 ground-water monitoring wells in the study design. The *relative standard deviation* was used as the parameter to estimate precision. The percent

relative standard deviation is defined as the sample standard deviation divided by the sample mean times 100, as shown below:

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

Here, X_i is one observation in a set of n replicate samples where \bar{x} is the average of all observations, and n is the number of observations in the replicate set. In our assessment of sampler precision, we used a statistical test 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, 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 parameter, *percent difference*, was used to represent sampler comparability for each of the target compounds in the sampling trials at the standpipe. Percent difference is defined as follows:

$$\%Diff = \frac{(\bar{x}_{tech} - \bar{x}_{ref})}{\bar{x}_{ref}} \bullet 100$$

where \bar{x}_{tech} is the average reported concentration of all technology sample replicates and \bar{x}_{ref} is the average reported concentration of all reference or port sample replicates. The statistical t-test for two sample means was used to assess observed differences between the reference and technology means for each sampling trial [Havlicek, 1988b]. The t-test gives the confidence level associated with the assumption that the observed differences between technology and reference mean values are

the result of random effects among a single population and that no significant bias between the technology and reference is observed. Following the convention in statistical analysis, a value of p that is 0.05 or less is taken to indicate that a statistically significant difference does exist.

Sampler 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 ground-water 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 sampling depths.

Field Deployment Logistics - This final category refers to the relative ease of deployment of the sampler in its intended scope of application. This is also a less objective category and incorporates field observations such as personnel numbers and training required for use, ancillary equipment requirements, portability, and others.

Sample Analysis

Two types of sample analysis were carried out during these trials. At the standpipe, selected samples were collected from the pipe during the various trials and hand-carried to an onsite laboratory for quick-turnaround analyses. Analysis results were used to confirm the expected contaminant concentrations in the standpipe following the addition of spiking inorganic cations and VOCs to the mixing tank. The analyses were performed at the NASA Environmental Services Laboratory, operated by Lockheed/G. B. Tech. Cations were analyzed by EPA Method 6010 (inductively coupled plasma atomic emission spectroscopy) and VOCs were analyzed by EPA Method 8260b (purge-and-trap, capillary gas chromatography/mass spectrometry) [EPA, 1996b].

In addition to the analysis of confirmatory samples at an onsite laboratory, all vendor and reference test samples from both the USGS Standpipe and Tyndall were shipped to DataChem Laboratories (Cincinnati, OH) for analysis. Cation and VOC

analysis were conducted at the DataChem using the same methods noted previously for the onsite NASA laboratory. A complete sample quality control package was generated by DataChem during the analysis sequence and submitted along with the results. These data quality control procedures are discussed in more detail in Appendix B.

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 thoroughly documented by verification organization field technicians using chain-of-custody forms.

Field Logbooks - Field notes were taken by observers during the standpipe and ground-water 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-verification Test Analytical System Audit - Prior to the actual demonstration, a visit was made in August 2002 to both the USGS Standpipe and the Tyndall site for site survey and limited sample collection. A number of replicate samples were collected from a limited number of Tyndall wells and these samples were analyzed by DataChem for cation and VOC content. Results from this preliminary investigation revealed acceptable performance of the overall laboratory analysis scheme. Replicate sample results revealed adequate sample precision and ground-water sample contaminant concentrations were comparable to those available from historical data provided to the Verification Organization by Tyndall personnel.

Field Spikes - For an additional check on laboratory performance, a number of field spike samples of target cations and VOCs were prepared during the verification test. A more complete description of the field spikes and the laboratory results is given in Appendix B.

Tube Sampler Decontamination Rinsate Samples - In certain instances during the Tyndall tests, the tubing sampler was deployed in more than one well and decontamination procedures were carried prior to deployment of the sampler in the second well. A sample of rinse water that was cycled through the tube sampler after decontamination was collected and analyzed to insure the adequacy of the decontamination. Results of rinsate sample analyses are also given in Appendix B.

Analytical Methods - Quality control measures associated with DataChem implementation of EPA Method 6010a and EPA Method 8260b included the analysis of a preparation blank, a laboratory calibration standard, a matrix spike, and a matrix spike duplicate in each batch of 20 samples. Other QC measures included: 1) the fulfillment of 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 Method 6010a and 8260b quality control data for the various batches of samples analyzed is provided in Appendix B.

Verification Test Plan

The preceding information, as well as that which follows, is summarized from the Ground-water Sampling Technologies Verification Test Plan [Sandia, 2003], which was prepared by SNL and Battelle personnel with concurrence of all vendor participants prior to the field demonstration. The test plan includes a more lengthy description of the site, the roles and responsibilities of the test participants, as well as a discussion of the experimental design and data analysis procedures.

Standpipe and Direct-Push Well Sampling Details

The sampling matrix for the USGS Standpipe phase of the verification test is given in Table 2. The standpipe tests included a pre-test and eight trials that were conducted over the course of two days. The pre-test trial involved flushing and filling the pipe with tap water, followed by sample collection at selected standpipe ports. These samples were run at the onsite laboratory and results were used to confirm the cleanliness of the pipe. Trial 1 was a blank trial in which the standpipe was filled with tap water. Vendor and

external port samples for both cations and VOCs were collected at a single depth of 35 feet. The standpipe was then filled with a cation-spiked solution such that the final cation concentrations were in the range of 5000 to 10,000 $\mu\text{g}/\text{mL}$ for Trials 2 and 3. Trial 2 was conducted with the vendor pump at a water depth of 35 feet and Trial 3 was done at a depth of 17 feet. The pipe was then drained and refilled with a spike level to raise the cation concentrations to the range of 12,000 to 15,000 $\mu\text{g}/\text{mL}$. Vendor and reference samples were again drawn from 17 feet water depth (Trial 4) and 35 feet (Trial 5).

Following draining and flushing of the standpipe, the pipe was refilled with VOC-spiked tap water such that the depth-to-water from the top of the pipe was approximately 50 feet, as measured by a calibrated pressure transducer at the bottom of the pipe. The approximate VOC concentration prepared in the mixing tank was 100 $\mu\text{g}/\text{mL}$. Trial 6 involved collection of samples from a position in the pipe that was 76 feet from the top of the pipe. In this trial, the height of the water column above the pump intake was about 26 feet and the total height the pump raised water was 76 feet. This trial was included to assess performance of the pump at water depths approaching the upper limit of the pump's useful deployment range in terms of water column lift potential. Following Trial 6, the standpipe was again drained and flushed and refilled to the top with spiked tap water. The target VOC concentration was again spiked at a nominal 100 $\mu\text{g}/\text{mL}$. Vendor pump and external port samples were collected at 17 feet (Trial 7) and 35 feet (Trial 8).

Sampling during each trial was conducted as follows: The vendor pump was deployed in the standpipe at the appropriate height and a 2-liter purge was carried out at flow rates typically in the

range of 100 to 200 mL/min. Following the purge, four replicate 250-mL samples for cation analysis were collected in series from the vendor pump while external port samples were collected simultaneously (Trials 2-5). In the case of volatile organics sampling (Trials 6-8), four replicate zero-headspace samples were collected with the vendor pump in 40-mL VOA vials while external port samples were simultaneously collected in similar vials. All cation and VOC samples were collected into containers that were previously spiked with acid preservative. All samples were stored in ice-filled coolers in the field; then transferred to and stored in laboratory refrigerators until overnight air shipment to DataChem in ice-filled coolers.

In selected trials, the tube sampler was also deployed in the standpipe and paired tube sampler and external port samples were collected in the same manner as noted above. See Appendix A for a complete description of the tube sampler performance verification.

