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Cost-Effective, Ultra-Sensitive Groundwater Monitoring for Site Remediation and Management

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14. ABSTRACT
This report outlines the cost analysis of ER-201122, whose objective was to to describe the development and demonstration of a new tool for monitoring contamination in ground and surface waters, the In Situ Sampler (IS2). The finished product provides an account of the theory, the engineering design process, and the first field data generated with this tool and method. This report can serve users and stakeholders as a preliminary guidance document for decision-making with respect to feasibility for future studies and field implementation.

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ACRONYMS AND ABBREVIATIONS

AC	alternating current
AFB	Air Force Base
AFCEC	Air Force Civil Engineer Center
amsl	above mean sea level
ASU	Arizona State University
bgs	below ground surface
BP	boiling point
BRAC	Base Realignment and Closure
BTEX	benzene, toluene, ethylbenzene, and xylenes
CAS	Chemical Abstract Service
COTS	commercial off-the-shelf
DC	direct current
DO	dissolved oxygen
DoD	U.S. Department of Defense
DOE	U.S. Department of Energy
EO	Executive Order
ER	Environmental Restoration
ft	foot/feet
HDPE	high density polyethylene
GC	gas chromatography
IC	ion chromatograph
IS2	In Situ Sampler
ITRC	Interstate Technology & Regulatory Council
JP	jet propellant
K_{ow}	octanol-water partition coefficient
L	liter
LNAPL	light non-aqueous phase liquid
µg/L	micrograms per liter
MDL	method detection limit
mg	milligram
mL	milliliter

MS	mass spectrometry
NAS	Naval Air Station
NASNI	Naval Air Station North Island
NOAA	National Oceanic and Atmospheric Administration
OD	outer diameter
OU	operable unit
PAH	polycyclic aromatic hydrocarbon
PDB	polyethylene diffusion bag
PDMS	polydimethylsiloxane
psi	pounds per square inch
PTFE	polytetrafluoroethylene (teflon)
QA/QC	quality assurance/quality control
RL	reporting limit
SBSE	stir bar sorptive extraction
SDB	styrene divinylbenzene
SPE	solid phase extraction
ST	storage tank
SVOC	semivolatile organic compound
TCE	trichloroethene
TPH	total petroleum hydrocarbon
USEPA	U.S. Environmental Protection Agency
UST	underground storage tank
V	volt
VOA	volatile organic analysis
VOC	volatile organic compound

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EXECUTIVE SUMMARY

OBJECTIVES OF THE DEMONSTRATION

Between 2004 and 2033, an estimated $200 billion will be spent on environmental restoration, of which 10-16% is estimated to be spent on site characterization. New methods and instruments that reduce costs, improve data quality, or provide complementary data at a reasonable cost, can be expected to have a significant impact on the direction of environmental restoration projects. The objective of this work is to describe the development and demonstration of a new tool for monitoring contamination in ground and surface waters, the In Situ Sampler (IS2). The finished product provides an account of the theory, the engineering design process, and the first field data generated with this tool and method. This report can serve users and stakeholders as a preliminary guidance document for decision-making with respect to feasibility for future studies and field implementation.

TECHNOLOGY DESCRIPTION

The IS2 is a method and instrument for solid-phase extraction in situ. The IS2 sampler is inserted to a desired depth in a monitoring well, where it meters 10s to 1000s of milliliters (mL) of fluid, such as groundwater, to an array of sorbent cartridge over a time-scale from hours to weeks. Unlike many passive technologies, the IS2 does not require compound-specific calibration—concentration data is derived directly from the mass of analyte recovered from the sorbent cartridge and the known volume of water processed. This preconcentration step provides significant magnification of analyte concentration, improving reporting limits (RL). The samples returned by the IS2, while weighing only a few grams, can represent chemical constituents concentrated from several kilograms of water. This makes the handling and shipment of large numbers of samples significantly more cost effective as well as "green," with respect to energy requirements and the carbon footprint of monitoring. The automation made possible by the IS2 reduces sample handling by technicians, with the potential to improve reproducibility, by limiting opportunities for contamination during processing in the analytical laboratory.

DEMONSTRATION RESULTS

The IS2 was demonstrated at two sites: the Former Williams Air Force Base (AFB) in Mesa, Arizona, and Naval Air Station North Island (NASNI). At the Former Williams AFB, the device was inserted to a depth of 200 feet (ft) and generated 24-hour composite samples from micrograms per liter (µg/L) quantities of fuel components including naphthalene. At NASNI, the sampler was deployed to generate 28-day composite samples in a shallow well with hexavalent chromium contamination that was demonstrated to be driven by tidal influence. In both cases, the sorbents used were commercially available and the analysis methods typical for the analytes. The IS2 system has been demonstrated to provide data comparable to liquid samples, while also providing short-term or long term-integrated data from the preconcentration of analytes in situ.

IMPLEMENTATION ISSUES

The IS2 groundwater monitoring strategy performed most reliably when collecting solid analyte samples only, as is the case in most typical monitoring applications. For technology validation

purposes, the device was modified to also capture the liquid that was extracted in situ. In this configuration, the challenge arises of preventing the hydrostatic pressure of water at depth to drive flow through the metering pumps. Passive check valves were used to counter the hydrostatic pressure but sourcing and properly sizing these turned out to be time-intensive. However, the most common and most desirable configuration of the device is one where only solid-phase samples are collected and processed water is returned to the well bore. This greatly reduces the engineering requirements for the instrument, as the equal inlet and outlet pressures enable a relatively simple valve system to control the flow precisely.

1.0 INTRODUCTION

The purpose of this project was to develop and validate a novel method for integrated groundwater sampling and sample processing, the In Situ Sampling (IS2) Technology. The IS2 technology provides the capabilities of contemporary laboratory bench techniques for liquid sample processing, including cleanup and concentration, in a package that is inserted directly into a contaminated, saturated geological formation by way of a monitoring well. The primary benefits of this technology include:

- Generation of time-integrated average concentration data, providing the best estimate of contaminant mass flux through a groundwater system.
- Cost benefits realized by greatly reducing the volume of groundwater shipped from sites to laboratories, enhancing the stability of samples for transport, and improving the sensitivity of the monitoring regimen.

Secondary benefits include the reduction of human handling steps in sample collection and processing, with the improvements in reproducibility that are typically associated with automation. This system is intended to be deployed without well purging where indicated by site hydrogeology, reducing hazardous waste generation.

1.1 BACKGROUND

The U.S. Environmental Protection Agency (USEPA) estimates that between 2004 and 2033, more than $200 billion will be spent on environmental remediation, 10-16% of which will be spent on site characterization including groundwater monitoring (USEPA, 2004). Included in that estimate is the U.S. Department of Defense's (DoD) own estimate that it will spend $33 billion for environmental remediation from 2003 forward, not including the costs of some sites where work was already taking place. A review of the cost information for the groundwater remediation program at the U.S. Department of Energy (DOE) Hanford Site agrees with the site characterization estimate, suggesting that performance monitoring (remediation system and groundwater monitoring) costs accounted for approximately 12% of the expenditures for that program in 2010, or more than 20% of the costs when capital investments are excluded (DOE, 2011).

The cost of groundwater monitoring can therefore be expected to be a significant contribution to the overall cost of managing a contaminated site. Making any significant cost reductions is complicated by the distribution of costs between many contributing elements:

- Construction of monitoring wells;
- Sampling and fieldwork labor;
- Capital equipment (pumps and other reusable systems);
- Consumables (bailers, sample bottles, reagents and preservatives);
- Transportation and shipping;
- Laboratory work; and
- Waste disposal.

With more than 40 years of development, the individual components of this process have been optimized to a degree, and several alternatives may be available for each element. Further improvements in the efficiency of the monitoring program–and its cost effectiveness for the site manager–may be possible by exploiting synergy between these components. IS2 is an example of a novel technology that takes this approach, by moving a component of the analytical process (cleanup and concentration) into the field.

While in situ analysis of many contaminants has been investigated (Carron et al., 1992; Li, et al., 2014), the typical path for characterizing environmental chemistry is to couple a sampling method in the field with an analytical method in the laboratory. Most groundwater sampling procedures move a significant volume of water (10s to 1000s of milliliters [mL]) from the well-bore to the laboratory. Significant care must be taken to preserve the viability of these samples, and a great deal of research has been performed to optimize the process of retrieving representative volumes of water (Britt et al., 2010; Parker and Britt, 2012; Pettyjohn et al., 1981). This includes several notable improvements in devices that take grab-samples, diffusion-based samplers (Verreydt et al., 2014), and an ongoing debate over the efficacy of purging the monitoring well before sampling (Barcelona et al., 2005).

In addition to the difficulty of acquiring and protecting volumes of water, most liquid sampling methods take time-discrete samples. While there are conditions where this will not affect data quality, groundwater is a dynamic environment, subject to many stresses including tidal influence, pumping, seasonal or engineered recharge, changing biological conditions and other factors that may cause contaminant concentrations to change on a time-scale that undermines data provided by discrete measurements. In a modeled system with changing contaminant concentrations, the choice of two random sets of discrete data can easily provide average observed values more than one standard deviation apart (Figure 1).

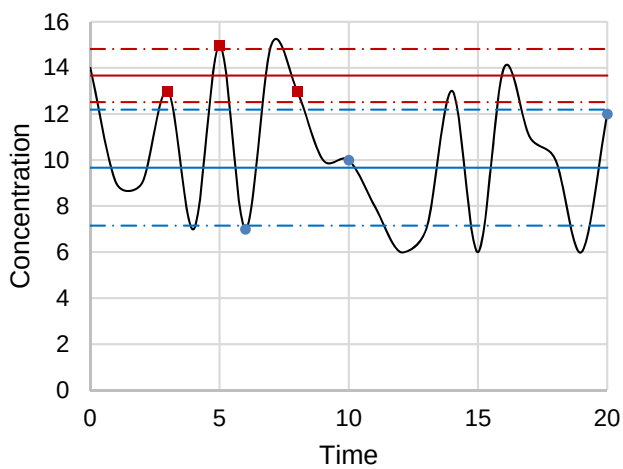

Figure 1. Modeled averages (solid lines) and standard deviations (dashed lines) obtained from two sets of three discrete samples (red and blue) taken randomly from an environment where the contaminant concentration (black) varies randomly between 50 and 150% of the average.

Contaminant mass flux in a plume is one of the most important site characterization activities that groundwater monitoring supports (Einarson and Mackay, 2001; Interstate Technology & Regulatory Council [ITRC], 2010; Stroo et al., 2012). If the difference between two averages is more than 40%, this could significantly affect mass flux calculations. The number of discrete measurements needed to characterize such an environment is prohibitively high, making the utility of time-averaging methods very attractive. This type of time-dependent concentration fluctuation is not hypothetical, has been documented in the field by the authors, and is presented in Section 5.5 of this report.

The approach of this project is to automate a standard laboratory method (solid phase extraction [SPE]) in a package that can be deployed in typical groundwater monitoring wells. SPE enables the extraction of trace contaminants from large volumes of water, providing both cleanup and preconcentration of analytes before quantification. This is a popular and mature technology, with a variety of vendors providing high-quality consumables (Hennion, 1999) and equipment for process automation. By controlling the volume and flow rate of water through the collection system, and collecting the entire contaminant mass, the IS2 provides a true average concentration of the contamination in the environment to which it is exposed.

By moving this process in situ, the investigators intend to avoid most of the challenges of maintaining the integrity of a liquid sample. Furthermore, this practice should yield many synergistic improvements in the efficiency of the entire process, namely:

- Reduced complexity of fieldwork, by generating dry solid-phase (sorbed) samples;
- Reduced consumption of consumables, by eliminating intermediary processes;
- Reduced shipping costs, by eliminating the weight of liquid samples;
- Reduced laboratory costs, by moving part of the analytical process out of the lab.

Additional gains in productivity should come from:

- Improved method detection limits, by pre-concentrating large (1000s of mL) samples; and
- Improved reproducibility, by reducing lossy sampling steps and increasing automation.

Finally, the in situ sample preparation process is intended to be a no-purge method, processing water taken from the screened interval and returning it directly to the well-bore; thus carrying with it the significantly lower waste production potential of such methods. While purging is a necessary step for some sampling methods (such as the use of bailers), studies suggest that it can be reasonably eliminated with a dedicated and properly designed sampler operating in the screened interval of the well, a principle that underlies polyethylene diffusion bag (PDB) sampling (Powell and Puls, 1993; Vroblesky and Hyde, 1997).

1.2 OBJECTIVE OF THE DEMONSTRATION

Field demonstration of the IS2 technology demonstrated; (i) field preparation of samples by SPE or stir-bar sorptive extraction (SBSE); (ii) reduction or elimination of liquid sample handling in the field; (iii) generation of time-integrated average concentration data; and (iv) agreement with

the measurements made by a traditional site monitoring program. Additionally, field demonstration provided the opportunity for the collection of data on the material and labor requirements associated with this technology, enabling comparisons with contemporary methods.

Points of contact for the management, development, and demonstration of the IS2 technology are provided in Appendix A.

1.3 REGULATORY DRIVERS

Regulatory drivers for this technology include:

- DoD Financial Management Regulation Volume 12, Chapter 2: Productivity Gain Sharing (DoD, 2012);
- Executive Order (EO) 13,423, *Strengthening Federal Environmental, Energy, and Transportation Management*. (EO No. 13,423, 2011); and
- EO 13,514, *Federal Leadership in Environmental, Energy, and Economic Performance*. (EO No. 13,514, 2010).

2.0 TECHNOLOGY

The technology developed under ER-201122 consists of a novel down-hole device for generating concentrated, non-aqueous-phase samples, and sequence of processes from deployment of the sampler to analysis of the samples. The method and systems associated with the technology have been described in international patent applications published under numbers US 2011/0003400 A1 (WO 2009/105241), "Methods and systems for ground and surface water sampling and analysis" (Halden, 2009); US 2013/0040290 A1 (WO 2011/140270), "Methods and systems for ultra-trace analysis of liquids" (Halden, 2011); and US 2014/0102182 A1 (WO 2012/145299), "Devices and methods for determination of bioavailability of pollutants" (Halden and Roll, 2012).

2.1 TECHNOLOGY DESCRIPTION

SPE and SBSE (Figure 2) are mature technologies used to concentrate and clean up the analytes of interest in aqueous samples before analysis by standard analytical methods including chromatography (gas and liquid) and mass spectrometry. In SPE, water is passed through a bed of resin beads, typically incorporated into a disposable plastic syringe. These beads are manufactured from sorbent materials or from inert materials that have been functionalized to promote the sorption of analytes from the aqueous phase. Selection of the functional groups and the bed volume enable the user to determine the specificity of the extraction and the capacity for material to be captured in the cartridge.

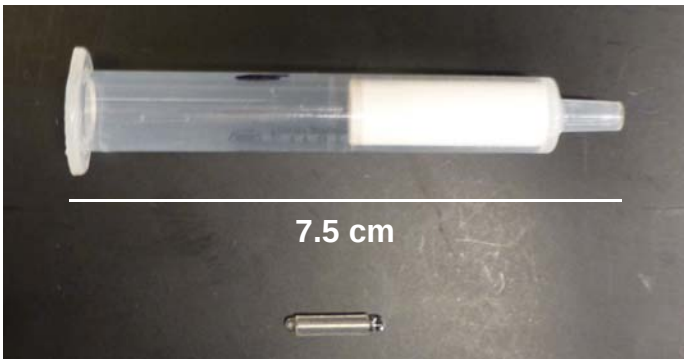

Figure 2. SPE cartridge (top) and polydimethylsiloxane (PDMS)-wrapped stir bar used with SBSE (bottom).

In SBSE, inert glass rods with magnetic cores are wrapped in a layer of PDMS. Hydrophobic analytes of interest partition from the aqueous phase into the PDMS layer, with the partitioning typically well-predicted by the octanol-water partition coefficient (K_{OW}) of the analytes (Baltussen et al., 1999). In practice, the sorbent capacities and affinities of SPE and SBSE sampling packages are selected such that they act as ideal sinks, capturing the entire contaminant mass to which they are exposed.

The IS2 sampler (Figure 3) is an extension of these concepts, packaging the sample preparation pipeline in a package that can be operated in environment. The IS2 sampler includes a bank of sorbent cartridges and the hardware necessary to take in water from the environment, dispense this water into the cartridges at a prescribed rate, and dispose of the water when it leaves the cartridges.

