GUIDANCE

PASSIVE SAMPLING FOR GROUNDWATER MONITORING: TECHNOLOGY STATUS

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Hans F. Stroo, Ph.D.
Stroo Consulting LLC

R. Hunter Anderson, Ph.D.
Air Force Civil Engineer Center

Andrea Leeson, Ph.D.
SERDP and ESTCP

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Passive samplers are devices designed to sample groundwater within a screened interval of a permanent monitoring well without pumping or purging. Given that the screened interval is in dynamic equilibrium with the adjacent formation groundwater, passive samplers can obtain representative groundwater samples when used appropriately. Several passive sampling devices have been developed, and testing has shown that passive samplers can replace traditional purge-based sampling and low flow purge methods without loss of data quality. The status of the passive sampling technology is provided in this summary.

Deployment of the Snap Sampler™

INTRODUCTION

Long-term monitoring (LTM) represents a large fraction of the annual costs and continued liability for the DoD's contaminated groundwater sites. Consequently, SERDP and ESTCP funded research on several technical solutions to reduce these costs. Solutions include passive samplers that can significantly reduce the labor needed and the waste generated during one sampling relative to traditional well purging methods, as well as sampling strategies that can reduce the number of individual sampling events necessary to differentiate between short- (i.e., random) and long-term (i.e., attenuation) variability.

The results of recent research designed to optimize LTM sampling is provided in this summary. All project descriptions and reports are available by project number at the SERDP and ESTCP website (www.serdp-estcp.org). The key findings are summarized below, with greater detail in the following sections:

Advantages of Passive Samplers

- Passive samplers are valid for most analytes, under a wide range of conditions.
- Their limitations are understood and credible guidance is available.
- These devices can greatly reduce monitoring costs, without sacrificing data quality.

Passive Sampling Strategies

- Frequent sampling at many sites is inefficient because attenuation rates are often slow.
- Annual or less frequent sampling may be appropriate for many sites with stable plumes.
- Understanding the sources of variability can result in more efficient LTM plans.

PASSIVE SAMPLERS

Passive samplers are devices designed to sample groundwater within a screened interval of a permanent monitoring well without pumping or purging. Given that the screened interval is in dynamic equilibrium with the adjacent formation groundwater, passive samplers can obtain representative groundwater samples when used appropriately. Several passive sampling devices

have been developed, and testing has shown that passive samplers can replace traditional purge-based sampling and low flow purge methods without loss of data quality.

There are three general types of passive samplers for groundwater:

1) **Equilibrium samplers** - devices that establish an equilibrium with the groundwater
2) **Sorptive samplers** - devices that accumulate analytes from groundwater over time
3) **Grab samplers** - devices that collect water samples at a specific depth and time

The first commercialized equilibrium sampler was the Polyethylene Diffusion Bag [PDB] sampler (USGS, 2001), and guidance on using PDBs has been available for a decade (ITRC, 2004). However, PDBs have important limitations. Only VOC contaminants can be monitored with the PDB, and many compounds typically monitored during monitored natural attenuation (MNA) cannot diffuse across the polyethylene barrier well enough to establish equilibrium concentrations in a reasonable time. In general, PDBs are valid only for VOCs (primarily chlorinated solvents and BTEX), and should not be used for inorganic compounds, hydrophilic volatile organic compounds (e.g., MTBE, 1,4-dioxane), or semi-volatile organics (PCB, PAH). Other equilibrium samplers (e.g., Regenerated Cellulose Dialysis Membrane [RCDM] samplers) have been developed to obtain representative samples for a broader range of analytes than PDBs.

Sorptive samplers are deployed in a monitoring well for a short period of time and rely on sorption of organic compounds to a matrix during the exposure period to accumulate a measurable mass. Time of exposure, temperature, and desorbed mass measured during analysis are used to calculate groundwater contaminant concentrations. These devices can be used for a wide range of organic constituents

Regenerated Cellulose Dialysis Membrane Equilibrium Sampler

Passive grab samplers are pre-deployed devices that are activated in place to directly obtain depth- and time-specific samples from monitoring wells. Passive grab sampling collects a whole water sample, so it can be used for any analyte, subject to volume limitations. All three types of passive samplers have been validated through ESTCP and guidance is available from the Interstate Technology & Regulatory Council (ITRC) (2004, 2007) and ASTM (Standard D7929-14-ASTM, 2014).

Advantages and Limitations of Passive Samplers

The key advantage of passive samplers is the cost savings from reduced time for sampling and decreased waste generation. However, there can be other important advantages, including: 1) no pumps or power supplies are needed; 2) less on-site time is needed, reducing risks to personnel and inconvenience to site operations; and 3) reduction of data artifacts associated with purging (e.g., excessive drawdown, turbidity).

Key limitations include: 1) some passive samplers cannot be used for all analytes; 2) some passive samplers may not be able to collect sufficient sample volume for all required analyses; 3) some passive samplers may not fit into wells smaller than the common 2-inch diameter well; 4) some devices are not appropriate for “total” or unfiltered sample analysis because of diffusive filtration; and 5) some methods (i.e., sorptive methods) produce a calculated concentration rather than a measured concentration.