The Tyndall Air Force Base ground-water sampling matrix is shown in Table 3. Six wells were chosen based on an interest in deploying the vendor pump over a range of water depths and in ground-water containing a variety of VOC contaminants. All wells sampled were direct-push-installed 1-inch internal diameter wells constructed of PVC with stainless steel mesh sections. Vendor and reference samplers were deployed by cable-tying the two pump strings together such that the inlets of the two samplers were in close proximity to each other before insertion into the well. This cable-tied sampler string was then lowered into the well such that the sampler inlets were positioned at the mid-point of the well screen.

Table 2. Standpipe Test Matrix

Trial	Analyte	Approx. Target Analyte Conc. (µg/L)	Standpipe Port Number	Depth (feet)	Vendor Samples	External Port Samples
Pre-test ^a	VOC/Inorganic	-	5, 12, 14	17, 35, 76	-	6
1 ^b	VOC/Inorganic	-	12	35	4	4
2	Inorganic	5-10,000	14	17	4	4
3	Inorganic	5-10,000	12	35	4	4
4	Inorganic	12-15,000	14	17	4	4
5	Inorganic	12-15,000	12	35	4	4
6 ^c	VOC	100	5	76	4	4
7	VOC	100	14	17	4	4
8	VOC	100	12	35	4	4
Total					32	38

Table 3. Tyndall Test Matrix

Well	Depth to center of screened interval (feet)	Number of Samples			
		Reference Sampler		Vendor Sampler	
		VOC	Inorganic	VOC	Inorganic
MW-2-P10	31	4	4	4	4
MW-5-P10	8	4	4	4	4
MW-8-P10	8	4	4	4	4
MW-9-P10	10	4	4	4	4
MWD-11-P10	17	4	4	4	4
T6-5-P10	13	4	4	4	4
Total		24	24	24	24

Sampling at Tyndall was conducted as follows: After deployment of the cable-tied reference and vendor samplers into the well, a low-flow purge was conducted while water quality parameters were monitored with flow-through cell water quality monitoring system (YSI, Model 6820). The in-line monitoring systems were performance-checked and/or calibrated immediately prior to use at each well. Water quality parameters (temperature, pH, conductivity, oxidative-

reductive potential (ORP), dissolved oxygen and turbidity) were monitored until stability conditions were met. Typically, stability conditions were met after sampling of approximately one liter of water (5-10 minutes). Stability criteria used in this investigation are shown in Table 4. A complete description of the flow-through monitoring procedures and calibration methods is given in the Verification Test Plan.

Table 4. Water Quality Stability Criteria for Low-Flow Purging

Ground-water Constituent	Criteria
Dissolved Oxygen	± 0.2 mg/L
Oxidation Reduction Potential	± 20 mv
Turbidity	± 10%
Specific Conductance	± 3-5% of reading
Temperature	± 3% of reading (minimum of ± 0.2 °C)
pH	± 0.2 units, minimum

Note: The above stability criteria are based on sequential measurements every 3-5 minutes.
Reference: [City of San Diego, 2003]

At three of the wells, parallel and simultaneous water quality parameter measurements were made on both the reference and vendor sampling lines. These measurements were carried out in order to demonstrate that ground-water stability conditions were reached at the same time with the vendor and reference sampling methods. At the remaining three wells, water quality parameters were measured on the reference sampling line only.

Following the low-flow purge and the attainment of ground-water stability conditions, four replicate cation samples were simultaneously collected in series into 250-mL high-density polyethylene bottles from both the vendor and reference sampling lines. Next, four replicate VOC samples were collected into 40-ml VOA vials from the vendor and reference sampler.

Chronological Summary of Demonstration Activities

The verification test began on Monday, February 24 and was concluded on Friday, February 28. The first two days of the demonstration were devoted to testing at the USGS Standpipe and the following three days were devoted to testing at Tyndall. The demonstration technical team observed and recorded observations associated

with the operation of the vendor technology during both standpipe and monitoring well trials to assist in the assessment of logistical requirements and technology ease-of-use. These observations also were used to document any pump performance anomalies as well as operator technical skills required for operation.

Deviations from the Verification Plan

In the following sections, a listing of the deviations from the test plan is summarized and an assessment of the resulting impact on the field test data set is discussed.

*Change in reference sampler configuration-*The configuration of the reference sampler included a length of 5/16-inch OD Teflon tubing that was connected to a 12-inch length of 1/8-inch ID tubing by means of a quick-connect stainless steel reducing union. Attempts to deploy this reference sampler configuration during the Tyndall field trials were unsuccessful as a result of insufficient clearance with the well inner diameter when the vendor and reference sampling lines were bundled together. To circumvent this problem, the tube sampler configuration was modified for the Tyndall field trials. The stainless steel quick-connector and 1/8-inch tubing were replaced with

a stainless steel check valve that was threaded directly onto the down hole end of the 5/16-inch tubing. This configuration provided adequate clearance for the cable-tied vendor and reference lines to be inserted into the well. The affect on of this configuration change on reference sampler performance is judged to be insignificant. See Appendix A for additional details on reference sampler design changes and performance.

Lost/dropped samples-One of the four replicate VOC sample vials from the standpipe reference sample port in Trial 7 was broken during shipment to the analytical laboratory. In this case the average external port value was based on three samples instead of the usual four. Dropping from four to three replicates in this case results in an insignificant impact on the overall results for this particular trial.

Lost of volatile target VOC species in field spike samples-The VOC target analyte list consisted of six compounds that were selected based on their likelihood of being encountered in typical ground-water sampling applications. The target compounds also were chosen such that a volatility range was represented. At the standpipe, a VOC-spiked solution was prepared in a mixing tank near the top of the standpipe and then drained into the standpipe with the total duration of this process being on the order of 10-15 minutes. Off-site lab analysis of the water samples collected from the standpipe from both the external port and the vendor bladder pump revealed that the two most volatile compounds, (vinyl chloride and ethyl

benzene) were at non-detectable (<1 µg/L) levels, despite the fact that they were mixed at an original concentration of about 70 µg/L. These observed VOC losses were corroborated by the on-site, quick-turnaround analysis of samples that were collected immediately after VOC spiking in the mixing tank. Thus, significant volatile losses occurred in the 10-15 minutes that it took to mix the solutions and fill the standpipe. Although it would be desirable to have the data from these most volatile compounds, data are available from the other four target VOC compounds such that pump performance over a range of compound volatility can be determined.

Non-detectable VOC target analytes in a Tyndall monitoring wells-Well selection for the Tyndall phase of the field study was based upon well samples that were collected during an August 2002 pre-verification test sampling effort at Tyndall. During that visit, a number of wells were sampled and a subset of six wells was chosen based upon the VOC analytical results that were obtained. During the verification test, all vendor and reference samples from one well (MW-9-P10) were non-detectable for VOC compounds. Since results were available from five other wells at Tyndall, the impact of this non-detect is judged to be of minor consequence in overall performance assessment of the pump. The reasons for observed differences in VOC concentrations at this particular well were not apparent and no further investigation was undertaken in this study.

Section 4 — Geoprobe GW1400 Series Pneumatic Bladder Pump Performance Evaluation

Test Design Summary

The test design consisted of a series of sampling trials for cation- and VOC-spiked tap water at the standpipe, followed by an additional series of trials at six, 1-inch internal-diameter, direct-push wells at Tyndall Air Force Base. In all sampling instances, a co-located, simultaneous reference sample was matched to each sample collected with the Geoprobe pump. The standpipe trials were designed to yield sampler performance parameters such as sampler precision and comparability with reference samples at a number of sampling depths and VOC concentration levels. The trials at Tyndall monitoring wells, in addition to providing additional performance data, also afforded the opportunity to observe the operation of the technology under actual conditions of use.

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 are reported in units of either $\mu\text{g/L}$ or mg/L for the cation and VOC target compounds selected for use in this study. 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 are compiled into data notebooks and are available from the EPA Project Officer through special request.