The instrument can be programmed to generate low-flow continuous, periodic composite, or high-flow time-discrete samples.

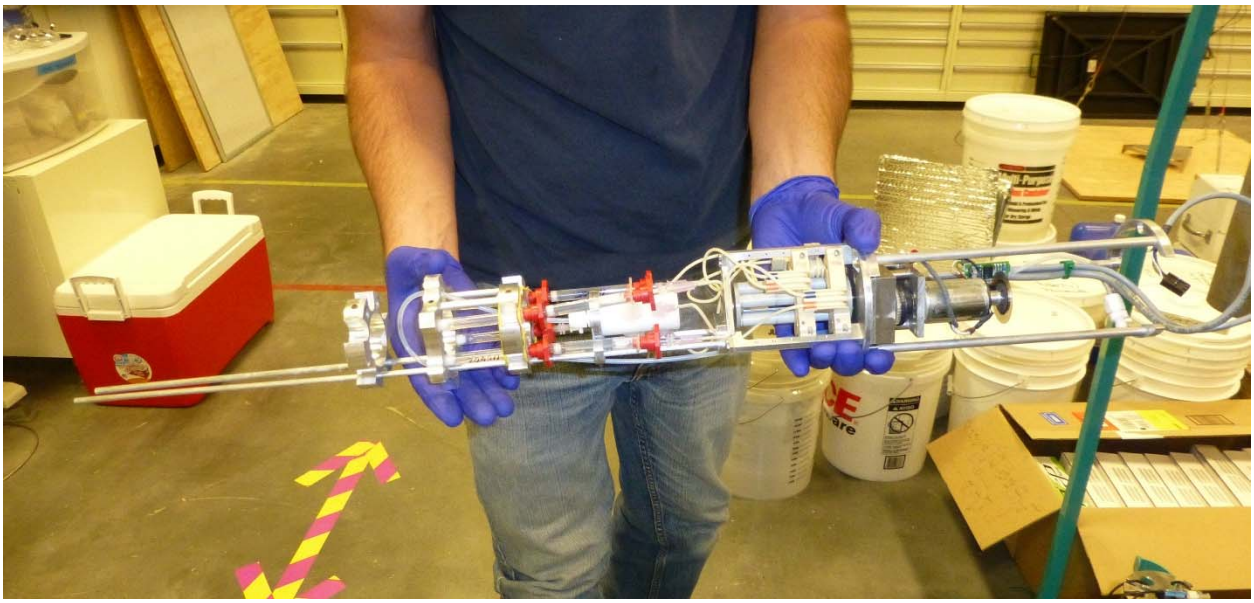

Figure 3. Field-prepared IS2 sampler with peristaltic pump.
From right to left, the unit comprises a peristaltic pump and an array of cartridges for solid phase extraction.

The IS2 sampler is an example of an active, time-integrative sampler. Fundamental properties of the sampler include:

- Sorbent cartridges that have negligible desorption rates during sampling; and
- Collection rates governed by advective flow through the sampler.

The rate of contaminant mass collection by the sampler proceeds according to Equation 2-1 (Vrana et al., 2005), where M_S is the contaminant mass captured on a cartridge; C_W is the concentration of the contaminant in the environmental water; R_S is the rate of advective flow through the cartridge; and t is the elapsed sampling time. After the samples are recovered and quantified, the environmental contaminant concentration can be determined according to Equation 2-2.

$$M_S = C_W R_S t \tag{2-1}$$

$$C_W = \frac{M_S}{R_S t} \tag{2-2}$$

This time-integrative approach provides concentration data and generates an average of the changing environmental concentration from the time sampling begins until it ends, yielding a significantly better estimate of the contaminant flux through the system when environmental concentrations are subject to temporal changes (Figure 4).

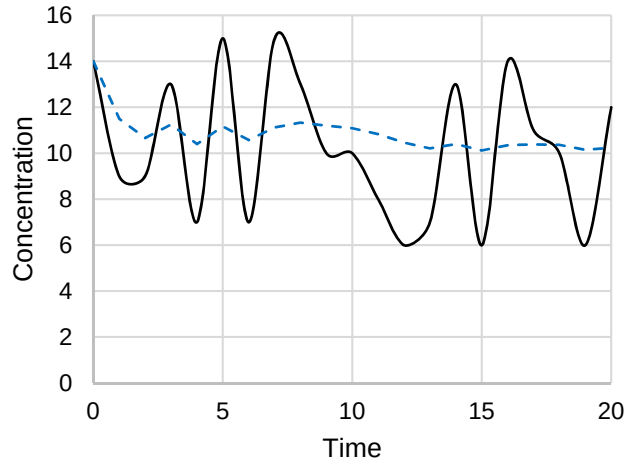

Figure 4. Modeled results for time-integrative data derived from the IS2 (dashed line) when the contaminant concentration (black) changes with time.
This model uses the same input data as Figure 1.

In the present embodiment (Figure 5), the IS2 sampler is deployed in the screened interval of a groundwater monitoring well. While in operation, the sorbent cartridges scavenge and concentrate target analytes. The water is returned to the well-bore through a discharge line or captured in internal storage bags, depending on the hydrogeological properties the requirements of the site. Upon return of the sampler to the surface, the loaded SPE or SBSE cartridges are returned to the laboratory for elution and analysis.

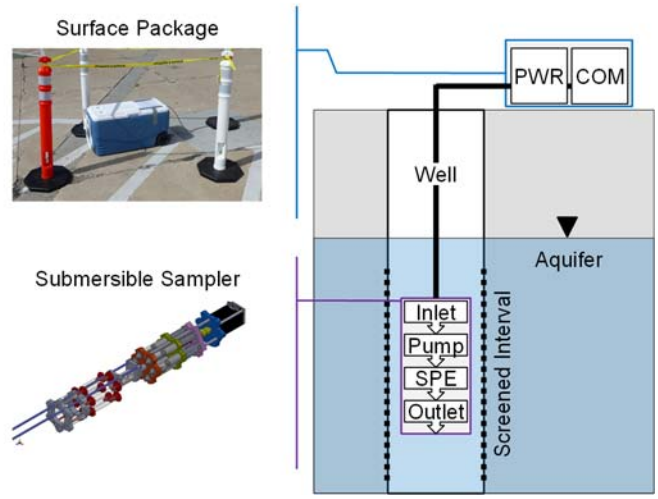

Figure 5. Schematic of a typical installation of the IS2 sampling technology.
The device is suspended from the surface and lowered to the desired sampling depth within the screened interval of a monitoring well. Power and communication are provided from a surface package via a multichannel control cable. The submersible handles water collection, processing, and expulsion or collection.

Development of the IS2 method and sampler under ER-201122 began in May 2011 and concluded in December 2014, with the following highlights:

May 2011	Project ER-201122 Commenced
July 2011	Peristaltic Sampling Unit for 4" Wells Designed
October 2011	Peristaltic Prototype Sampling Unit for 4" Wells Completed Gas Chromatography (GC)-Mass Spectrometry (MS)/MS with Automated Sample Handling Installed
December 2011	Site Selection Memo Delivered
March 2012	Draft Universal Demonstration Plan Delivered
November 2013	First Demonstration at the Former Williams Air Force Base (AFB)
April 2014	Reciprocating Sampling Unit for 4" Wells Designed
July 2014	Reciprocating Sampling Unit for 4" Wells Completed
November 2014	Second Demonstration at Naval Air Station North Island (NASNI)

Applications of in situ sample processing include:

- Improving the cost efficiency of the workflow in normal site monitoring programs;
- Improving limits of detection and quantification by concentrating large-volume samples;
- Improving reproducibility of data by automating sample handling and providing parallel replicates; and
- Acting as a sentinel technology, providing earlier detection of migrating contaminants.

2.2 TECHNOLOGY DEVELOPMENT

The IS2 apparatus consists of a submersible sampler, a power and control system that is connected via a waterproof cable, and the hardware used to secure the device in the deployment well. The sampler includes a pump, an array of solid phase extraction cartridges, and the liquid handling lines that enable the pump to load the cartridges with groundwater taken into the sampler from the environment. Development of the IS2 concentrated primarily on two submersibles: a 3.5-inch outer diameter (OD) unit with a peristaltic pump, and a 3.5-inch unit with a reciprocating pump.

Power and control for the sampling unit are provided by a multi-channel waterproof electrical cable that connects the subsurface sampling unit to a power and control package on the surface (Figure 6).

Figure 6. IS2 surface package at an installation.
Batteries and communication are stored in the waterproof container, and an electrical control cable extends into the well. The surface package location is determined by site safety considerations; here it is located at a restricted-access site, in a low-traffic location.

2.2.1 Development of 3.5-inch OD Peristaltic Sampling Unit

A 3.5-inch OD peristaltic sampler (Figure 7) was developed by coupling a high-precision, 6-channel peristaltic pump, a caddy for SPE cartridges, and an array of polymer bags for effluent capture. The entire sampler is housed within a 3.5" OD stainless steel case. The sampler can be configured with the effluent capture bags (effluent capture mode) or without them (effluent discharge mode) depending on site specific characteristics the requirements of the sampling program. The form factor of the device was determined by the dimensions required for deployment in the 4-inch monitoring wells commonly installed in the United States.

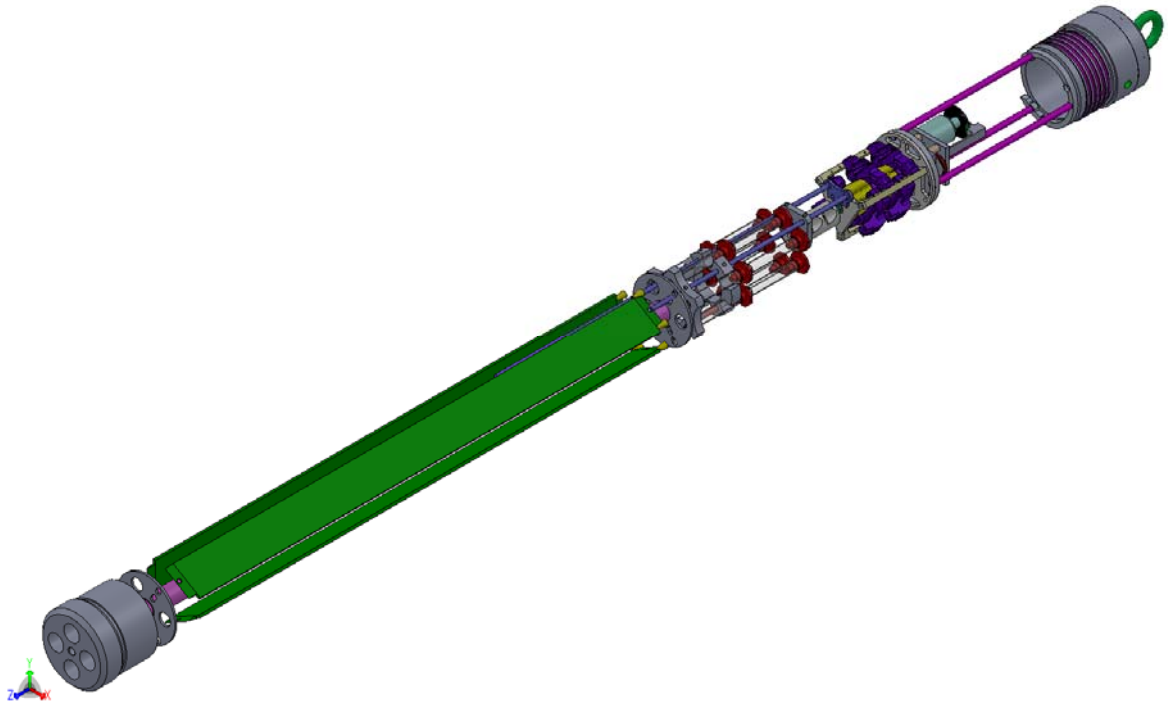

Figure 7. Rendering of IS2 sampling unit with peristaltic pump.
From top to bottom, the unit contains a six-channel peristaltic pump, distribution manifold, arrays of SPE cartridges (six cartridges in parallel, two arrays in series), and three effluent capture bags.

The peristaltic pump (Figure 8) is modified from a commercial off-the-shelf (COTS) Ismatec MiniClick 6 Reglo-E peristaltic pump unit (Part Number ISM1126; IDEX Health & Science, LLC; Oak Harbor, Washington, USA). Power and control for the unit is provided by a Reglo-E Digital control unit sourced from the same vendor (Part Number IS3187). Up to six channels are available for parallel/replicate extractions. This pump has been extensively tested on the bench and in shallow operation in the environment. Performing adequately at atmospheric pressure, such a pump is also expected to function well in effluent discharge mode, where the inlet and outlet pressures are equal. In effluent capture mode, excess inlet pressure has been demonstrated to cause liquid to bypass the pump, rendering the pump incapable of regulating dispensation.

Advantages of a peristaltic pump include high precision, low-flow operation, independent management of six channels, and a disposable fluid train that can be replaced with a manufacturer-validated clean fluid channel (the peristaltic pump tubing) before field deployment. Disadvantages of a peristaltic pump include wear of the peristaltic pump tubing during long-time scale use that may degrade the accuracy of the pump, as well as the limited material selection available for pump tubing, which may result in poor chemical compatibility with some site contaminants.

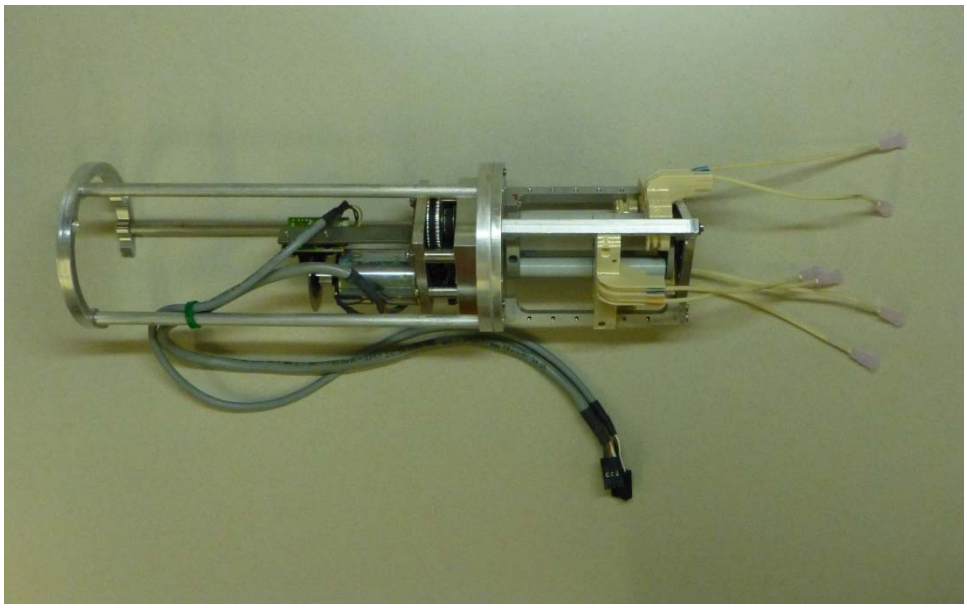

Figure 8. Six-channel peristaltic pump developed for the IS2 sampler.

The assembled sampler (Figures 3 and 9) is housed in a shell made of an inert material (stainless steel in the present embodiment), with ported, removable caps at both ends that allow for electrical power and control, and liquid inlet and outlet lines. In addition, a new framework for attaching internal functional units in the submersible was developed, as well as a variety of compatible units including a caddy for SPE cartridges and manifolds for splitting or collecting fluid handling lines.

Figure 9. IS2 sampler with peristaltic pump in its watertight shell.
Ports in the shell provide fluid inlets, gas pressure relief, and electrical connections.

Power and control for the peristaltic pump is provided by a Reglo-E Digital control unit (Figure 10). This unit provides motor power control via pulse-width modulation, and receives velocity feedback from an optical rotary encoder, with both signals transmitted using four channels of the electrical umbilical line. The transmission of both signals in an unshielded multichannel cable is not robust over very long cables, and crosstalk between the channels may affect the motor performance.

Figure 10. IS2 peristaltic pump control unit.
The control unit powers and controls the peristaltic pump in the sampler.

The control unit is calibrated with the pump before deployment in the field, and is capable of maintaining very low, nearly continuous flows (microliter per minute) or extremely low pulsed flows. The flow rate, which is programmed for sampling, is determined by the volume of water to be sampled, the time in which the composite sample is developed, the capacity of the sampler, and the expected aquifer flow rate through the well bore. In environments where the aquifer is very stagnant and communication with the surrounding media is poor, the flow rate through the device is expected to be held very low and/or the device will be operated in effluent capture mode. The pump control unit uses 120-volt (V)-alternating current (AC) power provided by an inverter and two 12-V batteries. The batteries, inverter, control unit, and the unused length of control cable are housed in a weatherproof container and constitute the surface package for the IS2 sampler (Figure 12).

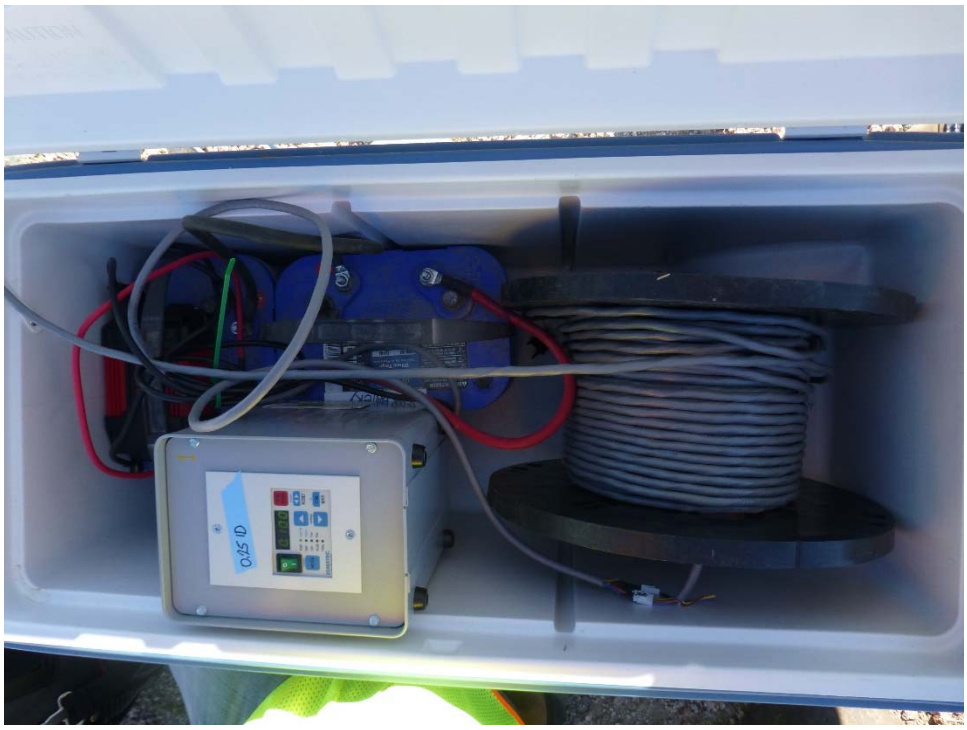

Figure 11. Field-prepared IS2 surface package for peristaltic pump sampler.
Clockwise from upper left: 12-V battery pack and 120-V AC converter, control cable and controller.

2.2.2 Development of 3.5-Inch Outer Diameter Reciprocating Sampling Unit

A reciprocating syringe pump design with check valves was generated and incorporated into the IS2 sampler (Figure 12). This pump utilizes a SilverPac C motor (Part Number CO-4118S-01, Lin Engineering, Morgan Hill, California, USA) to drive a custom six-channel syringe pump. Power and control for this unit are provided by a custom 24-V direct current (DC) system and software developed by the project team.

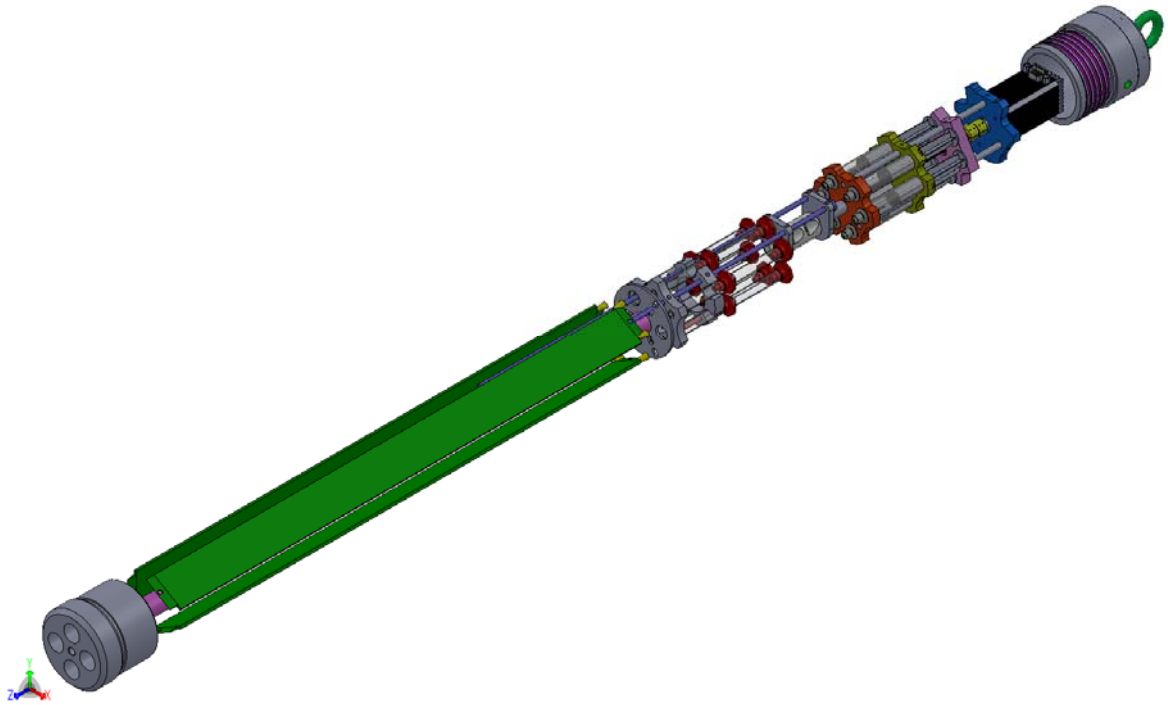

Figure 12. Rendering of IS2 sampling unit with reciprocating pump.
From top to bottom, the unit contains a six-channel reciprocating pump, distribution manifold, arrays of SPE cartridges (six cartridges in parallel, two arrays in series), and three effluent capture bags.

The reciprocating syringe pump (Figure 13 and 14) design includes inflow and outflow check valves, the break pressures of which are selected to provide cracking pressures that are slightly higher than the head on the inlet of the pump, enabling the pump to effectively control the intake of water at depth. The syringes used to drive fluids in this pump can be made of glass, providing a significantly more inert pathway than a polymer peristaltic pump tube. Trade-offs that come with this design include greater dead-volume within the fluid train, which may have implications for analytes prone to decomposition.

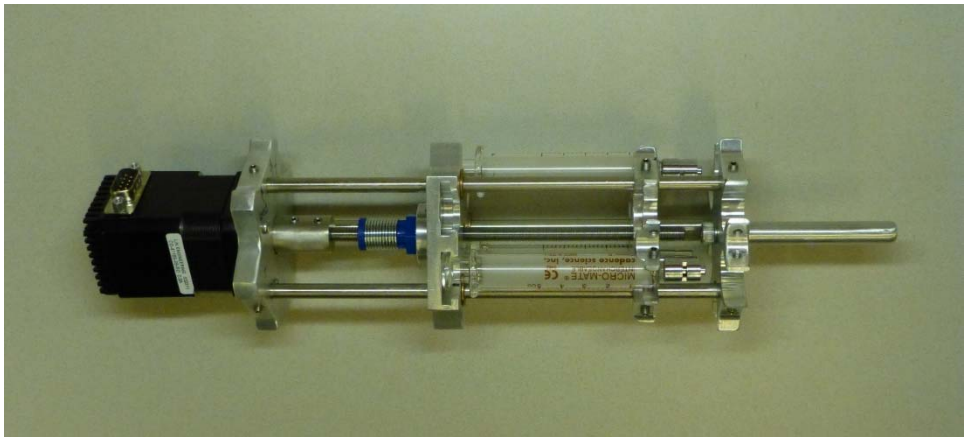

Figure 13. Six-channel reciprocating syringe pump developed for the IS2 sampler.

Figure 14. Field-prepared IS2 sampler with reciprocating syringe pump.

As a result of this redesign, the IS2 sampler with reciprocating pump also has a simpler control system that is both more adaptable and more tolerant of long control cables than the peristaltic pump system.

The motor controller for the reciprocating pump is integrated into the motor itself. Control is accomplished by sending command strings from a portable computer to the motor using a standard RS-232 interface over the control cable. Power for the motor is provided by a 24-V DC battery pack. This system also uses four channels in the control cable (two for command, two for power). Unlike the peristaltic pump system, this control system is robust over very long cables and is not subject to interference between channels. Additional motors can be integrated into the unit without additional control cables or channels, as the RS-232 interface allows motors to be daisy-chained and addressed individually.

A software interface for programming the pump was developed by the team (Figure 15). The interface allows the pump to be calibrated and a variety of continuous or periodic pumping modes to be programmed. The surface package for an IS2 sampler with a reciprocating pump consists of two 12-V batteries comprising the 24-V battery pack, the USB-to-RS-232 interface, and the unused portion of the control cable in a weatherproof container (Figure 16).

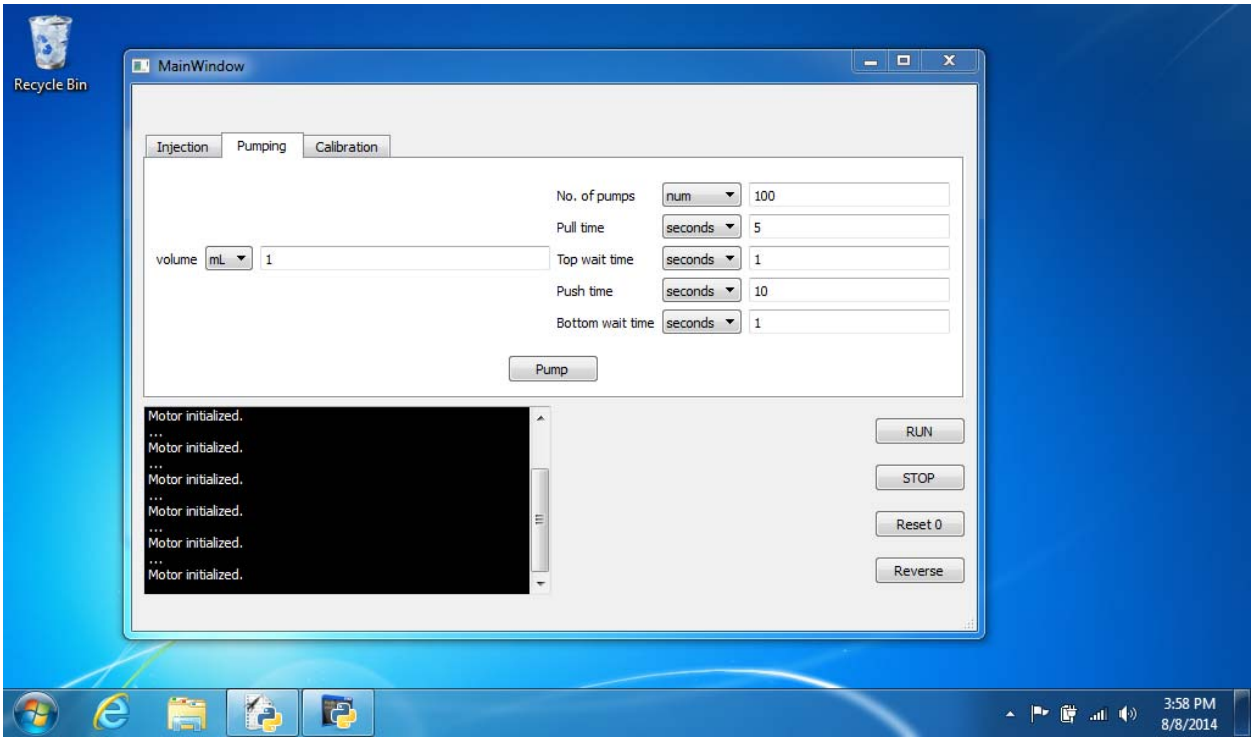

Figure 15. Screenshot of custom reciprocating pump control software.

Figure 16. Field-prepared IS2 surface package for reciprocating syringe pump.

2.3 ADVANTAGES AND LIMITATIONS OF THE TECHNOLOGY

The principal advantage of the IS2 technology over contemporary sampling methods is the elimination of many sample handling and processing steps, which will lead to:

- Reduced cost across the sampling process by reducing consumables, shipping and handling, and generation of hazardous and non-hazardous wastes; and
- Improved reproducibility by eliminating losses during handling.

Further, the IS2 technology has the advantage of using a single sampling cartridge to extract the analytes of interest from 100s of ml of water (Yamashita et al., 2004). The practical effect is that, after loading in situ, an array of six cartridges can represent more than 6 liters of site groundwater. This preconcentration, which represents a significant reduction in the volume of material that moves between the site and the laboratory, also suggests that the IS2 technology should improve the detection and quantification limits of any analytical method into which it is incorporated.

Limitations of this approach may include:

- Significant start-up costs in equipment (i.e., the IS2 sampling unit);
- Availability, in prefabricated cartridges, of sorbent materials with chemistry favorable for the contaminants of interest; and
- Well construction and site hydrology, which determine the mode of operation of the sampler (i.e., effluent capture or discharge modes).

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3.0 PERFORMANCE OBJECTIVES

The performance objectives from the ER-201122 Demonstration Plan are presented in Tables 1 and 2, and the subsequent subsections. Performance assessment and reflections of the demonstrations are presented in Section 6.0.

Table 1. Quantitative performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative Performance Objectives			
Demonstrate agreement with current methods (i.e., accuracy, precision)	Compare contaminant concentrations and coefficients of variability between replicate samples for data obtained using (a) the IS2 and (b) field practices currently in use at the site	IS2 measurements are within ± 30% of values obtained by co-analyses performed using typical field methods	Objective met at 2nd site*
Demonstrate time-averaged sampling capability	Analyze contaminants in two parallel systems: one representing IS2 collection cartridges, the other bags storing groundwater from bypass lines	No statistically significant difference between results from IS2 sampling and analysis of a time-averaged, composite sample, as determined by Student's *t*-test	Objective met
Demonstrate operability under environmental conditions	Compare volume of effluent generated in sampling and bypass mode. Compare IS2-generated concentration data with measurements for water collected in bypass mode.	No statistically significant difference between predicted and actual volumes of water processed, as determined by Student's *t*-test. Analytes from high-turbidity water shown to become concentrated within acceptable quality assurance/quality control (QA/QC) range (± 30% deviation)	Objective met

* Logistical requirements caused conventional samples from 1st Site to be taken at different depths and with different well preparation methods, which complicates direct comparisons to IS2 data.
QA/QC = quality assurance/quality control

Table 2. Qualitative performance objectives.

Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives			
Demonstrate favorable labor requirements	Characterization of effort by persons present during deployment activities (questionnaire)	Questionnaire results indicate that IS2 would not be rejected based on the amount of labor required	Objective met
Demonstrate utility of IS2's low MDL	Show presence of contaminants at trace levels in wells that yield non-detect values when determined by groundwater monitoring techniques other than the IS2	IS2 can detect contaminants in wells that show "non-detect" values when monitored with conventional groundwater monitoring strategies	Objective met
Demonstrate reduced generation of hazardous waste	Volume of excess waste generated per sample (L/sample)	Waste volume generated less than that of co-analyses performed using typical field methods	Inconclusive
Demonstrate favorable cost economics	Cost per sample including sampling, analysis, and waste disposal (dollars/sample)	Per-sample costs are for IS2 are comparable or lower than those of co-analyses performed using typical field methods	Objective met

MDL = method detection limits
L = liters

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4.0 SITES DESCRIPTION

Two sites were selected for demonstrations of the IS2 sampler: the former Williams AFB in Mesa, Arizona, and Naval Air Station (NAS) North Island in Coronado, California.