Sampler Precision at Standpipe

The precision data for both Geoprobe and reference samples from the cation and VOC standpipe trials are given in Tables 5 and 6. Relative standard deviation, as defined in Section 3, is the parameter used to represent precision for the Geoprobe and the reference samples. The results are listed by compound with test conditions (trial number, analyte concentration and sampling depth) also shown in the tables. The final column in each of the tables is the probability p associated

with the F-ratio statistical test. The F-ratio test was used to assess whether the technology and reference precision estimates can be regarded as statistically different from one another. The value p is a measure of the observed difference between the two values in probabilistic terms. Values of p that are less than 0.05 are indicative of statistically-significant differences that cannot be satisfactorily explained by random variation alone in the two sets of data being compared. For this test, the assumption is made that the vendor and reference precision estimates are statistically equivalent (e.g. from the same population). A value of p that is 0.05 under these assumptions indicates only a 5 percent likelihood that the two estimates are indeed from the same population. Conventional statistical interpretation is that a significant bias exists (e.g. the precision estimates are statistically different) when calculated p -values are less than 0.05.

Precision of the bladder pump and reference port samples for cations was comparable with relative standard deviations for both methods generally less than 2 percent. Statistical testing generally indicates that precision differences between the two methods are random and not significantly biased. In other words, values of p associated with the F-ratio test were all greater than 0.05 with only two exceptions (calcium in Trial 4 and iron in Trial 2).

The results for the VOC samples can be summarized as follows: Relative standard deviations for both the pump and port samples are less than 3 percent and the results of the F-ratio tests reveal method bias in only two of the twelve cases examined. Both results occurred in Trial 7, where a sample vial was damaged and lost. Consequently, only three replicate samples were used in the F-test. In light of the overall good precision, these infrequent indications of bias are not of major importance. Overall, the precision of the pump and reference samples for VOC samples is comparable.

Table 5. Geoprobe and Reference Precision Summary for Inorganic Species at the Standpipe

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (Feet)	Geoprobe Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test <i>p</i>
Calcium	2	8980	17	0.6	1.1	0.31
	3	8830	35	1.6	1.1	0.48
	4	14,830	17	0.5	0.1	0.03
	5	14,700	35	0.9	0.7	0.74
Iron	2	6720	17	0.2	1.1	0.02
	3	6800	35	1.9	2.9	0.47
	4	12,900	17	0.5	0.5	0.98
	5	12,300	35	0.8	0.7	0.86
Magnesium	2	5630	17	0.0	0.9	--
	3	5750	35	1.6	1.0	0.43
	4	11,700	17	0.5	0.1	0.08
	5	11,800	35	0.7	0.8	0.73
Potassium	2	7480	17	1.1	1.3	0.80
	3	7450	35	2.7	0.8	0.10
	4	14,400	17	0.4	0.3	0.50
	5	15,200	35	1.0	1.0	0.86
Sodium	2	103,600	17	0.6	1.2	0.24
	3	101,900	35	2.8	1.0	0.15
	4	111,100	17	0.4	0.2	0.19
	5	115,200	35	0.5	0.9	0.45

Notes: The concentration level shown is the mean reference port value.

Table 6. Geoprobe and Reference Precision Summary for VOC Species at the Standpipe

Compound	Trial No.	Conc. Level µg/L	Sampling Depth (Feet)	Geoprobe Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test <i>p</i>
Vinyl Chloride	6	ND	76	--	--	--
	7	ND	17	--	--	--
	8	ND	35	--	--	--
MTBE	6	68	76	0.7	1.8	0.16
	7	77	17	2.7	1.1	<0.01
	8	81	35	1.6	0.6	0.15
cis-1,2-DCE	6	64	76	2.8	1.5	0.37
	7	73	17	0.8	2.6	<0.01
	8	18	35	1.3	1.0	0.80
Benzene	6	72	76	1.7	2.1	0.68
	7	82	17	1.3	2.0	0.57
	8	86	35	1.0	0.6	0.44
TCE	6	67	76	1.5	1.9	0.64
	7	74	17	1.4	1.7	0.82
	8	78	35	0.3	0.4	0.69
Ethyl Benzene	6	ND	76	--	--	--
	7	ND	17	--	--	--
	8	ND	35	--	--	--

Notes: The concentration level shown is the mean reference port value.

Geoprobe pump precision for Trial 7 excludes a broken vial (number of samples = 3)

Sampler Comparability at Standpipe

The Geoprobe pump and reference sampler comparability data are shown in Tables 7 and 8 for cation- and VOC-spiked water, respectively. Percent difference, as defined earlier in Section 3, is used to assess the comparability between vendor and reference port samples. Percent difference values were computed for each of the target cation and VOC compounds in the standpipe trials. The difference data are given by compound for each of the variables in the trials (e.g., sampling depth and concentration).

For the cation trials, the difference values for the Geoprobe pump range from -14.8 to 6.5 percent with a median value of -1.0 percent and 18 of the 20 reported results fall on the negative side. The t-test results reveal ten instances of method bias. When considering the comparability of the pump to a reference method, two measures of comparability, namely percent difference and the t-test result, should be considered together. As an example, consider an average percent difference of -2 percent that is determined to be a statistically significant difference in contrasted to an average percent difference of -15 percent that is also determined to be a significant difference. In the former case, the determination of a significant bias is much less a concern since the degree of difference between the two methods is very small. In the latter case, the degree of difference is considerably larger and the t-test result would add credence to the observed difference by indicating that some biasing factor is present when the two methods are compared. Four of the seven indications of statistically significant bias are associated with absolute percent difference values in excess 4 percent.

For the VOC trials, the difference values for the Geoprobe pump range from -5.6 percent for TCE in Trial 6 to 0.9 percent for MTBE in Trial 7, with an overall median value of -2.3 percent. Furthermore, all but one percent difference values are negative. In light of the volatile nature of the target analytes, losses from the pumping system, however small they might be, are expected relative to the port samples where the exposure of the water sample to air is of much shorter duration. Six instances of significant bias ($p < 0.05$) are

observed in the t-test results; however, in all cases the absolute percent difference is less than 6 percent and consequently these statistical indications of method bias are of only minor importance.

Two non-target VOC compounds, namely chloroform and bromodichloromethane, were consistently present in the tap water used during these tests at levels of approximately 17 and 6 $\mu\text{g/L}$ respectively. While they were not spiked compounds, their presence yields some additional comparative data between the bladder pump and the reference port samples. Percent difference values for chloroform ranged from -6.7 to 2.9 for the four trials in which it was encountered as a background compound. Percent difference values for bromodichloromethane ranged from -8.1 to 4.8 in the same four trials.

Blank and High Water-Column Standpipe Trial Results

The analysis of pump and reference port samples from the non-spiked tap water trial (Trial 1) at the standpipe revealed non-detectable levels for all of the target VOCs. Some of the target cation compounds (e.g. potassium and sodium) were detected as background constituents in the tap water used for the blank trial. The other three target cations were not detected. These results indicate that the pipe was clean prior to the verification trials, and furthermore, that a new or decontaminated pump does not contaminate a clean sample of water.

Pump flow rates were measured in selected trials to illustrate typical pumping rates under varying depth and water-column heights. Summary flow rate data are shown in Table 9. Flow rates ranged from a high of 90 mL/min for a 35-foot distance between the top of the well and the pump intake, with a water-column height above the pump inlet of 33 feet, to a low of 15 mL/min for a 76-foot deployment and a water-column height above the pump inlet of 27 feet. In this latter case, the pump had to lift water approximately 49 feet for purging and sampling.

Table 7. Comparability of Geoprobe and Reference Cation Data from Standpipe Trials

Compound	Trial No.	Conc. Level ^A (µg/L)	Depth (Feet)	Difference (%)	t-Test ^B <i>p</i>
Calcium	2	8980	17	-0.6	0.39
	3	8830	35	4.0	<0.01
	4	14,830	17	-0.9	0.01
	5	14,700	35	-0.4	0.46
Iron	2	6720	17	-4.6	<0.01
	3	6800	35	-2.6	0.19
	4	12,900	17	-2.1	<0.01
	5	12,300	35	-2.4	<0.01
Magnesium	2	5630	17	-0.4	0.36
	3	5750	35	6.5	<0.01
	4	11,700	17	-0.7	0.03
	5	11,800	35	-0.9	0.13
Potassium	2	7480	17	-1.0	0.28
	3	7450	35	-14.8	<0.01
	4	14,400	17	-0.4	0.20
	5	15,200	35	-2.1	0.03
Sodium	2	103,600	17	-1.6	0.05
	3	101,900	35	-7.3	<0.01
	4	111,100	17	-0.4	0.13
	5	115,200	35	-1.1	0.08

Notes:

A Concentration levels shown are the mean reference port values.

B The t-test was used to compare the mean value of the Geoprobe samples to the mean value of the reference port samples for each compound in each trial. Small values of *p* (<0.05) are suggestive of method bias. See text for further details.

Table 8. Comparability of Geoprobe and Reference VOC Data from Standpipe Trials

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (Feet)	Difference (%)	t-Test <i>p</i>
Vinyl Chloride	6	ND	76	--	--
	7	ND	17	--	--
	8	ND	35	--	--
MTBE	6	68	76	-1.5	0.19
	7	77	17	0.9	0.39
	8	81	35	-1.5	0.12
cis-1,2-DCE	6	64	76	-4.7	0.02
	7	73	17	-1.9	0.32
	8	78	35	-2.2	0.03
Benzene	6	72	76	-3.8	0.03
	7	82	17	-2.4	0.12
	8	86	35	-2.6	<0.01
TCE	6	67	76	-5.6	<0.01
	7	74	17	-1.0	0.44
	8	78	35	-3.6	<0.01
Ethyl Benzene	6	ND	76	--	--
	7	ND	17	--	--
	8	ND	35	--	--

Note: The concentration level shown is the mean reference value

Table 9. Pumping Rates for Various Sampler Depths

Sampler Depth ^A (Feet)	Trial No.	Depth to Water ^A (Feet)	Water Column (Feet)	Gas Pressure (psig)	Vacuum Assist?	Flow Rate (mL/min)
17	2	3	14	80	No	60
17	2	3	14	80	Yes	70
35	1	2	33	80	No	90
76	6	49	27	100	Yes	15

Note: ^A Measured from top of standpipe

Water Quality Parameter Stability Monitoring at Tyndall

Water quality parameters were measured in parallel with the pump and the reference tube sampler in three of the six Tyndall wells selected for sampling. Parameters were measured with each sampling system using calibrated flow-through cells that were connected to the outputs of the pump and the reference tube sampler. Water quality parameters that were measured included: temperature, pH, conductivity, dissolved oxygen (DO), oxidation/reduction potential (ORP) and turbidity. Typically, DO and turbidity were the

two parameters that were the most sensitive and last to stabilize according to the criteria given in Table 4. A typical time series plot of DO and turbidity for both sampling systems drawing from Tyndall Well Number MW-8-P10 is shown in Figure 3. This result is typical of those encountered at the other two wells. Water parameter stability was reached at essentially the same time with both sampling systems. These results show that the pneumatic bladder pump does not alter the physical characteristics of the water sample when compared to a reference sampling technique.

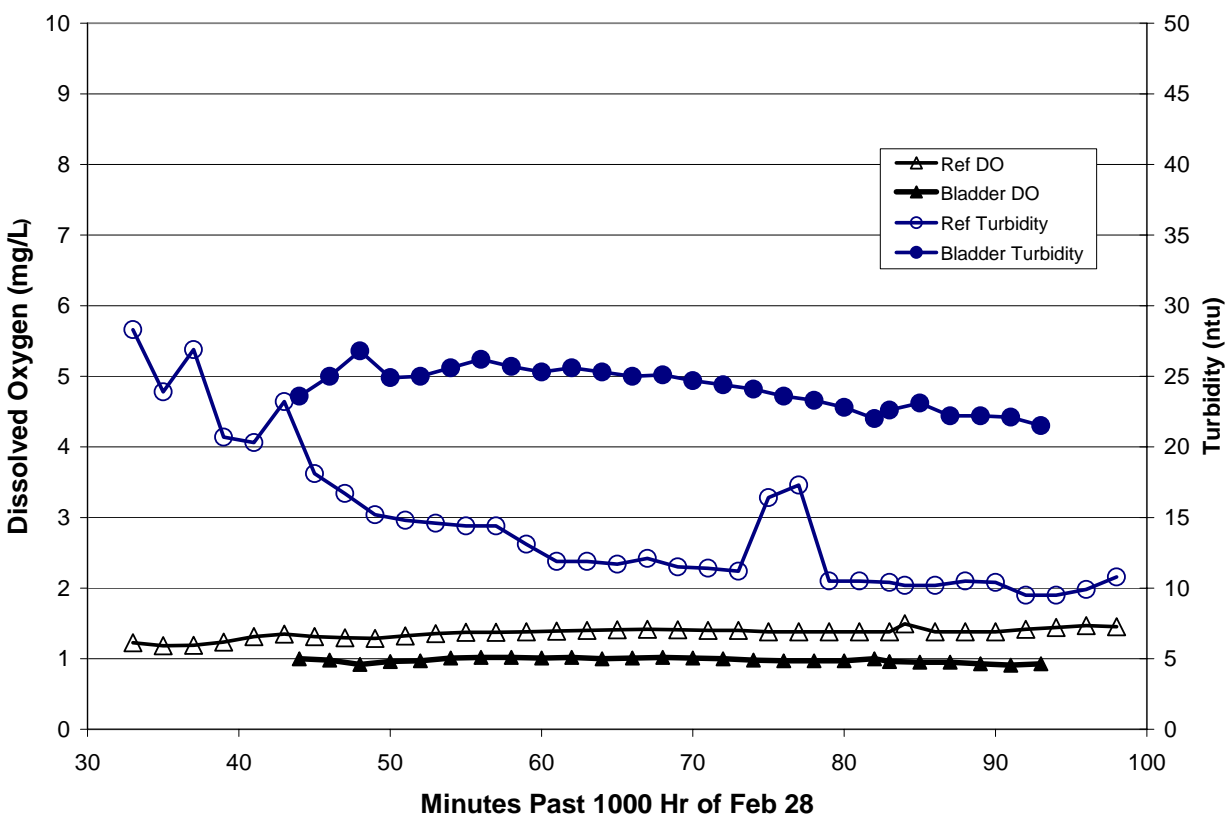


Figure 3. Simultaneous dissolved oxygen (DO) and turbidity measurements from Tyndall Well MW-8-P10 measured through the pneumatic bladder pump (Bladder) and a reference tube sampler (Ref).

Comparison of Pump and Reference Samples at Tyndall Monitoring Wells

Geoprobe pump sample results for the target cations from six different Tyndall direct-push ground water monitoring wells are shown alongside reference sampler data from the same wells in Table 10. Four replicate samples were taken using the Geoprobe pump with the

simultaneous collection of paired reference samples. For each of the five target cations, the Geoprobe pump average concentration, Geoprobe pump precision, reference pump average concentration, reference pump precision, and the percent difference between Geoprobe and reference are shown in the table. The data in the table can be summarized as follows: Precision, as

reflected by the relative standard deviation, is moderate for both Geoprobe and reference samples, with RSD values ranging from 0.2 to 4.1 percent for the Geoprobe pump and 0.2 to 3.0 percent for the reference method. Percent differences between Geoprobe and reference are significant in some cases ranging from a low of – 9.7 to a high of 53.5 percent. In 16 of the 25 cases shown, the Geoprobe pump reported higher values than the reference method. Spatial inhomogeneity

of the down-hole sampling volume even within the locale of the co-located sampling inlets may be the explanation for these differences. Given the limitations of the experimental design, definitive conclusions cannot be drawn. The results of the Tyndall trials should be considered in combination with those from the standpipe, where additional experimental control was achieved, for an overall understanding of pump performance.