4.1 FORMER WILLIAMS AIR FORCE BASE, MESA, AZ

4.1.1 Site Location

The former Williams AFB (Figure 17) covers more than 4,000 acres of land located in Mesa, Arizona, approximately 30 miles southeast of Phoenix. Williams AFB operated as a flight training school from 1941 until the base was closed under the Base Realignment and Closure (BRAC) in 1993. Much of the converted property is now in use by public and private entities, including the Phoenix-Mesa Gateway Airport and the Arizona State University (ASU) Polytechnic Campus.

Figure 17. Former William AFB, Mesa, AZ.
The site of the former fuel storage tanks (ST)-12 is highlighted (Former Williams AFB, 2011).

The Former Fuel Tank Storage Site (ST-12) in operable unit (OU) 2 was operated from 1977 to 1989. This site was impacted by up to 1.5 million gallons of jet propellant (JP)-4 from leaking underground storage tanks (UST) and their associated fuel distribution lines. Free-phase recovery, a thermal-extraction pilot plant, and soil vapor extraction have all been performed at this site, which continues to be impacted by benzene, toluene, ethylbenzene, and xylenes (BTEX) fuel components, benzene and toluene in particular. Contaminants monitored at ST-12 include total

petroleum hydrocarbons (TPH) (both diesel and gasoline associated), volatile organic compounds (VOCs) (including benzene, toluene, and naphthalene), semi-volatile organic compounds (SVOCs), and metals (Air Force Civil Engineer Center [AFCEC], 2011b).

4.1.2 Site Geology/Hydrogeology

The former Williams AFB lies at an altitude of 1340 feet (ft) on generally flat land that slopes gently to the west. The underlying geology is characterized by alluvium-filled depression. The six geological layers underlying the site, from deepest to shallowest, are crystalline rocks, extrusive rocks, Red Unit, Lower Unit, Middle Unit and the Upper Unit. These layers are described briefly in Table 3.

Table 3. Geological formations underlying the former Williams AFB.
(AFCEC, 2011a; AMEC Environment & Infrastructure, 2013)

Stratigraphic Lithology	Depositional Conditions	Approximate Thickness (ft bgs)	Type of Aquifer	Unit
Gravel, sand, silt, and clay	Open basin; channel, floodplain, alluvial fan	0 to 300	Unconfined	Upper unit
Interbedded coarse- and fine-grained layers		0 - 160	Unconfined	Vadose zone
Coarse-grained, permeable		145-160	Unconfined	Cobble zone
Interbedded coarse- and fine-grained layers		160-195	Unconfined	Upper water bearing zone
Silty clay layer		195-210	Unconfined	Low permeability zone
Interbedded coarse-and fine-grained layers (coarsest and most permeable unit)		210-240	Semi-confined	Lower saturated zone
Low permeability clay		240-260	Semi-confined	Aquitard
Silt, siltstone, silty sand, and gravel.	Closed basin; playa, alluvial fan, fluvial	<100 to 1,000	Unconfined, leaky confined	Middle unit
Clay, silt, mudstone, evaporites, sandstone, gravel, conglomerate, and andesitic basalt.	Closed basin; playa, alluvial fan, fluvial	600 to 10,000+	Unconfined, leaky confined	Lower unit
Breccia, conglomerate, sandstone, siltstone, and local basaltic to rhyolitic flows and pyroclastic rocks.	Alluvial fan, fluvial	2,000+	Confined	Red unit

bgs – below ground surface

The Upper, Middle, Lower, and Red Units contain the regional groundwater supplies, with the Middle Unit being the largest and most productive water-bearing unit in the basin. Beneath the former Williams AFB, the Upper and Middle Units are separated by a clay aquitard. Water levels declined markedly during the 1960s and 1970s, but have been rising steadily since 1978. The primary (Middle Unit) aquifer is presently approximately 290 ft bgs.

4.1.3 Contaminant Distribution

This source of this site is extensive light, non-aqueous phase liquid (LNAPL) contamination, which resulted from long-term leakage from the former fuel tank site and was subsequently smeared by rising groundwater levels. From this source, a dissolved plume of fuel components spreads largely to the west. A site map illustrating the distribution and concentration of benzene is presented in Figure 18. The contamination is largely limited to the upper unit by the aquitard that separates it from the middle unit, thus sparing the most important units for water in the community.

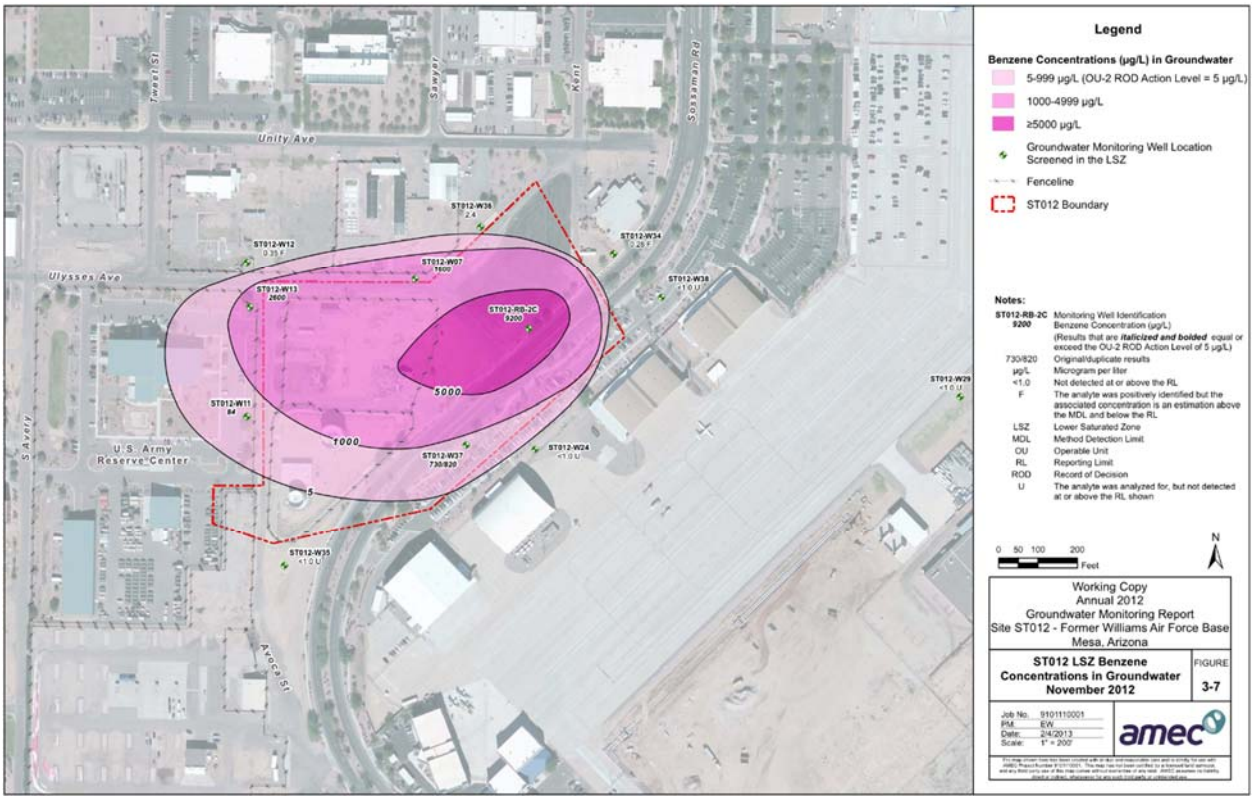

Figure 18. Site map of ST-12, showing concentrations for BTEX components in groundwater.
(AFCEC, 2011b)

4.2 NASNI, CORONADO, CA

NASNI is located in San Diego County, California; southwest of the city of San Diego, on the tip of the Silver Strand peninsula with the city of Coronado adjacent and to the east (Figure 19). The remainder of NASNI is surrounded by water, the Pacific Ocean to the south and San Diego Bay on the west and north. NASNI was commissioned in 1917, and is currently an active military base. Since 1935, NASNI has been occupied exclusively by the Navy.

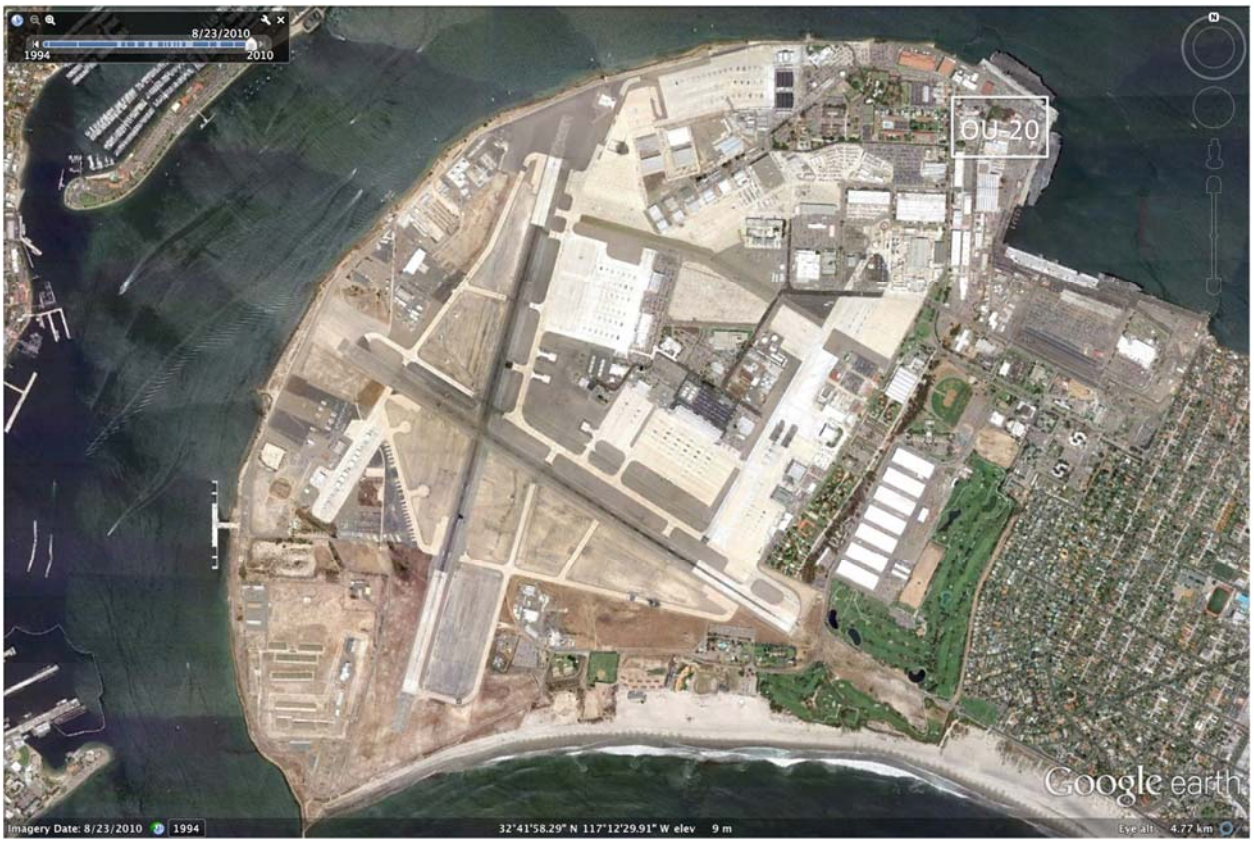

Figure 19. NASNI, Coronado, CA.
OU-20 is highlighted (NASNI, 2010).

4.2.1 Site Location

OU-20 is located in the northeast portion of the island. Metal-plating processes performed in Buildings 1 and 2 at OU-20 are the likely source of chromate in groundwater. Former operations at Building 1 included the repair and maintenance of helicopter blades, as well as the manufacture and repair of fiberglass components. Activities in support of these operations included parts grinding, cleaning, anodizing, paint stripping, and painting. Additional contributions to the subsurface contamination may have included overflow of subsurface pits used for temporary waste storage, and the cleaning of aircraft fuel tanks outside of the buildings (Halden, 2012).

4.2.2 Site Geology/Hydrogeology

NASNI is located on relatively flat land with an average elevation of approximately 20 ft above mean sea level (amsl). The island was enlarged beginning in the 1930s through placement of hydraulic fill dredged from San Diego Bay onto tidal flats and near-shore areas. The peninsula has been entirely graded for development, and the area surrounding Buildings 1 and 2 is covered with asphalt, concrete, or maintained landscaping. The hydraulic fill consists of medium-grained to coarse-grained, poorly graded sands and silty sands. In some areas, the fill is underlain by organic silts and clays.

Groundwater recharge is minimal and occurs primarily from irrigation. Shallow groundwater beneath NASNI is unconfined, and groundwater occurs at depths from approximately 4 to 25 ft bgs. Groundwater in the investigation area is found at approximately 5 ft amsl and flows north-northeast, in communication with San Diego Bay. The groundwater gradient across the study area is relatively flat and ranges from 0.001 to 0.002. Aquifer transmissivity values calculated from slug and pumping tests in the Building 379 area ranged from 0.5 to greater than 1000 ft^2/min, with an approximate value of 400 ft^2/min calculated nearest to the proposed deployment location (SES-TECH, 2010).

4.2.3 Contaminant Distribution

VOC and chromate plumes have been well-characterized in the northeastern portion of NASNI. The VOC plume originates from the vicinity of Building 379 and extends down gradient to the northeast for approximately 2000 ft, with several sources contributing. The chromate plume originates in the vicinity of Building 2, the former anodizing shop in Building 2 being most likely source of chromate, and extends down gradient approximately 700 ft (Figure 20).

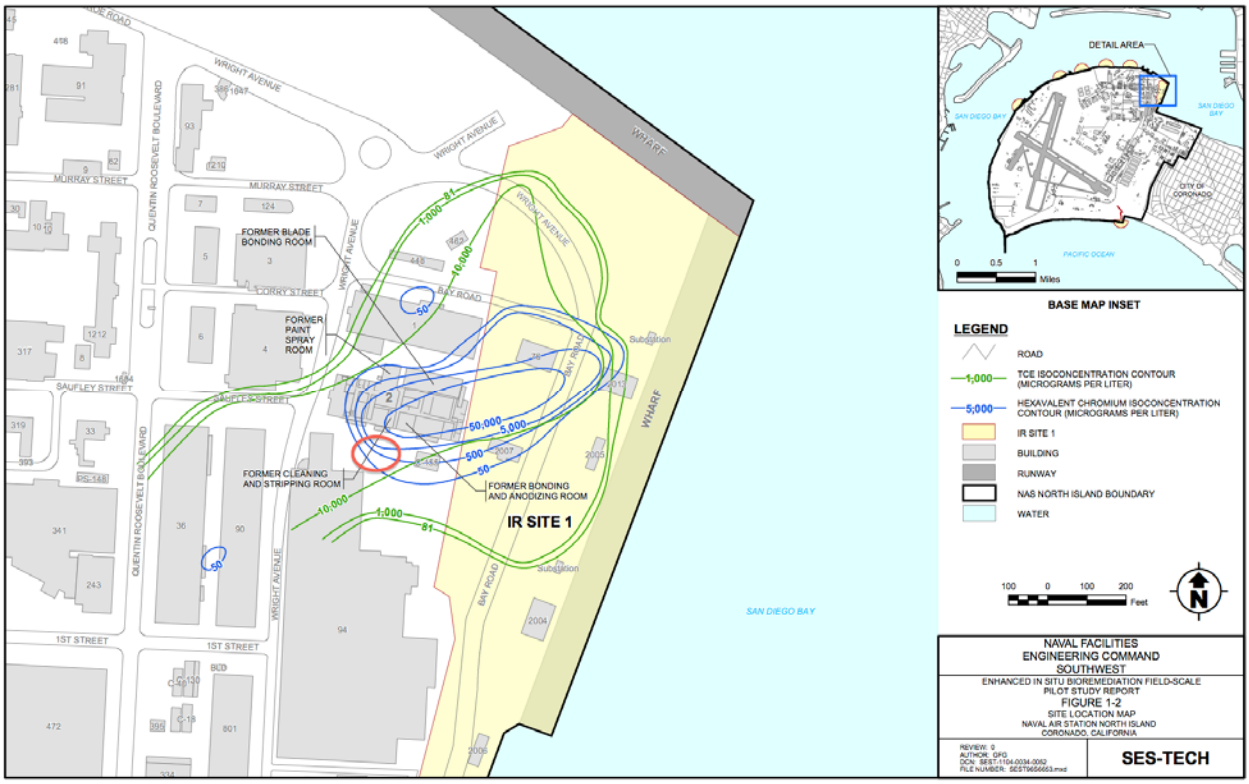

Figure 20. VOC and chromate plumes at NASNI OU-20.
(SES-TECH, 2010)

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5.0 TEST DESIGN

Broadly, the experiments performed are comparisons of contaminant concentration results obtained in closely-timed sampling events performed by the site manager using conventional methods and by the IS2 team using the IS2 sampler. The process of designing and executing a sampling event with the IS2 sampler provides the opportunity to gather data that supports all of the performance objectives.