Table 10. Geoprobe and Reference Sampler Cation Results from Ground Water Monitoring Wells

Well Number	Cation	Pump AVG (µg/L)	Pump RSD (%)	Reference AVG (µg/L)	Reference RSD (%)	Percent Difference (%)
MW 2-P10	Ca	7400	1.6	5030	3.0	47.3
	Fe	1100	1.1	920	1.4	18.6
	Mg	2780	1.8	1950	3.0	42.3
	K	5450	1.1	3550	1.6	53.5
	Na	6620	1.2	7200	0.4	-8.2
MW-9-P10	Ca	69,800	3.8	67,500	0.9	3.3
	Fe	ND	--	ND	--	--
	Mg	3680	4.1	3550	1.6	3.5
	K	4530	2.1	4530	2.1	0.0
	Na	4500	2.6	4500	1.8	0.0
MW-8-P10	Ca	15,250	3.0	16,890	0.8	-9.7
	Fe	ND	--	ND	--	--
	Mg	1740	1.8	1830	0.2	-5.2
	K	2580	1.9	2580	1.9	0.0
	Na	4880	1.0	5380	1.8	-9.3
MW-5-P10	Ca	34,600	0.4	29,100	1.6	18.9
	Fe	ND	--	ND	--	--
	Mg	2500	0.8	2280	0.9	9.8
	K	2870	0.5	2800	1.0	2.4
	Na	5330	3.2	4950	1.2	7.6
T6-5-P10	Ca	80,200	0.2	75,400	0.5	6.5
	Fe	ND	--	ND	--	--
	Mg	6810	0.3	6180	0.5	10.2
	K	2690	0.3	2510	0.5	7.4
	Na	4100	0.6	4070	0.8	0.8
MWD-11-P10	Ca	15,000	0.2	15,260	1.6	-2.0
	Fe	ND	--	ND	--	--
	Mg	2690	0.4	2690	0.6	0.0
	K	6130	1.6	5080	1.0	20.7
	Na	10,900	0.8	8520	0.7	27.8

Geoprobe pump and reference sample results for the VOC compounds detected in the five Tyndall monitoring wells are given in Table 11. The well number is listed in the table and is followed by the VOC compounds detected at that particular well. Also shown in the table are the pump average value, pump precision (percent relative standard deviation), reference sampler average value and reference sampler precision. The percent difference between the pump and the reference sample is given in the final column. VOC concentrations vary from low µg/L to low mg/L levels and the number of compounds detected in the ground water varies from well to well. Relative standard deviation values are generally higher than those encountered during the VOC

trials at the standpipe and are attributable to many additional factors that are encountered during field sampling. Two important factors are the degree of spatial and temporal homogeneity of the pump and reference ground water samples. The study design specified the collection of co-located samples from each of the wells by the pump and the reference sampler. Furthermore, reasonable attempts were made to collect samples at the same time and only after water quality parameters had stabilized during a low-flow purging protocol. Temporal coincidence of the two sampling activities was difficult to achieve precisely, since the sampling rate of the pump was lower than that of the reference system.

Table 11. Pump and Reference Sampler VOC Results From Ground water Monitoring Wells

Well Number	Compound	Pump AVG (µg/L)	Pump RSD (%)	Ref. AVG (µg/L)	Ref. RSD (%)	Percent Difference (%)
MW 2-P10	Benzene	240	3	490	7	-51
	Toluene	ND	--	6	4	--
	m,p-Xylene	155	6	139	1	12
	o-Xylene	11	5	34	2	-69
	1,3,5-Trimethylbenzene	7	9	ND	--	--
	1,2,4-Trimethylbenzene	23	10	16	3	46
	Naphthalene	108	5	66	2	62
MW-8-P10	cis-1,2-DCE	329	1	267	1	23
	Trichloroethene	105	5	98	3	8
MW-5-P10	Trichloroethene	2184	7	2193	1	-1
	cis-1,2-DCE	6	5	6	2	9
T6-5-P10	Vinyl chloride	7	9	6	8	4
	Benzene	103	1	84	3	22
	Ethyl benzene	30	1	44	2	-32
	Isopropyl benzene	10	2	14	1	-25
	Propyl benzene	12	1	15	2	-24
	Naphthalene	108	5	123	4	-12
MWD-11-P10	m,p-Xylene	37	3	7	20	425
	o-Xylene	33	3	7	15	404
	Ethyl benzene	9	6	ND	--	--
	1,3,5-Trimethylbenzene	13	4	ND	--	--
	Naphthalene	8	18	ND	--	--
	1,2,4-Trimethylbenzene	40	1	6	14	571

Furthermore, it is nearly impossible to ascertain the stability of the VOC concentrations in formation ground water with time or location. The data presented here implicitly assume temporal and spatial stability of the ground water source, however; that assumption may not necessarily be valid. Consequently, both the Tyndall and standpipe trial results should be considered in combination to best understand overall pump performance.

A comparison of compounds detected by pump and reference sampler indicates that with a few exceptions, the same VOCs were detected in both sets of samples. In several cases, VOCs were reported very near the method detection levels (typically in the vicinity 5 µg/L) and detected by one sampling method and not the other. Precision data are generally comparable between the Geoprobe and the reference method; however, the reference method precision from well number MWD-11-P10 is generally higher than observed at the other wells, ranging from 14 to 20 percent. Percent difference values for the pump relative to the reference sampling device range from -69 to 571 percent; however, some of the larger values are associated with measurements near the method detection level. At these low concentration levels, differences between the mean concentration levels can result in large percent difference values. The three high percent difference values observed for m,p-xylene, 1,3,5-trimethylbenzene, and 1,2,4-trimethyl benzene at well MWD-11-P10 appear to be questionable high values from the pump. All measurements of these particular compounds at this well during testing of the other Geoprobe mechanical pump are consistent with the reference method data reported in Table 11. Ten of the 17 reported Geoprobe pump VOC percent difference values are positive.

Pump Deployment Logistics

The following observations were made during testing of the pneumatic bladder pump at both the standpipe and ground water monitoring wells.

- Only one person is required to operate the pump and controller. Training requirements are minimal with several hours of training required for a ground water sampling technician to become proficient in routine field use of the equipment. The assistance of a second person can be advantageous, particularly when configuring the pump tubing for deployment into the well.
- The pump can be disassembled in the field for repair or decontamination.
- The inlet filter screen of the pump has a limited surface area and is prone to clogging when sampling in turbid water conditions.
- A gas cylinder (with associated safe transport issues) or a generator of sufficient power to power the portable air compressor is required. A small, 1-Kilowatt generator was insufficient to power the compressor and a larger 5-Kilowatt unit was required.

Pump Performance Summary

A summary of the Geoprobe Pneumatic Bladder pump performance is given in Table 12. Summary categories include precision, accuracy, comparability with reference method, versatility, and logistical requirements. Cost and physical characteristics of the equipment are also summarized in the table.

The results of this verification test show that the Geoprobe pneumatic bladder pump and accessories can be used to collect VOC-contaminated water samples that are statistically comparable to a reference method with regard to both precision and accuracy.