Site-specific experimental parameters are discussed in sections 5.4 and 5.5.

5.1 CONCEPTUAL EXPERIMENTAL DESIGN

Solid phase extraction chemistry typically requires an *a priori* understanding of the classes of contaminants that are of interest, in order to obtain acceptable recovery from the matrix. While the IS2 sampler could be used to prospect for contaminants from a few desired classes, it is anticipated that this system will be used more frequently to obtain time-averaged composite samples, large-volume extractions to improve detection limits, or both, in sites where the contaminant chemistry is already largely known.

The design of a sampling event with the IS2 incorporates some or all of the following steps:

i. Determination of the appropriate SPE material or combination of materials for the contaminants of interest;
ii. Preparation of the sampling unit with a suitable SPE material;
iii. Preparation of the well if necessary (i.e., by purging);
iv. Placement of the device in the screened portion of the targeted well;
v. Equilibration of the well as necessary (i.e., giving time for water levels to return to equilibrium with the surrounding formation);
vi. Sampling at a prescribed rate for the duration of the event;
vii. Retrieval of the device; and
viii. Analysis of the exposed and loaded cartridges therein.

For demonstration and validation purposes, this activity will be bracketed by:

- An initial, regularly scheduled sampling event by the site manager using standard practices. The analytical results from this event establish the basic performance parameters for the IS2 technology;
- A pre-deployment sampling event by the IS2 team using a bailer; and
- A post-deployment sampling event by the IS2 team using a bailer.

The pre- and post-deployment sampling events by the IS2 team will be used for QC and to provide working data for the analysis of the results of the IS2 deployment for the period of time in which official results are not yet available.

5.2 BASELINE CHARACTERIZATION ACTIVITIES

Baseline characterization for each site was established by:

i. Reviewing site documentation and the results of previous studies;
ii. Scheduling the demonstration to coincide with a sampling event performed by the site restoration manager; and
iii. Independently sampling the well pre- or post-demonstration.

5.2.1 Document Review

A review of the documentation for the site and the demonstration wells was conducted in order to establish the baseline parameters for the experiment. This review focused on the concentrations and trends in concentration of the contaminant of interest. Other data and trends that were established (if possible) during document review included the depth to groundwater, the hydraulic gradient, the linear velocity of the groundwater, the sediment type, the porosity, and the hydraulic conductivity of the aquifer.

5.2.2 Independent Sampling

In addition to the documented sampling events conducted by the site restoration manager, the IS2 sampling team also conducted an independent sampling event using standard bailers and prepared samples for an independent laboratory analysis.

5.3 TREATABILITY OR LABORATORY STUDY RESULTS

Laboratory studies were performed to demonstrate the feasibility of the method, and in anticipation of any field studies. This was typically accomplished by replicating aspects of field studies on the bench with groundwater sourced from relevant sites, with the site contaminants intact or spiked with a simulated contaminant mixture. In addition to bench studies before any field demonstration, there were a series of early field deployments of the IS2 sampler to test the mechanism and develop the standard operating procedure for field work.

5.3.1 Feasibility Study: Cartridge Obstruction by Fouling

An early concern of the authors and reviewers was the potential for the available SPE cartridges to become obstructed by sediments accumulated during large-volume extractions. This effect was tested by loading a common SPE cartridge (Strata C-18; Phenomenex, Torrance, California, USA) with large volumes of groundwater. Three of the cartridges additionally protected by glass fiber filters (Acrodisc AP-4523; Pall GmbH, Dreieich, GE).

A peristaltic pump was programmed to deliver groundwater at 5 mL/hour to the cartridges. The groundwater samples used for the test were taken from perchlorate-contaminated aquifer, which the team had access to and which were known to contain significant amounts of salts (Table 4). Over 23 days, the average flow rate decreased by approximately 20% in all cartridges (Figure 21). This was not a significant impediment, and much of this decrease can also be attributed to wearing of the peristaltic pump tubing. Measurements of the pressure at the entrance to each cartridge were

also taken (Figure 22), and it was noted that the filters appeared to be accumulating enough particulate matter to influence the pressure in the cartridges, the absolute difference between the two groups was not very large.

Table 4. Example anion concentrations in groundwater used for feasibility studies.

Anion	Concentration (mg/L)
Chloride	210 ± 4
Sulfate	45 ± 1
Nitrate	7.9 ± 0.3

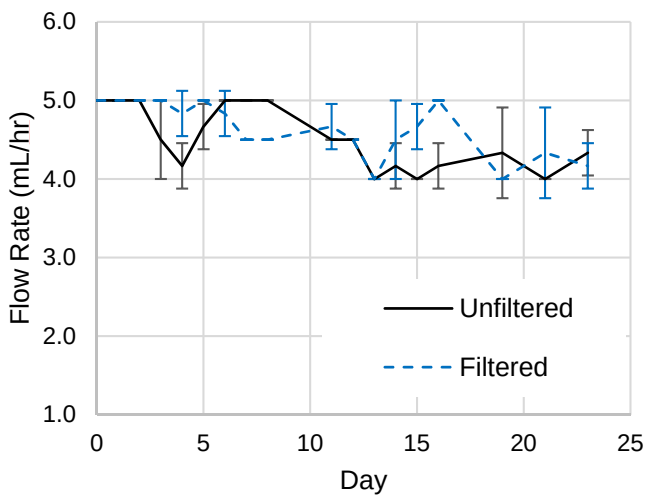

Figure 21. Flow characteristics through C-18 SPE cartridges over several weeks.

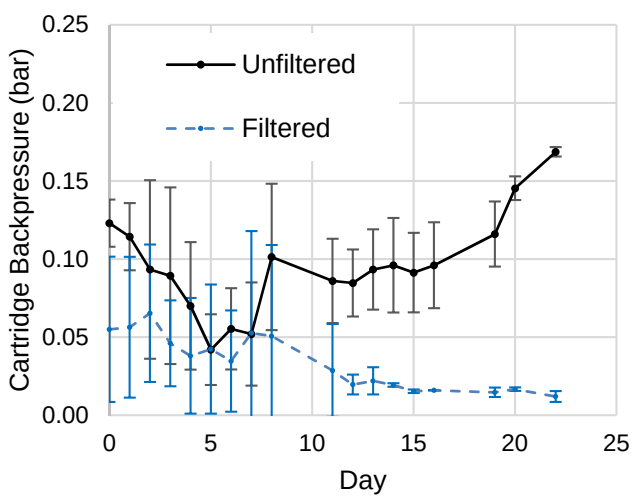

Figure 22. Pressure observed upstream of C-18 cartridges over several weeks.

While groundwater is not typically high in turbidity, surface waters contain significantly greater quantities of particulate matter, particularly suspended organic matter. The project team has tested the feasibility of using the IS2 sampler and method in surface waters and to sample sediment pore waters in lacustrine environments. Visible accumulation of suspended organic matter upon the entrance frit of SPE cartridges (Figure 23) has been noted, but there is no evidence that this accumulation restricted flow through the cartridge appreciably.

Figure 23. Accumulation of surface water sediments upon the frit of an SPE cartridge.

5.3.2 Feasibility Study: Contaminant Applicability

A number of compounds were screened for applicability to the IS2 method from either contaminated site samples or from groundwater spiked to environmentally relevant contaminant concentrations. Contaminants that were screened in the laboratory include those listed in Table 5.

Table 5. Compounds screened in the laboratory for IS2 sampling.

Chemical Name	CAS No.	Typical Uses	SPE-Relevant Properties
Perchlorate ion	14797-73-0	Oxidizer	Anion
Chromate ion	11104-59-9	Metal plating	Anion
Benzene	71-43-2	Fuel component	Aromatic
Toluene	108-88-3	Fuel component	Aromatic
Ethylbenzene	100-41-4	Fuel component	Aromatic
Isopropylbenzene	98-82-8	Fuel component	Aromatic
Parabens (methyl-, ethyl-, propyl-, butyl-, benzyl-)	Multiple	Antimicrobial	Aromatic (benzoates)
Naphthalene	91-20-3	Fuel component	Polycyclic aromatic
Dibenzofuran	132-64-9	Insecticide	Polycyclic aromatic
Fipronil	120068-37-3	Insecticide	Polycyclic aromatic
Triclosan	3380-34-5	Antimicrobial	Polycyclic aromatic
Triclocarban	101-20-2	Antimicrobial	Polycyclic aromatic
Bisphenol-A	80-05-7	Plastic monomer	Polycyclic aromatic
Tetrabromobisphenol-A	79-94-7	Flame retardant	Polycyclic aromatic
N-Nitrosamines	Multiple	Disinfection byproducts	Nitrosamine

5.3.3 Preliminary Study: Perchlorate

The perchlorate ion is an emerging contaminant frequently associated with spent munitions. A preliminary study targeting perchlorate was conducted using groundwater samples acquired from an impacted aquifer in the Salt River Valley near Mesa, Arizona. The site is characterized by good hydraulic conductivity with water at 187 ft bgs in fluvial material consisting of silty sands and gravels, poorly and well-graded sands, clayey sands, and clayey gravels. Access to the aquifer was provided by a 4-inch monitoring well screened from 109 to 259 ft bgs. Groundwater samples were recovered from the well for characterization and bench development of the IS2 sampler using a bailer or Hydrasleeve (GeoInsight, Las Cruces, New Mexico), transferred to 1-liter high density polyethylene (HDPE) sample bottles, and refrigerated at 4°C until used. Aliquots of the groundwater samples were filtered and characterized for a suite of anions by ion chromatography; the most significant components are presented in Table 4.

Perchlorate can be effectively removed from aqueous solution by applying ion exchange SPE (Medina et al., 2005). Interference is a challenge when perchlorate exists as a minor co-contaminate in solution with other anions at concentrations 3 to 5 orders of magnitude greater, as the weakly-charged perchlorate ion often exhibits lower affinity for the ion exchange media. For this trial, Strata X-AW 3 mL/500 mg (Phenomenex, Torrence, California) weak anion exchange cartridges were selected. Bench trials showed that when presented with high ionic-strength solutions, this resin exhibited relatively low capacity before breakthrough (less than 10 mL at the salt concentrations noted in Table 4) but also offered favorable selectivity and recovery for perchlorate. Quantification was performed on an ion chromatograph (IC) with a conductivity detector.

To simulate a sampling event with the IS2, a bench model of the unit was prepared with three sampling channels (for replicate samples), each with three SPE cartridges in series (increasing sorbent volume to offset the low specific capacity of the sorbent). A fourth channel (bypass) was

prepared to collect a composite sample of the same groundwater without solid phase extraction. The bench unit was programmed to deliver 50 mL of groundwater to each channel. The volumes of water actually delivered per channel were recorded, and the liquid composite sample from the bypass was directly characterized for perchlorate. The concentration detected in the bypass sample and the volumes delivered to the sorbent channels were used to estimate the mass delivered to the sorbent channels, and subsequently to estimate the recovery for perchlorate in this experiment. The average recovery was determined to be 77% (Table 6).

Table 6. Mass balance data for feasibility experiments with perchlorate.

Sample	Processed Volume (mL)	Groundwater Perchlorate Concentration (µg/L)	Recovery (%)
Unprocessed Groundwater	49.7	30.2	-
SPE Eluate	47.2 (±3.3)	23.2 (±0.7)*	77 (±2)

*Calculated from eluate concentration and processed volume.
µg/L - micrograms per liter

In the field, the IS2 sampler is configured either to capture the processed water post-processing or to discharge it back into the well. While the bench trial captured effluent, the programmed dispensation volume values (which differed from the actual values by a few percent) could be used to determine the concentration values that a user of the device would have reported had the device been configured for effluent discharge. A comparison of the data that was generated in each mode is presented in Figure 24, illustrating the propagation of the error in the dispense volume values. Though the uncertainty increases, the results are not significantly different.

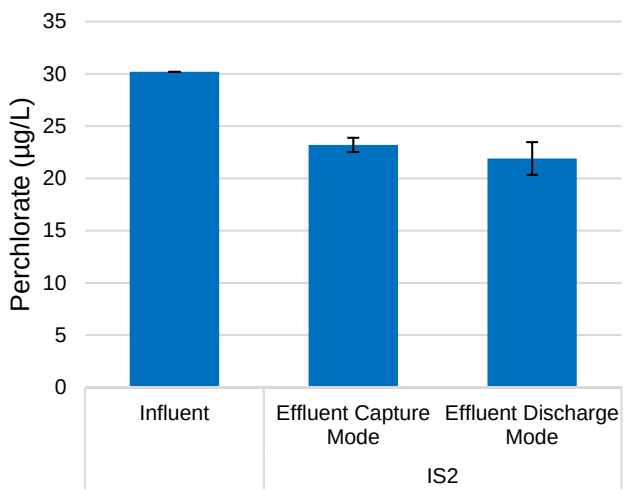

Figure 24. Comparison perchlorate concentration data quality observed during preliminary study using effluent capture or effluent discharge mode.

Due to the relatively large sorbent bed volumes required to effectively process such a low volume of groundwater, the present method was determined to be a poor match for an IS2 demonstration.

As the purpose of this project was to demonstrate the application of standard methods in the field, further development of an applicable perchlorate method was determined to be outside of the project scope.

Though the perchlorate extraction chemistry demonstrated here was not efficient enough for field use, the site presented an opportunity to test the mechanical operation of the IS2 sampler in situ and to develop the deployment procedures. The sampler was deployed twice to a depth of 190 ft bgs. This experience informed the standard operating procedure; most importantly, that while the device as currently embodied can be manually inserted to significant depths, an experienced well support crew with a boom truck (crane) should be employed for depths greater than 60 ft. This experience also lead to the development of the cable management system and significant changes to the internal layout of the device, making it more robust.

5.4 FIRST DEMONSTRATION: FORMER WILLIAMS AFB

The former Williams AFB was selected for the first demonstration of the IS2 sampler. Fuel components such as those present in the upper aquifer at ST-12, and particularly heavier constituents such as naphthalene, are a good target for a demonstration of the IS2 because they have favorable partitioning characteristics and mature techniques exist for separating and quantifying them. This demonstration was carried out using the peristaltic pump-driven sampler.

5.4.1 Preparation

In consultation with the site remediation contractor, two wells were selected as potential demonstration sites in the periphery of the plume: W11 and W36 (Table 7). Considerations included the expected concentration of fuel components, ease of access for the investigators, and type of instruments already deployed (e.g., water depth transducers). Both wells are in the upper, unconfined unit, approximately 250 ft deep and screened below 200 ft.

Table 7. Construction details for candidate wells at Former Williams AFB.

Well	Year Built	Diameter (inches)	Depth to Screen (ft bgs)	Screen Length (ft)	Depth to Water (ft)
ST012-W11	1989	4	208	40	153 (2010)
ST012-W36	2010	4	210	35	156 (2012)

The site is impacted by a significant amount of LNAPL, which is present in many of the monitoring wells. A visit to the site to collect preliminary samples found LNAPL present in W11. The demonstration was therefore performed in W36, since it lies exclusively in the dissolved plume. If W36 had been rendered unavailable by remediation activities at the site, W11 could possibly have been substituted provided that care was taken to remove the free product as much as possible before introducing the IS2 sampler.

The primary analyte of interest at this site was naphthalene, a polycyclic aromatic hydrocarbon (PAH). Naphthalene is considered semivolatile, and the aromatic rings in this compound make it a good candidate for solid phase extraction with a styrene divinylbenzene (SDB). Two other common fuel components (Table 8) were identified from groundwater sampling data as secondary

analytes of interest. Lighter and more volatile compounds would likely be more difficult to recover effectively than heavier and less volatile compounds. EPA methods 8260B and 8270C were selected for quantification of these compounds from liquid samples, and an SPE and GC-MS method was developed by the project team for IS2 sampling and analysis.