Table 12. Geoprobe GW1400 Series Bladder Pump Performance Summary

Performance Parameter	Performance Summary
Precision	<p>Inorganic cations: For 5 target cations at concentrations ranging from 5 to 115 mg/L, and at 17- and 35-foot standpipe sampling depths: Relative standard deviation range: 0.0 to 2.8% Median relative standard deviation: 0.6%</p> <p>VOC Compounds: For 4 target VOCs at an approximate 70 µg/L concentration level and 17-, 35- and 76-foot standpipe sampling depths: Relative standard deviation range: 0.3 to 2.8% Median relative standard deviation: 1.3%</p>
Comparability with Reference Samples	<p>Inorganic Cation Standpipe Trials: For cation target compounds at concentrations ranging from 5 to 115 mg/L, and at 17 and 35-foot sampling depths: Percent difference range: -14.8 to 6.5 Median percent difference: -1.0</p> <p>VOC Standpipe Trials: For VOC target compounds at an approximate concentration level of 70 µg/L and at 17-, 35- and 74-foot sampling depths: Percent difference range: -5.6 to 0.9 Median percent difference: -2.3</p> <p>Inorganic Cation Field Trials: For cation target compounds at concentrations ranging from 4 to 7 4 µg/L and at sampling depths ranging from 8 to 31 feet below the surface: Percent difference range: -9.7 to 53.5 Median percent difference: 3.5</p> <p>VOC Field Trials: For VOC target compounds at concentrations ranging from 5 to 1500 µg/L and at sampling depths ranging from 8 to 31 feet below the surface: Percent difference range: -68.7 to 570.8 Median percent difference: 8.4</p>
Sampler versatility	<p>The GW1400 Series pump demonstrated consistent performance across the tested range of compound volatility and sampler depth.</p> <p>The pump was successfully used with a low-flow sampling protocol and flow-through cell monitoring of water quality parameters</p> <p>Reduced pump flow rates at depths in excess of 50 feet may be incompatible with certain sampling protocols.</p> <p>Small inlet screen is prone to clogging when sampling turbid wells</p>
Logistical requirements	<p>Pump can be operated by one person with several hours of training.</p> <p>The pump requires either an external pressurized gas supply or a compressor powered from a line source or 5-kilowatt gasoline-powered generator.</p>
Completeness	<p>System was successfully used to collect all of the samples prescribed in the test plan.</p>
Purchase cost	<p>Pump: \$700 Pneumatic controller: \$1300 Tubing costs: HDPE/FEP \$114 (50-foot roll); FEP/FEP \$396 (50-foot roll)</p>
Size and weight	<p>GW1400 Series: 0.5-inch diameter x 23.8-inch length, 0.5 lbs. Pneumatic controller: 13x10x5 inches, 8.2 lbs.</p>

Section 5 – Pneumatic Bladder Pump Technology Update and Representative Applications

Note: No additional material was been submitted by the vendor for this section.

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Appendix A – Reference Sampler Method and Performance

Introduction

This appendix contains information on the reference sampler that was used alongside the vendor's pump during the Tyndall field trials. One of the challenges of this verification test was the inclusion of a reference sampler with a small cross sectional profile such that it could be co-located with the vendor pump in the 1-inch internal-diameter wells used in the study. Included in this summary is a brief description of the reference method as well as a summary of the performance of the reference sampler as determined during the standpipe portion of the test.

Method Summary

The reference method, hereafter referred to as the tube sampler, was used to collect a co-located sample alongside the vendor technology from the USGS Standpipe and the narrow-diameter wells at Tyndall AFB during the verification test. The sampler is simple in concept and is designed to provide a sample with minimal volatile organic compound losses during sample handling. The sample is collected by inserting a length of inert tubing into the standpipe or well alongside the vendor technology such that the two inlets are co-located at the desired point along the well screen. A sample is then collected by purging a fixed volume of sample through the tube with a peristaltic pump. Following this purge, the flow is stopped and a vacuum is applied at the top of sampling tube. The tube is then withdrawn from the well and sample is dispensed from the bottom of the tube. Only the bottom two-thirds of the water column in the tube is used for sample. The top third of the water column in the tube is discarded as this water is expected lose some volatiles through the air/water interface at the top of the tube. A diagram of the sampler as deployed during the Tyndall tests is shown in Figure A-1.

Sampler Parts Specification

25-foot section of FEP Teflon tubing (5/16-inch ID, 3/8-inch OD, 1/32-inch wall thickness)

1-foot section of FEP Teflon tubing (1/8-inch ID, 3/16-inch OD, 1/32-inch wall thickness)

Stainless steel quick connect fittings: female 1/4-inch ID (Fisher Cat. No. 15-340-6) and male 1/8-inch ID (Fisher Cat. No. 15-340-10)

10 to 20-foot section of Tygon tubing (3/8-inch ID, 1/32-inch wall thickness)

3-foot section of Masterflex tubing for peristaltic pump (Cole Parmer Cat. No. U-96500-17)

Peristaltic pump motor and pump head (Cole Parmer Cat. Nos. A07520-40 and A07518-00 or equivalent)

Hand vacuum pump (Fisher Cat. No. 13-874-614A)

40-mL VOA vials and labels

Clamp (for holding tubing in place when installed in well)

AC power source

Stainless steel check valve (5/16-inch ID)

Note: Two sampler design variations were used in this verification test. At the standpipe, a 12-inch length of 1/8-inch ID tubing was connected to the 5/16-inch tubing via a stainless steel quick connect fitting. This section of narrow tube was used to reduce the loss of water sample prior to the dispensing of samples into the VOA vials when the tubing string was withdrawn from the standpipe. At the Tyndall field site, due to clearance limitations, the design with the quick-connect fitting could not be deployed in the narrow-bore wells alongside the vendor's pump so an alternative design was used. The narrow tubing and quick-connect fitting were replaced with a stainless steel check-valve fitting (See Figure A-1) that was threaded directly onto the lower end of the 5/16-inch OD tubing. This design gave sufficient clearance for the reference and vendor sampling systems to be co-located in the narrow-bore wells. The check valve prevented any loss of sample from the reference tubing when it was withdrawn from the well. Following withdrawal of the tubing from the well, a paper clip was used to dislodge the check-ball and release water into the sampling vials.

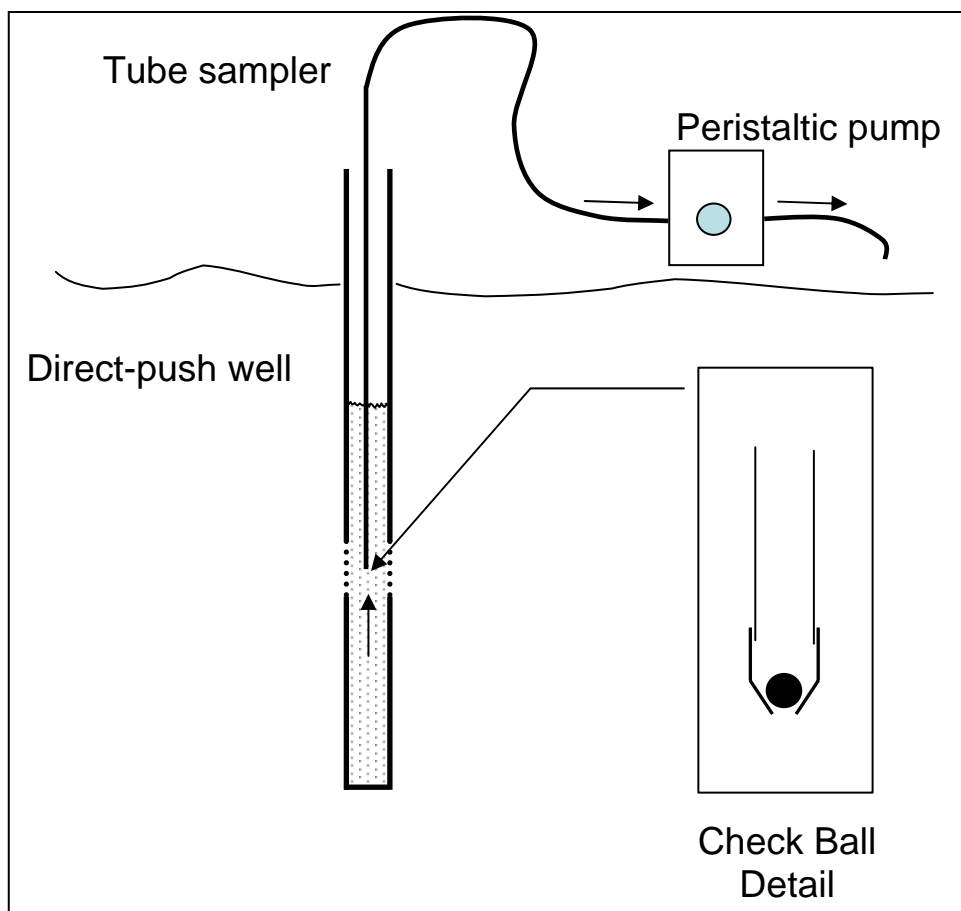


Figure A- 1 Schematic diagram of the reference tube sampler. Inset figure shows detail of the check ball fitting at the down-well end of the tube.