Table 8. Analytes of interest for IS2 demonstration at the former Williams AFB.

Analyte	CAS No.	Monitoring Well	BP[1] (°C at 1 atmosphere)	Log K_{OW}[1]
Ethylbenzene	100-41-4	106	136	3.21
Isopropylbenzene	98-82-8	120	152	3.56
Napthalene	91-20-3	128	222	3.45

[1]Values predicted by the ACD/Labs Suite.
BP – boiling point
CAS - chemical abstract service

The SPE cartridges chosen for this study (Table 9) contain 25 milligrams (mg) of an SDB resin housed between two frits in a 1 mL disposable syringe body. This resin mass was chosen because it was determined to have ample capacity for analyte capture beyond the quantity required for experiment, in order to provide a factor of safety in case the contaminant concentrations in the well had increased or the volume of water processed by the IS2 differed from the programmed value.

Table 9. Sampling matrix for IS2 demonstration at the former Williams AFB.

Wells	Analyte (Quantification Method)	Sorbent (Extraction Method)	Sample Type	Cartridge Quantity	Holding Time*
W36	SVOCs by ASU GC-MS	Strata SDB, 1 mL, 25 mg	Quantification	3	14 days at 4EC
			Breakthrough	3	
			Field blank	1	
			Trip blank	1	
			Method blank	1	N/A
	VOCs by GC-MS (EPA 8260C)	N/A	40 mL VOA vial	3	14 days at 4EC
	SVOCs by GC-MS (8270C)	N/A	1 L amber bottle	2	14 days at 4EC

*Maximum allowable holding time.
VOA – volatile organic analysis

Preliminary work was conducted with a benchtop IS2 sampling unit and grab samples of site groundwater to assess the methods and mechanism before field deployment. During this work, the material used for the internal plumbing of the sampler was tested and several poorly performing materials (e.g., tygon and viton) were replaced with polytetrafluoroethylene (PTFE) for the liquid handling lines upstream of the sampling cartridges wherever possible.

Once the sampling and sample processing methods were considered ready, a sampling matrix was created for the demonstration (Table 9). The samples to be collected included those prepared by the IS2 sampler and a suite of liquid grab samples to be processed by a commercial laboratory for comparison. The demonstration was scheduled to occur shortly after a quarterly sampling event by the site restoration contractor, the methods (sampling by bladder pump and analysis by EPA

methods 8260B and 8270C) and results of which were also provided to the ASU project team for comparison.

Before delivering the sampler to the field site, pre-prepared sampling cartridges were loaded into the sampling mechanism. Three sampling channels were prepared, each loading a quantification cartridge in series with a breakthrough detection cartridges. A field blank cartridge was loaded into the sampler but not connected to a liquid handling line. A trip blank cartridge was carried to the site but not loaded into the sampler. A method blank was retained at the laboratory and later loaded with deionized water to provide a method blank.

5.4.2 Deployment

The IS2 sampler was inserted to 200 ft bgs (50 ft underwater). Due to the depth required to reach the target formation at this site, the project team elected to use a crane to assist with the deployment. The sampler was programmed to continuously dispense 250 mL over 24 hours.

The sampler was recovered and returned to the laboratory shortly after the control unit indicated that the dispensation had been completed. The recovery team observed a decontamination procedure that included:

- The use of nitrile gloves when handling surfaces that had been in contact with contaminated water;
- Decontamination of the sampler with a dilute soap and water solution;
- Hand-washing; and
- Disposal of all waste according to the ASU hazardous waste management guidelines.

The sample cartridges were removed from the sampler, capped to retain the entrained fluid, and refrigerated before being extracted. The volume of water collected in the storage bag for each channel was determined gravimetrically and recorded.

After allowing the well to equilibrate for another day, a disposable bailer was used to collect the liquid samples (Table 9), which were immediately returned to a commercial laboratory for analysis.

5.4.3 Results

The volume of water dispensed per channel was greater than expected (Table 10), particularly for channel 3. This was a significant concern, as the sampler is intended to be used in some cases without effluent capture, and inaccurate dispensation would significantly affect the results generated in those cases. This source of this dispensation error was investigated, as a number of conditions can result in poor accuracy including pump wear, communication problems via the control line, overpressure of the inlet, and initial calibration error.

Table 10. Fluid volume dispensed by the IS2 peristaltic pump.

Channel	Programmed (mL)	Dispensed (mL)	% Deviation
1	250	285	14
2	250	268	7.2
3	250	470	88
Average (standard deviation)	-	341 (±112)	36 (±44)

Overpressure of the inlet was determined to be the problem through testing in the pressure chamber (Section 2.2.1). The inlet pressure was varied over the range of pressures that the submersible would have experienced during the deployment and it was determined that pressure as low as 5 pounds per square inch (psi) (approximately 12 ft of head) could cause leakage of the pumps. While this would not be a problem in a flow-through system (i.e., one where the inlet and outlet of the pump are at equal pressure, as on the surface), this conclusion lead directly to a redesign of the pump system to improve tolerance of inlet overpressure, through the application of a reciprocating pump with check valves.

After elution, the concentration of naphthalene, ethylbenzene, and isopropylbenzene were determined by GC-MS. It was noted that the concentration of the analytes in the breakthrough cartridges was below the limit of detection, indicating that the quantification cartridge had sufficient capacity to collect all of the analyte mass without breakthrough. The QC cartridges were also noted to contain no detectable concentration of the analytes (Figure 25).

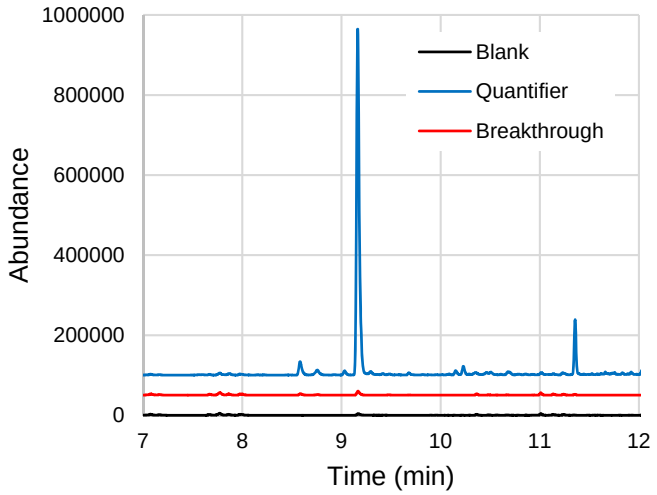

Figure 25. Gas chromatograms for naphthalene recovered from quantification and breakthrough cartridges.
No breakthrough was indicated.

For all of the analytes, a reporting limit (RL) was determined by multiplying the lowest calibrated concentration for the analyte by the ratio of the prescribed volume of the eluate (2 mL) to the prescribed volume of water programmed for the channel (250 mL). With the lowest calibrated concentration for all three analytes being 10 µg/L, the RL for the IS2 is conservatively estimated at approximately 0.1 µg/L for this study. Compared to the RLs provided by the commercial labs that analyzed liquid samples, this is a significant improvement of between 1 and 2 orders of magnitude (Table 11, Figures 26 and 27).

Table 11. Reporting limits for discrete and composite sampling of naphthalene.

Sampling Method	Species	Quantification Method	RL
Liquid Grab Sample (40 mL)	Naphthalene	EPA 8260B[a]	1.0 – 5.0 µg/L
Liquid Grab Sample (1 L)	Naphthalene	EPA 8270C[a]	9.5 – 10.0 µg/L
IS2 sorbed sample, 24-hour composite (250 mL pre-concentrated on 500 mg resin; eluted to 2 mL)	Naphthalene	ASU GC-MS[b]	0.10 µg/L

[a]RL based on results from a certified laboratory, [b]RL generated by the IS2 team at ASU.

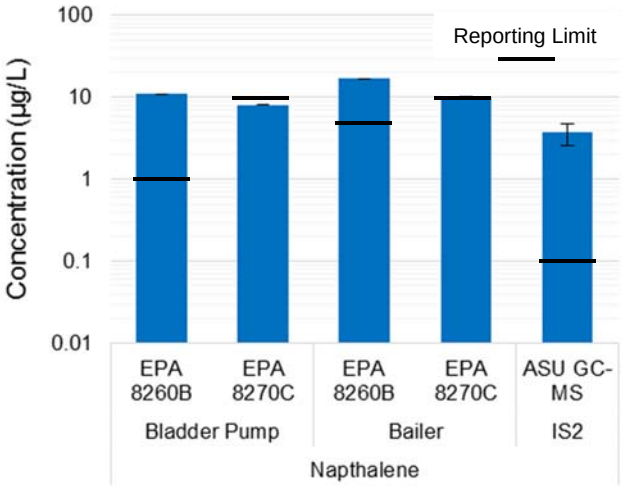

Figure 26. Concentrations and RLs of naphthalene reported in demonstration well using samples generated by a bladder pump, a bailer, and the IS2, and analysis by EPA methods 8260B, 8270C, and the ASU GC-MS method.

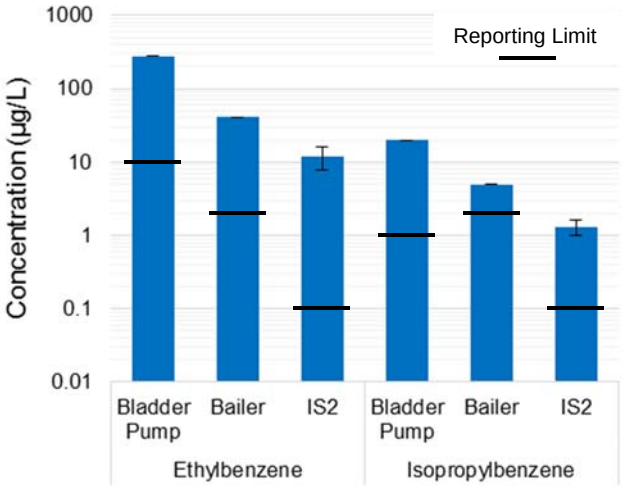

Figure 27. Concentrations of ethylbenzene and isopropylbenzene reported in the demonstration well using samples generated by a bladder pump (by EPA 8260B), a bailer (by EPA 8260B), and the IS2 (by the ASU GC-MS method).

The concentration of the primary analyte of interest, naphthalene, reported by the IS2 and the ASU GC-MS method was observed to be within an order of magnitude of that reported by samples generated by the bladder pump and the bailer, and analyzed by EPA Methods 8260B and 8270C. As expected, the reported values of the more volatile ethylbenzene and isopropylbenzene were lower. However, it should be noted that there are many inconsistencies between the methods that could drive these differences, including the date of sample collection, the depth of sample collection (Table 12), the use of a 24-hour composite sample versus time-discrete sampling, material differences between the samplers, and handling techniques of the different sampling teams.

Table 12. Sampling depths and depth of screen at demonstration well.

Method	Depth to Screen (ft bgs)	Sampling Depth (ft bgs)
Bladder Pump	210	215
Bailer		155
IS2		200

While the recovery of the IS2 technique could likely be improved, the differences between techniques and the natural variation in concentration between sampling events make direct comparison of concentrations a challenge, and the project team notes that for concentrations below the RL of the other techniques, the IS2 should have a significant advantage.

5.5 SECOND DEMONSTRATION: NASNI

5.5.1 Preparation

Two candidate wells were identified from documents provided by the site management (Table 13). Considerations included placement in the dilute fringe of the chromate plume (>100 µg/L). Well OU20-PEW-01 typifies the location and construction of a candidate well. This well is located on the southwest edge of the plume, in the parking lot located between Buildings 2 and 94, and marked in Figure 20 with a red circle. This well was also the subject of an investigation performed under ER-200914 (Halden, 2012), and as a result of that investigation, it was identified as a candidate for sampling with the IS2. During that experiment, the well was found to be appropriately sized for the IS2 sampler, outside and up-gradient of previously-conducted field pilot-tests, and in a location minimally disruptive to traffic and logistically easy to access.

Table 13. Construction details for candidate wells at NASNI.

Well	Year Built	Diameter (inches)	Depth to Screen (ft bgs)	Screen Length (ft)	Depth to Water (ft)	Chromate Conc. (mg/L, year)
OU20-PEW-01	2006	4	25	10	5 (2006)	25 (2012)
S1-MW-09	NA	4	9	10	4 (2014)	0.25 (2013)

A second candidate well, S1-MW-09, was identified and proposed as an alternative, due to lower contaminant concentrations. After a visit to the site, well S1-MW-09 was selected for the

demonstration, primarily because it is located near a painted island in the parking lot, facilitating placement of equipment without interfering with traffic.

This site is impacted by commingled plumes of hexavalent chromium (present as chromate) and chlorinated solvents, largely trichloroethene (TCE). During a preliminary visit to the site, an Isco 3700 (Teledyne Isco, Lincoln, Nebraska) sequential portable sampler was deployed to take 1-L samples at 2 hour intervals, in order to provide baseline data for the IS2 demonstration. These samples were collected from 15 ft bgs, the same depth at which the IS2 would sample. The average concentrations of relevant anions, hexavalent chromium, and TCE (from site documentation) are presented in Table 14. Observations were also made of the depth to water in the well, and local tide data was collected from the National Oceanic and Atmospheric Administration (NOAA) database for the San Diego observatory (Station 9410170).

Table 14. Concentrations of analytes relevant to the IS2 demonstration at NASNI.

Analyte	Concentration	Method	Date Measured
Chloride	21 mg/L	EPA 300.0	November 2014
Sulfate	32 mg/L	EPA 300.0	November 2014
Nitrate	3.2 mg/L	EPA 300.0	November 2014
Chromium-VI	1.2 mg/L	SM 3500 CR D	November 2014
Trichloroethene	6.6 µg/L	NA	July 2013

The depth to water in S1-MW-09 was always observed to be 4.1 ft, which suggested that this location was outside of the influence of the tide. However, when the chromium-VI concentration in the well is plotted on the same time axis as the tidal data (Figure 28), it is clear that tidal action is influencing the groundwater at this location, and is responsible for swings in the chromate concentration of up to 0.5 mg/L (± approximately 50% from average). This provides a good example of a location where time-discreet and time-averaged measurements could provide significantly different data.

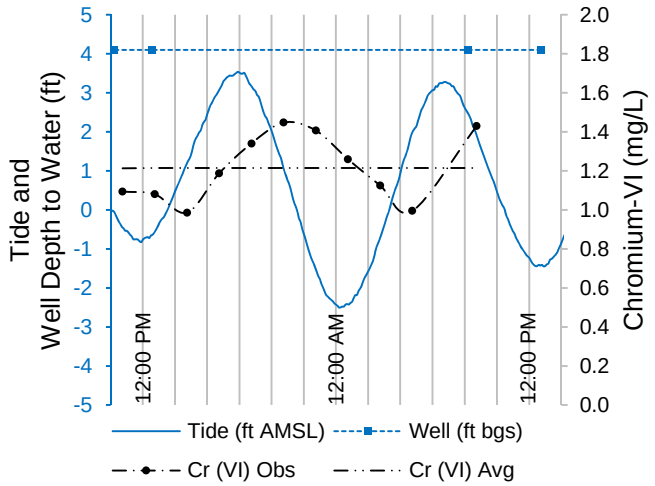

Figure 28. Tide, depth to water, and contaminant concentration data for well S1-MW-09 over a 24-hour time period.

The contaminant concentration is observed to follow the tide.

The SPE cartridges selected for this study contain 1.0 g of SIR-100-HP (ResinTech, West Berlin, New Jersey) strong base anion resin. This resin has demonstrated good affinity and high capacity for chromate in the presence of other salts including chloride (Bowen et al., 2014). During preliminary work in the laboratory, the resin provided recovery of over 80% from both deionized water and contaminated site groundwater, and enough capacity to process more than 400 mL of site water per cartridge without breakthrough.

The sampler was configured with a reciprocating syringe pump driving six fluid channels. Three of these channels included a single SPE cartridge. The fluid from all six channels was collected in inert polymer bags. Breakthrough, which was not anticipated, would be detected in the effluent from the cartridges. The sampler was programmed to take in 1.25 mL of water every second hour, process it at 0.5 mL/min, and pause until the next sampling period. Twenty-eight days of sampling every 2 hours would process a total of 420 mL of groundwater.