Detailed Sampling Procedure

1. Prepare and label four 40-mL VOA vials for sample collection
2. Assemble tubing in the following order from down-hole end to top: 1/8-inch Teflon tubing, quick connectors, 5/16-inch Teflon tubing, 3/8-inch Tygon tubing [length cut to allow positioning of tubing inlet at desired point along well screen], pump tubing.
3. Mark the exposed tubing such that the alignment of the mark with the top of the well will position the inlet at the desired point along the well screen.
4. Gently install the tubing in the well. [A careful, slow installation will minimize the increase in well water turbidity.] Use a clamp to hold the tubing in place at the well head.
5. Insert the pump tubing into the peristaltic pump head, turn on pump and flush 1 liter of water through the tubing at a flow rate of approximately 200 mL/min.
6. At end of purge, stop pump, attach hand-held vacuum pump at outlet end of tubing and apply vacuum to maintain the water column in the tubing.
7. Remove the tubing from the peristaltic pump head.
8. Withdraw tubing from well, keeping the end with the vacuum pump attached at least 10 feet above the inlet end of the tubing. A stepladder may be necessary to accomplish this.
9. Hold inlet end (1-8-inch tubing) over 40-mL vial and slowly dispense sample into the 40-mL vial by using the vacuum release lever on the hand pump.
10. Dispense the sample into the four VOA vials in a continuous fashion. (A third person should be available to take the VOA's and cap them immediately after filling.)

11. Following collection, verify correct labeling on VOA vials
12. Disassemble and decontaminate the lengths of Teflon tubing and quick connectors if they are intended for use in another well.

Note: For the alternate sampler design used at Tyndall, Step 2 and Step 9 are changed as follows:

2. Thread the stainless steel check valve on the end of the 5/16-inch OD tubing. The top end of the 5/16-inch tubing is connected to the Tygon tubing and the Tygon is in turn connected to the short length of peristaltic pump tubing.
9. Hold end of 5/16-inch tubing over 40-mL vial and using the end of a paper clip, release sample from the tubing by pushing the check ball upward. The vacuum pump lever should continuously be released during this sample dispensing procedure.

Tube Sampler Performance

In order to ascertain the tube sampler's performance characteristics, it was deployed in selected tests during the standpipe trials. Tube samples were collected from the standpipe at the same time as reference port samples for target cation and VOCs. Each test included four paired tube sampler and reference port samples such that tube sampler precision and accuracy relative to the port samples could be determined. The precision and accuracy results for the tube sampler for the target cations are given in Tables A-1 and A-2 respectively.

Table A- 1 Tube Sampler and Reference Port Precision for Cations

Compound	Trial No.	Conc. Level µg/L	Sampling Depth (feet)	Tube Sampler Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test p
Calcium	2	9500	17	0.6	0.5	0.82
	4	15,200	17	0.9	1.5	0.42
Iron	2	6400	17	1.3	2.2	0.39
	4	13,000	17	0.9	1.8	0.26
Magnesium	2	5800	17	0.3	0.7	0.25
	4	11,700	17	0.9	1.8	0.32
Potassium	2	5900	17	0.4	3.8	0.39
	4	14,800	17	1.3	2.3	0.36
Sodium	2	89,800	17	0.1	4.0	0.47
	4	115,500	17	1.2	1.8	0.49

Table A- 2 Tube Sampler and Reference Port Comparability for Cations

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (feet)	Difference (%)	t-Test <i>p</i>
Calcium	2	9500	17	-1.8	<0.01
	4	15,200	17	0.5	0.58
Iron	2	6400	17	-1.6	0.27
	4	13,000	17	-0.4	0.73
Magnesium	2	5800	17	0.7	0.11
	4	11,700	17	-0.1	0.92
Potassium	2	5900	17	3.4	0.40
	4	14,800	17	0.0	0.98
Sodium	2	89,800	17	3.1	0.44
	4	115,500	17	-0.4	0.71

Tube sampler precision for cations is as good as or better than that observed with the reference port samples. The percent relative standard deviations for the tube sampler ranged from 0.1 to 1.3 percent whereas the range was 0.5 to 3.8 percent for the reference port samples. Statistical testing shows precision differences between tube sampler and reference port samples were not significant in all test cases. The comparability of the tube sampler with the reference port sample data is quite good with percent difference values ranging from -1.8 to 3.4 percent for all target cations. Results of the paired t-test also shown in Table A-2 indicate one statistically different result (Trial 2, Calcium) however the -1.8 percent difference noted is small.

Similar results for precision and accuracy are shown in Tables A-3 and A-4 for target VOC compounds that were detected during the standpipe trials. Tube sampler precision for the VOCs is comparable to that observed for the port samples. The percent relative standard deviations for the tube sampler ranged from 0.6 to 1.9 percent whereas the range was 0.7 to 1.6 percent for the reference port samples. Statistical testing further shows that observed precision differences between tube sampler and reference port samples were not significant. The comparability of the tube sampler with the reference port sample data is good with percent difference values ranging from -1.3 to 0.8 percent for all detected VOCs. Results of the paired t-test, also shown in Table A-4, reveal that none of the observed differences were statistically significant at the 0.05 level.

Table A- 3 Tube Sampler and Reference Port Precision for VOCs

Compound	Trial No.	Conc. Level (µg/L)	Sampling Depth (feet)	Tube Sampler Precision (RSD %)	REF Precision (RSD %)	F-Ratio Test <i>p</i>
MTBE	7	76	17	1.3	1.0	0.37
cis-1,2-DCE	7	74	17	1.9	1.6	0.27
Benzene	7	81	17	0.6	0.7	0.06
TCE	7	73	17	0.8	0.8	0.12

Table A- 4 Tube Sampler and Reference Comparability for VOCs

Compound	Trial No.	Conc. Level µg/L	Sampling Depth (feet)	Difference (%)	t-Test p
MTBE	7	76	17	0.8	0.36
cis-1,2-DCE	7	74	17	-0.9	0.52
Benzene	7	81	17	-1.3	0.06
TCE	7	73	17	-1.1	0.12

Tube Sampler Performance Summary

The results of the testing at the standpipe reveal that the tube sampler performs acceptably both with regard to precision and accuracy for target cations and VOCs when used as a co-located reference sampler in the narrow-diameter wells during the Tyndall ground water sampling portion of this verification test.

Appendix B – Analytical Method and Quality Summary

Introduction

DataChem Laboratories in Cincinnati, OH conducted the analysis of all samples collected during this study. For cation analysis, EPA Standard Methods 3010A (Acid Digestion of Aqueous Samples and Extracts For Total Metals by FLAA or ICP Spectrometry) and 6010B (ICP Atomic Emission Spectrometry) were used for analysis. For VOC analysis, EPA Standard Method 8260B (Volatile Organic Compounds by Gas Chromatography/Mass Spectroscopy) was used. Various data quality measures were incorporated into both the field sampling and the laboratory analysis components of this study. This appendix summarizes those data quality measures.