For this demonstration, the sampler was inspected after the first, second, and fourth weeks to ascertain its function and collect liquid samples. The collected water was recovered for analysis and the internal mechanism of the sampler inspected for faults.

5.5.2 Deployment

The IS2 sampler was inserted into the well, with an inlet positioned at 15 ft bgs (11 ft under water) (Figure 29). For this shallow deployment, the sampler was installed and deinstalled manually. The sampler was programmed to take in 1.25 mL of water every second hour, process it at 0.5 mL/min, and pause until the next sampling period. Twenty-eight days of sampling every 2 hours would process a total of 420 mL of groundwater.

Figure 29. Field assembly and installation of the IS2 at NASNI.

The maintenance and recovery team observed a decontamination procedure that included:

- Use of nitrile gloves when handling surfaces that had been in contact with contaminated water;
- Decontamination of the sampler with deionized water;
- Hand-washing; and
- Disposal of all waste according to the ASU hazardous waste management guidelines.

After the fourth week of sampling, the sample cartridges were removed from the sampler, capped to retain the entrained fluid, and refrigerated before being extracted. The volume of water collected in the storage bag for each channel was determined gravimetrically and recorded.

5.5.3 Results

The volume of water processed by the sampler is a particularly important parameter. The ultimate embodiments of this system in a production environment would be operated in effluent discharge mode, which requires confidence in the predicted sample volumes to provide confidence in the calculated average contaminant concentration. The experimental device used in this demonstration has many adjustable parts that would likely be non-adjustable in a production system. To ensure accurate dispensation for this experiment, the sampler pump was adjusted after the first week of operation (Figure 30), and a significant improvement in performance was observed after the second week. This resulted in the equipment being left in place for the remainder of the experiment without adjustment.

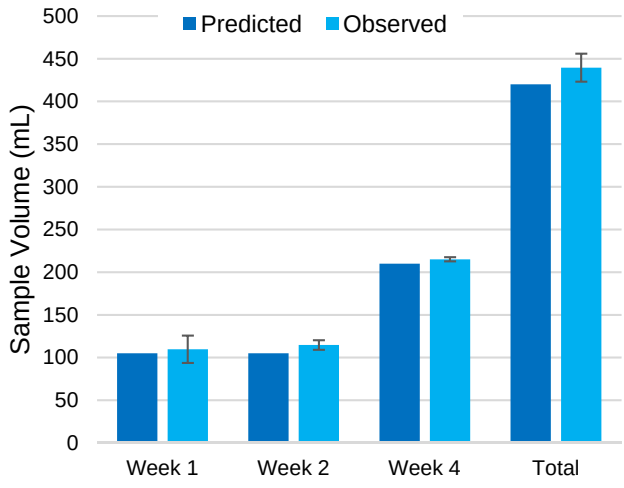

Figure 30. Predicted and observed volumes of water processed by the IS2 sampler during the demonstration at NASNI.

All of the liquid samples (post-cartridge effluent and unprocessed composite samples) were analyzed for chromate and total chrome. Chromium was not detected in any of the post-cartridge effluent samples, indicating that there had been no detectable breakthrough during sampling. A comparison of the total chrome and chromate data suggests that the majority of the total chrome

was present as chromate (Figure 31), which further indicated that there was no significant change in speciation between the sorbed and liquid composite samples. For consistency, total chrome data is presented subsequently.

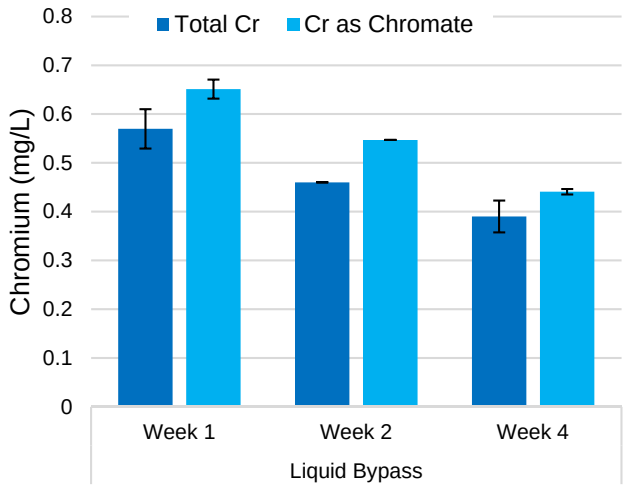

Figure 31. Speciation of chromium observed in the liquid bypass channels.

Upon recovery after 28 days, the cartridges were eluted twice and the eluates similarly analyzed. It was observed that the recovery from elution was lower than expected (approximately 55% of the value observed in the bypass samples), so the resin was destructively tested using EPA Methods 3050B and 6010B. The results improved the recovery to approximately 77% of the value observed in the bypass samples (Figure 32), which meets performance objective 31 and the EPA recommended recovery of 70% to 130%.

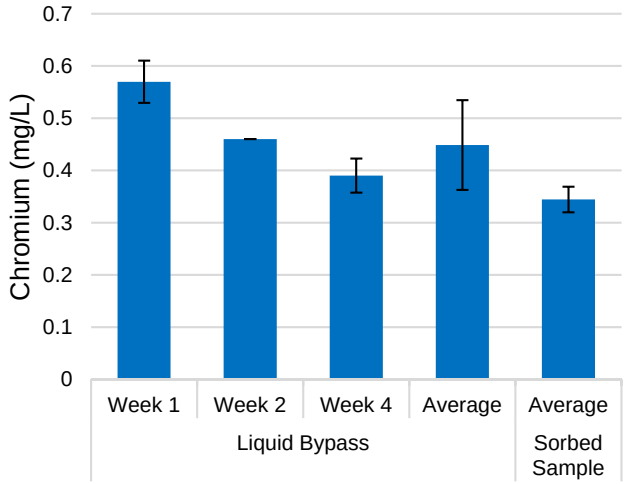

Figure 32. Concentrations of chromium reported by 7 and 14-day liquid composite sample and a 28-day sorbed composite sample.

The elution recovery for field deployment was lower than that observed in bench studies, likely due to diffusion of the target species into the resin matrix. These results indicate that very long

time averages can be collected for metal species where speciation is not a concern, as the sampling plan can call for the resin to be destructively tested with good results. For situations where metal speciation is a concern and the anions must be recovered through elution, shorter time averages are recommended, to reduce losses of analytes. This method still allows for time averages to be conducted on significantly longer time scales than the short-term tidal fluctuations.

As in the first demonstration, the IS2 enabled lower RLs for the sampling method than liquid grab sampling. This is due to the preconcentration process, by which the accumulated mass in the SPE cartridge can provide detectable quantities even when the environmental concentration cannot. Using the results of the demonstration method, a selection of RLs is provided in Table 15.

Table 15. RLs for discrete and composite sampling of chromium-VI.

Sampling Method	Species	Quantification Method	RL (mg/L)
Liquid grab sample (400 mL)	Total Cr	EPA 200.7[a]	0.01
	Cr (VI)	SM 3500 CR D[a]	0.05
	Cr (VI)	EPA 7196A[b]	0.1
IS2 sorbed sample, 1-week composite (400 mL pre-concentrated on 1.0 g resin; elute to 50 mL)	Total Cr	EPA 200.7[a]	0.001
	Cr (VI)	EPA 7196A[b]	0.01
IS2 sorbed sample, 4-week composite (400 mL pre-concentrated on 2.0 g resin; resin acid digested)	Total Cr	EPA 3050B and EPA 6010B[a]	0.01

[a]RL based on results from a certified laboratory, [b]RL generated by the IS2 team at ASU.
Cr = Chromium
Cr(VI) = Hexavalent Chromium

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6.0 PERFORMANCE ASSESSMENT

A summary of all data analysis in support of the assessment of performance objectives is provided in the following section.

6.1 DEMONSTRATE AGREEMENT WITH CURRENT METHODS

This quantitative performance objective requires IS2 to demonstrate agreement with current sampling and analysis methods. The original performance objective required measurements within 30% of the values obtained by co-analysis.

6.1.1 Supporting Data

Table 16 is a summary of the results of IS2 sorbed-sample analysis and co-analysis of liquid samples at the two demonstration sites, as well as the percent difference between the methods.

Table 16. Summary of contaminant quantification data for two demonstrations.

Demonstration	Sample	Result	Difference (%)
First Demonstration: Former Williams AFB	Naphthalene discrete liquid sample by bladder pump (8260B)	11 µg/L	--
	Naphthalene discrete liquid sample by bailer (8260B)	17 µg/L	--
	Naphthalene composite solid sample by IS2, uncorrected for recovery	3.7 µg/L	67 – 78
	Naphthalene by IS2, corrected for recovery (70%)	5.3 µg/L	52 – 69
Second Demonstration: NASNI	Cr(VI) liquid composite sample	0.45 mg/L	--
	Cr(VI) solid composite sample by IS2, uncorrected for recovery	0.34 mg/L	24
	Cr(VI) solid composite sample by IS2, corrected for recovery (80%)	0.43 mg/L	4.4

6.1.2 Performance Assessment

The performance of the IS2 for the proposed fuel contaminant (naphthalene) at the Former Williams AFB was below expectation, but the difference was of not much more than the difference observed between the results of two other sampling and analysis methods (maximum difference = 9 µg/L, standard deviation = 3.8).

There were a number of confounding factors that made direct comparisons difficult at the first demonstration site. The depths of the three sample methods were different, the samples were taken on different days, and two discrete methods were compared with a time-averaged method. Naphthalene and the secondary analytes are prone to losses in a system that includes plastic components. Additionally, it was not feasible at the time of the demonstration to align all of the sampling logistics between the three methods, so the bailed and IS2 samples were performed in an undisturbed well, while a low-flow purge was performed prior to taking the bladder pump sample. The bladder pump sample was taken by a different team, and the samples were processed by three different laboratories. Refinement of the IS2 method, coupled with comparison sampling better matched to the IS2 sampling conditions (e.g., depth), may potentially improve comparability.

At the second demonstration site, the results were significantly closer; a statistical analysis is provided in Section 6.2. Without correcting for the known recovery of the analyte, the sorbed sample yielded a concentration only 24% less than the liquid composite sample. When corrected for recovery, this difference fell to 4.4%. The excellent performance at this demonstration can be attributed to the robust SPE method, the non-volatile, conservative properties of the metal anionic analyte, and the ability of the IS2 instrument to collect split liquid and sorbed composite samples.

It is clear from Figure 32 that had the liquid sample been collected one week and the composite sample the next, the difference between the results would have been much larger. For example, a comparison was not made between the IS2 results and the results of the 24-hour discrete survey, where the average concentration was nearly three times what the IS2 sorbed samples reported. This was an indication that short- and long-term changes in concentration make it difficult to compare samples that were not taken simultaneously.

This quantitative performance objective has been met.

6.2 DEMONSTRATE TIME-AVERAGED SAMPLING CAPABILITY

This quantitative performance objective requires the IS2 to demonstrate agreement between a liquid composite sample and a solid-phase composite sample. The original performance objective required agreement to be demonstrated using Student's *t*-test.

6.2.1 Supporting Data

Tables 17, 18, and 19 present a summary of the statistical data generated to support this performance objective.

Table 17. Samples and concentration values use for comparison of liquid and solid composite sampling.

Two points (week 2 for channels 1 and 3) were lost in handling.

Sample Set	Sample Name	Chromium-VI Concentration (mg/L)
Liquid Composite Samples	Channel 1 Week 1	0.59
	Channel 2 Week 1	0.61
	Channel 3 Week 1	0.52
	Channel 2 Week 2	0.46
	Channel 1 Week 4	0.39
	Channel 2 Week 4	0.35
	Channel 3 Week 4	0.43
Solid-Phase Composite Samples (Uncorrected)	Channel 4 Week 4	0.32
	Channel 4 Week 4	0.38
	Channel 4 Week 4	0.34

Table 18. Results of F-Test for the equality of variances of liquid and solid composite sample results.
Statistics generated by Microsoft Excel.

	Liquid Composite Samples	Solid-Phase Composite Samples
Mean	0.479	0.345
Variance	0.00975	0.000895
Observations	7	3
Degrees of Freedom	6	2
F	10.9	
P(F<=f) one-tail	0.0865	
F Critical one-tail	19.3	

Table 19. Results of *t*-Test for the equality of means of liquid and solid composite results.
Statistics generated by Microsoft Excel.

	Liquid Composite	Solid-Phase Composite
Mean	0.479	0.345
Variance	0.00975	0.000895
Observations	7	3
Pooled Variance	0.00753	
Hypothesized Mean Difference	0	
Degrees of Freedom	8	
t Stat	2.23	
P(T<=t) one-tail	0.0280	
t Critical one-tail	1.86	
P(T<=t) two-tail	0.0560	
t Critical two-tail	2.31	

6.2.2 Performance Assessment

As indicated in Section 6.1.2, the results generated by sorbed and liquid composite samples were quite similar, with the sorbed samples reporting 24% lower than the liquid composite samples before being corrected for recovery, and reporting only 4.4% lower after being corrected for recovery.

Though the number of samples available for statistical analysis is relatively low, a simple analysis of the variance and means has been prepared. The samples included in the analysis are presented in Table 17. The sorbed sample results were taken without correction for recovery, to provide a more conservative test. The week 2 samples for channels 1 and 2 were lost in the field, and are not presented.

The first analysis performed was an F-test. The null hypothesis was that the sample variances are equal. The F-statistic calculated from the samples (Table 18) is less than the critical F-value, so the null hypothesis is accepted and the variances cannot be assumed to be different.

The second analysis performed was a *t*-test. The null hypothesis was that the sample means are equal. The *t*-statistic generated from the samples (Table 19) is between the critical one-tail and

two-tail *t*-values, so the null hypothesis is accepted and the means are assumed to be equal, at a significance level of up to 0.056.

This quantitative performance objective has been met.

6.3 DEMONSTRATE OPERABILITY UNDER ENVIRONMENTAL CONDITIONS

This quantitative performance objective requires the IS2 to demonstrate equivalence between the volume of water processed by the solid-phase cartridge and the programmed volume of water. The original performance objective requires agreement to be demonstrated using a *t*-test. The demonstration is further considered successful if there is no more than 30% difference between the concentration results obtained from solid-phase composite samples and liquid composite samples.

6.3.1 Supporting Data

A t-test is not practical for this application as originally described because the variance in the predicted values is zero. Instead, a *t*-test was performed to determine whether or not the data support a hypothesis that the mean volume of water pumped through the SPE cartridges is equal to the mean volume of water pumped directly to storage for the liquid composite sample. While the number of data points is still impractically small, this was done to further address the early concern that SPE cartridges may become fouled during environmental use, reducing fluid flow. The volumes used for the analysis were those measured between weeks 2 and 4 of the NASNI deployment. The results are presented in Table 20.

Table 20. Results of *t*-Test for the equality of mean volumes of water collected for liquid and solid composite results.
Statistics generated by Microsoft Excel.

	Liquid Composite	Solid-Phase Composite
Mean	216.3	213.8
Variance	9.97	0.703
Observations	3	3
Pooled Variance	5.34	
Hypothesized Mean Difference	0	
Degrees of Freedom	4	
t Stat	1.31	
P(T<=t) one-tail	0.131	
t Critical one-tail	2.13	
P(T<=t) two-tail	0.261	
t Critical two-tail	2.78	

Supporting data regarding the difference between the concentration results derived from solid-phase and liquid composite samples is presented in Sections 6.1 and 6.2.

6.3.2 Performance Assessment

The null hypothesis of the statistical assessment for the first part of this objective was that the sample volume means are equal. The *t*-statistic generated from the samples (Table 19) is between the critical one-tail and two-tail *t*-values, so the null hypothesis is accepted and the means are assumed to be equal, though at a very low significance level of 0.26. This analysis is not very strong, due to the limited number of comparable samples available. However, it is supported by other data, including the preliminary flow data presented in Section 5.3.1. At present there is no indication that SPE cartridges are subject to unacceptable fowling or obstruction that would preclude their use in sampling wells.

The second part of the objective required a demonstration of results derived from sorbed samples that are no more than 30% different from liquid composite samples; this data was provided in Section 6.1 with an accompanying statistical analysis in Section 6.2, and the demonstration at NASNI was successful.

This quantitative performance objective has been met.

6.4 DEMONSTRATE FAVORABLE LABOR REQUIREMENTS

This qualitative performance objective requires that the complexity of operating the IS2 system be acceptable when compared to other water sampling techniques. Personnel associated with IS2 demonstrations were asked to give their subjective analyses of the practicality of the IS2 in this context.

6.4.1 Supporting Data

In discussion with the team members, there was consensus that approximately 1 hour was required to install or deinstall the device, including staging of equipment, safety precautions for traffic areas, recording well parameters such as depth to water, checking the device function and preparing it for the well, inserting or removing the device, decontamination of the device upon removal, and cleanup.

6.4.2 Performance Assessment

While the IS2 sampler requires some preparatory work, the consensus of the team is that the requirements are qualitatively similar or not much greater than the preparation required for other mechanical sampling devices (e.g., bladder pumps). Additionally, while deep insertion (>100 ft) requires the use of a crane, the team found that installation and deinstallation at all depths takes approximately an hour, and is qualitatively similar to sampling with other mechanical sampling devices.

This qualitative performance objective has been met.

6.5 DEMONSTRATE UTILITY OF IS2'S LOW MDLS

This qualitative performance objective requires the IS2 to demonstrate improvement in MDL. The original performance objective describes two goals: improving MDLs in a well where

contaminants are detectable but not quantifiable, and detecting contaminants in a well where contaminants are not quantifiable but expected to exist at trace quantities.

6.5.1 Supporting Data

It was not possible to follow the original requirements of this performance objective, as many other well selection factors limited the number of wells appropriate for demonstration. These included accessibility, security, traffic concerns, well design, and other considerations. However, the demonstrations that were performed produced data that supports a claim that the IS2 method improves the resolution of groundwater sampling. Specifically, the improvements in RL that were observed are collected Table 21.

Table 21. Sampling methods and RLs from two demonstrations of the IS2.

Sampling Method	Species	Quantification Method	RL
Liquid Grab Sample (40 mL)	Naphthalene	EPA 8260B[a]	1.0 – 5.0 µg/L
Liquid Grab Sample (1 L)	Naphthalene	EPA 8270C[a]	9.5 – 10.0 µg/L
IS2 sorbed sample, 24-hour composite (250 mL pre-concentrated on 500 mg resin; elute to 2 mL)	Naphthalene	ASU GC-MS[b]	0.10 µg/L
Liquid grab sample (400 mL)	Total Cr	EPA 200.7[a]	0.01 mg/L
	Cr (VI)	SM 3500 CR D[a]	0.05 mg/L
	Cr (VI)	EPA 7196A[b]	0.1 mg/L
IS2 sorbed sample, 1-week composite (400 mL pre-concentrated on 1.0 g resin; elute to 50 mL)	Total Cr	EPA 200.7[a]	0.001 mg/L
	Cr (VI)	EPA 7196A[b]	0.01 mg/L
IS2 sorbed sample, 4-week composite (400 mL pre-concentrated on 2.0 g resin; resin acid digested)	Total Cr	EPA 3050B and EPA 6010B[a]	0.01 mg/L

[a]RL based on results from a certified laboratory, [b]RL generated by the IS2 team at ASU.

6.5.2 Performance Assessment

While the specifically proposed tests were not logistically feasible for this project, the demonstration data support the original project objectives, namely that:

a. The IS2 method provides concentration data that is detectable and quantifiable at lower concentrations than methods that do not perform in situ preconcentration.

b. The IS2 has the potential to provide detection in wells where the concentration would be below detection limits for other methods.

This qualitative performance objective has been met.

6.6 DEMONSTRATE REDUCED GENERATION OF HAZARDOUS WASTE

This qualitative performance objective required the IS2 to demonstrate a lower rate of generation of hazardous waste than other water sampling methods.

6.6.1 Supporting Data

All sampling methods generate some hazardous waste: used gloves, consumables (pump tubing, pump bladders, etc.), water or other liquids used for decontamination, and hand washing. Some particularly waste-intensive groundwater sampling processes, such as well purging, are not necessarily appropriate for comparison, as the decision to purge and the purging regime should be dictated by the site hydrogeological properties (Barcelona et al., 2005). At present, no-purge operation of the IS2 is indicated anywhere that passive sampling would otherwise be indicated. In either case, while the IS2 is capable of reducing purge waste by operating in no-purge settings, the advantage is not unique.

Logistical considerations during the demonstrations led to commingling of other hard and liquid wastes, so the demonstrations did not provide adequate evidence to support any conclusions about the relative amount of waste generated during sampling. Observation of the demonstrations suggest that an IS2 sampling event generates similar quantities of hazardous waste to other sampling methods.

6.6.2 Performance Assessment

At present, there is not enough data to support a conclusion that the IS2 has a lower rate of generation of hazardous waste than other sampling methods.

6.7 DEMONSTRATE FAVORABLE COST ECONOMICS

This performance objective requires the IS2 to demonstrate per-sample costs comparable to those expected for sampling with other methods.

6.7.1 Supporting Data

The cost assessment (Section 7.0) provides an analysis of the costs associated with IS2 sampling, and provides some estimates of comparable costs for other instruments. Broadly, the per-sample costs of the IS2 are similar to other methods, with potential savings in shipping and sample handling costs. A summary is presented in Table 22, and the actual costs associated with the demonstrations are presented in Section 7.0.

Table 22. Cost elements for groundwater sampling and qualitative analysis of the relative cost of the IS2 method.

Per-Sample Cost Element	IS2 Sampling versus Other Methods
Consumables (gloves, pump tubing, etc.)	Similar
Labor (technician time)	Similar or slightly worse
Sample Handling (size, weight, shipping)	Better; advantage grows with number of samples
Analysis (laboratory costs)	Similar
Labor (shallow sampling, <100 ft bgs)	Similar
Labor (deep sampling, >100 ft bgs)	Worse

6.7.2 Performance Assessment

Simultaneous analyses using the IS2 and other techniques were performed; additionally, the IS2 team has experience taking samples with other instruments, providing baseline samples for this and other studies. The IS2 was broadly similar in cost to other methods, with logistical advantages in sample volume and mass versus liquid samples, and additional costs (crane rental) when extremely deep samples are taken. The IS2 provides unique data, however, and with additional future demonstrations the advantages and disadvantages may be shown to offset.

This performance objective has been met.

7.0 COST ASSESSMENT

Cost is a fundamental driver in the development of in situ sample preparation technology. Anticipated cost benefits include reductions in:

- Consumables use and disposal costs;
- Packaging and shipping costs for prepared samples;
- Handling and disposal of contaminated water; and
- Analytical labor cost.

The IS2 technology demonstration provided an opportunity to generate estimates for the operational cost of the technology when scaled up to site-wide or multi-site contractor use. In each instance where a field trial is performed, a well was selected for which recent monitoring data are available. The methods employed to collect these data may be considered a reasonable alternative to the method being developed in this program.

The following cost assessment provides both an analysis of the direct costs of demonstrations using experimental equipment and an assessment of the potential costs associated with a production system competing with other methods and equipment.

7.1 COST MODEL

The IS2 Cost Model breaks the costs associated with the technology into two broad categories: capital investment and operating costs (Tables 23 and 24). The capital investment category is related to the initial outlay required to procure an appropriate IS2 system for sampling at a field site, while the operating costs include consumables, labor, waste management, shipping, analysis, and other recurring charges.

Table 23. Capital investment cost model for ER-201122.

Category	Cost Element	Unit Cost (2015 dollars)
IS2 Peristaltic Sampler (Research Model)	Peristaltic Pump	2200
	Peristaltic Pump Control	750
	Shell and Caps	800
	Internal Structure	400
	Control Cable (500 ft)	500
	Assorted Hardware	300
	Total	*4950*
IS2 Reciprocating Sampler (Research Model)	Reciprocating Pump	2200
	Shell and Caps	800
	Internal Structure	400
	Control Cable (500 ft)	500
	Assorted Hardware	300
	Total	*4200*

Table 24. Operating costs model for ER-201122.

Category	Cost Element	Unit Cost (2015 dollars)
IS2 Groundwater Sampling (all depths)	SPE Cartridges	$1 to $2 / sample
	Other Consumables (gloves, waste bags, etc.)	$1 / sample
	Shipping	$40[1]
	Labor	$240[2]
	Total Sampling	*$280[3]*
Sample Analysis	Certified Laboratory	$60 to $200[4] / sample
IS2 Deep Well Sampling (>60 ft bgs, optional)	Crane Rental and Operation (install & deinstall)	$1500

[1]Example shipping cost: FedEx Standard Overnight from San Diego to Los Angeles, 1 kilogram package including Styrofoam cooler, samples, and ice or ice substitute.
[2]Example labor cost: Two technicians, $60 per technician-hour, 2 hour for install-deinstall.
[3]Example installation: One well, triplicate samples, one contaminant or class of contaminant.
[4]Example analyses: $60/sample for Cr (VI), $100/sample for EPA 8260B, $200/sample for EPA 8270C.

7.1.1 Capital Investment Cost Model

Producing a precision, remotely operated, submerged sampler is complex. As much as possible, the IS2 team has incorporated off-the-shelf in the unit to provide the best cost efficiency and uniformity, with the fabrication and integration of the remainder of the device is at the ASU Machine Shop. The vendor parts and costs, as well as the machinist hours and costs were tracked. While a significant discount can be expected when a higher-volume device is produced commercially, the cost of the experimental IS2 samplers is similar to the cost of other contemporary systems.

7.1.2 Operating Costs Model

Labor is the largest component of the deployment costs. A comparison of the labor cost associated with the IS2 and that of the methods currently in place at the deployment sites is critical to establish the cost competitiveness of the new technology. The labor, materials, shipping, and waste disposal costs of the deployment will be tracked for comparison with the standard sampling methods.

7.2 COST COMPETITIVENESS

The capital cost of these research instruments is largely in line with that of other commercially available instruments that might be deployed in order to develop similar datasets (Table 25).

Table 25. Comparison of capital costs associated with several sampling instruments.

Instrument	Configuration	Capital Cost (2015 dollars)
IS2 (Research Model)	Composite Samples	4200
	Reciprocating Pump	
	500 ft Control Cable	
ISCO Model 6700	Composite or Sequential Samples	4100
	25 ft lift	
Solinst 407 Bladder Pump	Discrete Samples	3100
	Solinst 125 psi Controller and Tubing Cart	
	Solinst Air Compressor	
	Solinst 407 Bladder Pump (Stainless Steel, 1” x 2’)	
	100 ft lift, PTFE-lined tube	
Solinst 407 Bladder Pump	Discrete Samples	4400
	Solinst 250 psi Controller and Tubing Cart	
	Solinst Air Compressor	
	Solinst 407 Bladder Pump (Stainless Steel, 1” x 2’)	
	>200 ft lift, PTFE-lined tube	
Solinst 408 Double Valve Pump	Discrete Samples	4200
	Solinst 250 psi Controller and Tubing Cart	
	Solinst Air Compressor	
	Solinst 408 Bladder Pump (Stainless Steel, 5/8” x 1’)	
	>200 ft lift, PTFE-lined tube	
AquiStar Multi-Parameter Smart Sensor and Data Logger	Discrete Samples (High-frequency time series)	6200
	Pressure, Conductivity, pH, DO, and Temperature sensors	
ProHydro Snap Sampler	Discrete Samples	1500
	3x 40-mL VOA	
	Sampling at >200 ft	

DO = dissolved oxygen

In addition to researching capital costs, the IS2 team tracked or estimated operating costs for the IS2 demonstrations and for other samples taken during the demonstrations using the cost-comparison matrices shown in Table 26 and 27. These estimates support the conclusion that IS2 composite samples are similar in cost to discrete samples. Taking significantly more samples (10s instead of 1s) would substantially impact the per-sample cost of all methods, with the IS2 cost-efficiency improving significantly due to the lower weight of sorbed samples when compared to liquid samples.

Table 26. Cost data for first demonstration at former Williams AFB.

	Site Sampling Plan (2015 dollars)		
	Method Used by Site Manager (Solinst 407) Nov. 2013	Bailed Sample Nov. 2013	IS2 Deployment Nov. 2013
Capital Costs			
Equipment	4400[1]	400	4950[2]
Installation	0	0	0
Total	4400	400	4950
Operating Costs			
Equipment Rental	0	0	0
Consumables	0	6.75 Bailer	10 (6x cartridge) 25 (4x pump tube)
Deployment Labor	60 Pump Tech (1 hr)	60 Bailer Tech (1 hr) (salary+overhead)	1140 crane two workers two days (2 h) 120 IS2 Tech (2 h)
Packaging and Shipping	0	0	0
Analysis	100	100	160
Waste Disposal	NA	NA	NA
Total	160 (single time-discrete sample)	170 (single time-discrete sample)	250 shallow 1400 deep (24-hour composite sample in triplicate)

[1]Estimate based on configuration required for 200 ft lift.
[2]Estmate for research model with peristaltic pump.

Table 27. Cost data for second demonstration at NAS North Island.

	Site Sampling Plan (2015 dollars)		
	Method Used by Site Manager (Unknown Bladder Pump)	ISCO 3700 Oct. 2014	IS2 Deployment Nov. 2014
Capital Costs			
Equipment	2600[1]	0	4200[2]
Installation	0	0	0
Total	2600	0	4200
Operating Costs			
Equipment Rental	0	450/week	0
Consumables	0	20 Pump Tubing	5 (3x cartridge)
Deployment Labor	60 Technicians (1 Tech., 1 hr)	120 Technicians (1 Tech., 2 hr)	240 Technicians (2 Tech., 2 hour)
Packaging and Shipping	40 (2kg, FedEx Standard Overnight, San Diego to Los Angeles)[3]	80 (15kg, FedEx Standard Overnight, San Diego to Los Angeles)[4]	40 (1kg, FedEx Standard Overnight, San Diego to Los Angeles)
Analysis	60 (1 sample)	720 (12 samples)	180 (3 samples)
Waste Disposal	NA	NA	NA
Total	160 for one time-discrete sample	Including Rental: 70 per sample 800 for 24-hr time series Excluding Rental: 30 per sample 350 for 24-hr time series	155 per sample for 28-day composite in triplicate

[1]Estimate based on Solinst Model 407 configuration required for 100 ft lift.
[2]Estimate for research model with reciprocating pump.
[3]Estimate based on 1 L of quantification and QC samples.
[4]Estimate based on 12 samples taken for 24-hour, 2-hour interval sampling.

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8.0 IMPLEMENTATION ISSUES

No regulations or regulatory barriers have been identified that may apply to the use of this technology; rather, we see an opportunity for this technology to enter an already crowded field and provide a new and complementary data set. While the IS2 uses active transport to move contaminated groundwater to the sorbent cartridges, it is best described as an integrative, accumulative sampler and as such should be implemented using the best practices for such samplers as described in ASTM Standard D7929-14, "Standard Guide for Selection of Passive Techniques for Sampling Groundwater Monitoring Wells."

At present, the biggest challenge for development of the IS2 is the case in which the sampling agency desires simultaneous liquid composite and solid composite samples to be taken at depth. The design and sourcing of precision passive valves to prevent inlet pressure from driving the fluid flow has been a significant engineering challenge. However, the most common and most desirable configuration of the device will be one that produces only solid-phase samples and returns processed water to the well bore. This greatly reduces the engineering requirements for the instrument, as the equal inlet and outlet pressures enable a relatively simple valve system, or a peristaltic pump, to control the flow very precisely.

The IS2 sampler as currently embodied is a research instrument fabricated from a mixture of COTS parts, and parts designed in-house and fabricated by the ASU machine shop. These instruments work as intended, but are heavier, more complex, and more expensive than a commercial embodiment would be. As such, the best way for this technology to improve and to reach the intended audience is for a commercialization effort to design and build a series of devices for sale or for use by a monitoring consultant. Such an effort could simplify the instruments and improve maintainability by providing a standard parts set. Such simplification, standardization, and serial production would also reduce the cost of the instrument. To this end, the team participated in the 2012 ASU Venture Catalyst program, and has reached out to other potential collaborators. The project team sincerely hopes that this report will provide an asset in a continuing effort to bring the concept of in situ solid phase extraction to a wider audience.

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APPENDIX A

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