Data Quality Measures

Performance measures used to track overall laboratory data quality for inorganic cation and VOC samples are given in Tables B-1 and B-2. These measures are used to verify acceptable instrument performance and the adequacy of the final analytical results. Cation and VOC lab performance measures are essentially the same and included field spikes, method or preparation blanks, lab calibration standards as well as matrix spikes and matrix spike duplicates. The VOC method also included the addition of surrogate VOC spikes in each sample. This appendix provides only a general summary of the data quality control measures in order to provide an overall indication of the quality level of the laboratory data. All quality control data are available in the Data Notebook associated with this test which is available from the EPA Project Officer via special request.

Table B-1 Cation Analysis Quality Control Measures

Quality Control Check	Description	Frequency
Field Spikes	Six replicate 10 ppm spike samples made up in distilled water	One set per site
Prep. Blanks	Laboratory blank	Every 20 th sample
Lab Calibration Standard	Laboratory spike sample	Every 20 th sample
Matrix Spike	Lab spike into a field sample	First sample in batch
Matrix spike duplicate	Repeat analysis of matrix spike	First sample in batch

Table B-2 VOC Analysis Quality Control Measures

Quality Control Check	Description	Frequency
Field Spikes	Six replicate 10 ppm spike samples made up in distilled water	One set per site
Prep. Blanks	Laboratory blank	Every 20 th sample
Lab Calibration Standard	Laboratory spike sample	Every 20 th sample
Matrix Spike	Lab spike into a field sample	First sample in batch
Matrix Spike Duplicate	Repeat analysis of matrix spike	First sample in batch
Surrogate Standards	Spike of three unique VOCs	Every sample

Data Quality Examples

The following sections present examples of system performance throughout the course of the study. In the interest of brevity, all quality control data is not shown in this appendix. A complete tabulation of all quality control data is included in the GW SAMPLING II VERIFICATION TEST DATA NOTEBOOK and is available for viewing through special request to the EPA Project Officer.

Preparation Blanks

Preparation blanks for each batch cation samples were reported as not detected (<1 ppm) for each of the target analytes. Preparation blanks for each VOC analysis batch were also reported as not detected (<10 ppb) for each of the target analytes.

Laboratory Calibration Standard Results

Cation Analysis—The inorganic method criteria for the laboratory calibration standards specify a recovery of ± 10 percent or within documented laboratory-specific acceptance ranges for the particular sample matrix being analyzed. Normal LCS percent recovery ranges for the six target analytes were as follows: Calcium 68-143, Iron 81-115, Magnesium 71-127, Potassium 67-126 and Sodium 55-146. Recovery data are best for Ca, Fe and Mg and more variable for K and Na. None of the reported cation results were flagged by the laboratory as being out of normal LCS recovery range for six the target analytes. An example of the batch-to-batch LCS performance for Stennis cation analysis is given in Figure B-1. None of the LCS recovery data were flagged by the laboratory as being outside recovery ranges encountered during normal operation of the instrument.

VOC Analysis—LCS percent recovery ranges encountered by the laboratory under normal instrument operating conditions are as follows: 1,1-dichloroethene 59-129; hexane 48-143; benzene 76-127; trichloroethene 69-121; toluene 69-123; chlorobenzene 74-122. None of the LCS recovery data were flagged by the laboratory as being outside the recovery ranges encountered during normal operation of the instrument.

Matrix Spike and Matrix Spike Duplicate Results

Cation Analysis—One sample batch was reported outside the normal recovery range for the MS and MSD quality control checks (Standpipe, Batch No. 2, Calcium) however the spike was done in a tap water sample that had low calcium background. According to method guidelines, the calcium concentration in the sample should be 10--fold higher than the method detection limit, thus the results from this matrix check should be viewed accordingly. All other MS and MSD quality checks met laboratory acceptance criteria. The recovery ranges are similar to those given for LCS checks however for the sake of brevity they are not reproduced here.

Complete information is available in the Data notebook from the verification test available by special request from the EPA project officer.

VOC Analysis—The MS and MSD results from all batches of VOC samples met laboratory acceptance criteria. The recovery ranges are similar to those given for LCS checks however for the sake of brevity they are not reproduced here. Complete information is available in the Data notebook from the verification test available by special request from the EPA project officer.

Surrogate Standards

Each VOC sample was spiked with a mixture of dibromofluoromethane, toluene-d8, and bromofluorobenzene. Recovery levels for these spiked compounds are calculated for each sample as an additional quality control measure. All recoveries for these three surrogate standards were within the normal recovery range encountered by the laboratory under normal instrument operating conditions.

Field Spikes

Cation Analysis—Field spikes containing the target cation compounds were prepared during the standpipe and Tyndall portions of the verification test. Laboratory analysis results are shown in Tables B-3. Recoveries range from 95 to 118 percent and the relative standard deviations are all less than 5 percent. The results show acceptable sample cation recovery from the field spikes.

Table B-3 Target Cation Field Spike Results

Location/Target Cation	Average (µg/L)	Recovery (%)	Precision (%RSD)
Standpipe			
Calcium	10,250	103	5
Iron	11,000	110	0
Magnesium	10,250	103	5
Potassium	9300	93	2
Sodium	9575	95	2
Tyndall			
Calcium	10,000	100	0
Iron	10,667	107	5
Magnesium	9883	99	1
Potassium	9850	99	1
Sodium	11,833	118	3

VOC analysis—Field spikes containing the target VOC compounds were also prepared during the standpipe and Tyndall portions of the verification test and results are shown in Table B-4. During the standpipe trials, an initial attempt at spike preparation was made by injecting a spike solution through the septa of VOA vials that were pre-filled with distilled water. Evidence of leakage through the septa was observed however so these samples were discarded. Alternatively, four replicate samples were drawn from the standpipe mixing tank just prior to filling the standpipe in order to derive a measure of overall sampling and analytical precision. Since the concentration level of the VOCs in the mixing tank was not known precisely, spike recovery for the standpipe samples could not be determined. Spikes at Tyndall were prepared in a different manner by filling VOA vials with distilled water, injecting 2 µl of chilled VOC spiking solution and then quickly topping off the VOA vials with distilled water and capping them.

The spike sample results from the standpipe show very rapid losses of vinyl chloride and ethyl benzene from the mixing tank. This loss was also observed in all of the vendor and reference samples. As a result, spike analysis results for these two compounds invalidate the use of these two compounds in the standpipe test matrix. Precision of the other four compounds ranges from 0 to 5 percent RSD and is acceptable. Tyndall recoveries range from 82 to 125 percent with the highest observed for vinyl chloride, further evidence of the

difficulty associated with sampling and analysis of this volatile compound. Overall, the VOC recoveries are judged to be acceptable and within the anticipated range.

Table B-4 Target VOC Field Spike Results

Location/Target Cation	Average (µg/L)	Recovery (%)	Precision (%RSD)
Standpipe			
Vinyl Chloride	ND	--	--
MTBE	80	--	1
cis-1,2-DCE	76	--	2
Benzene	84	--	2
TCE	76	--	3
Ethyl Benzene	ND	--	--
Tyndall			
Vinyl Chloride	125	125	7
MTBE	89	89	7
cis-1,2-DCE	81	81	9
Benzene	87	87	8
TCE	82	82	8
Ethyl Benzene	82	82	11

Overall Summary of Quality Control Measures

The results of various quality control measures applied both in the field and in the laboratory and summarized in this appendix indicate that the quality of the data produced during this verification test is acceptable and at the level anticipated for an analytical laboratory that is proficient in carrying out the EPA standard methods for determination of cations by inductively coupled plasma atomic emission spectroscopy and VOCs by purge-and-trap followed by capillary-column gas chromatography/mass spectrometry.