A common concern during the transition to passive sampling is that the results may not agree entirely with conventional or low-flow purging methods. Inconsistencies can happen and are largely due to flow changes associated with pumping (or not pumping) the well. Occasional differences within individual wells should be expected, but statistical equivalence has been observed in these demonstrations when comparing results over several wells. Individual well differences can be attributed to the depth-specificity of passive samplers, or a limited integration of the sample zone, whereas purging may provide an integrated sample from a larger volume (i.e., the screen length and beyond). As a result, both methods may be internally “accurate”, but each may represent the aquifer slightly differently.

Performance of Passive Samplers

The three passive sampler validation projects funded by ESTCP (ER-200630, ER-200921, and ER-200313) have shown that passive sampling approaches can overcome the limitations of PDB samplers (Table 1). These projects have focused on one grab sampler (the Snap Sampler™), a broad-range equilibrium sampler (the RCDM sampler), and a sorptive sampler (the GORE® Sorbers, now referred to as AGI Universal Samplers), respectively. These are among the most developed passive samplers, and many of the lessons learned from testing these samplers should also apply to other types of devices and technologies.

Table 1: Results of Passive Sampler Demonstrations

Project No.	Sampler	Analytes	Status	Comparison to Low Flow Purging
ER-200313	**RCDM** *(Equilibrium)*	Cl VOCs Explosives Inorganics Perchlorate MNA parameters	Final (2011)	▪ Excellent for most analytes ▪ Linear relationships with slopes = 1.0 ▪ Close correlation with PDBs (100%) ▪ Detection limits within 2-5x MCLs ▪ Estimated cost savings of 45-70%
ER- 200630	**Snap™** *(Grab)*	VOC, Cl VOCs Inorganics Explosives Perchlorate MNA parameters MTBE	Final (2011)	▪ Excellent for most analytes ▪ Linear relationships with slopes = 1.0 ▪ Estimated cost savings of~70%
ER-200921	**AGI** *(Sorptive)*	Cl VOCs BTEX Alkyl benzenes PAHs	Final (2014)	▪ Excellent for most analytes ▪ Linear relationships with slopes = 1.0 ▪ Detection below MCLs (ng/L range) ▪ Estimated cost savings of 30-45%

The results of these passive sampler demonstration projects are highly encouraging. All three devices, tested under ESTCP, have shown excellent agreement with traditional low-flow sampling results for almost all of the analytes present at several field sites. In 2007, ITRC concluded that these samplers, as well as others, "provided reliable and accurate data when used appropriately" (ITRC, 2007). These results support that conclusion, and should greatly increase confidence in the use of these passive samplers for LTM.

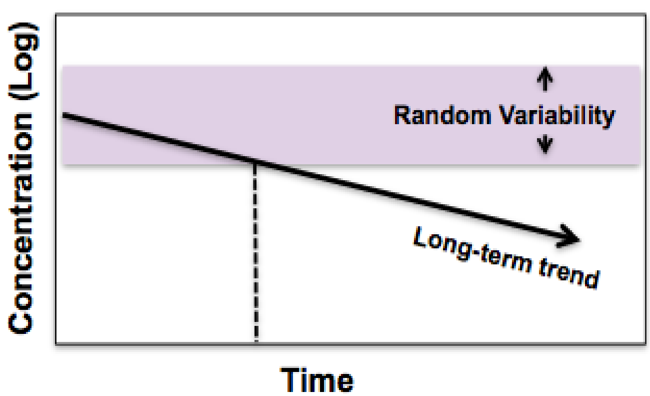
AGI Universal Sampler – A Sorptive Sampler

Precautions that should be followed to ensure accurate data include: 1) use of appropriate samplers for the suite of analytes of concern; 2) avoid problematic monitoring wells (e.g., fouled, bent, long screen >20ft, small diameter [for some methods]); 3) avoid monitoring wells with LNAPL; and 4) recognize potentially problematic analytes (e.g., total Fe). Site-specific evaluations may be desired for unusual site conditions. Such evaluations can be based on comparisons of passive sampler results to historical data, or on paired testing. A conversion evaluation several years after conversion may be useful to understand how the method transition has affected results at individual wells.

The cost savings from converting to passive samplers can be considerable. Savings results largely from the reduced labor and reduced waste compared to traditional purge-based methods. The ESTCP-funded demonstrations suggest that a reduction of 50% in LTM costs is a conservative expectation for grab samplers and equilibrium samplers, while a reduction of at least 30% can be expected when using sorptive samplers. Such savings are significant given that sampling is the dominant cost at MNA sites and sampling may continue for decades.

IMPROVING PASSIVE SAMPLING

Recent SERDP and ESTCP projects have focused on optimizing LTM sampling frequencies, with and without the use of passive samplers. The goal is to increase the efficiency of LTM by defining the monitoring frequencies needed to quantify long-term trends (see below).



Optimizing Monitoring Frequencies

Project ER-1705 demonstrated that changes in concentrations of chlorinated solvents are generally very slow, with attenuation half-lives typically over 5 years. As a result, the variability in typical quarterly or semi-annual monitoring programs is often dominated by shorter-term (i.e., seasonal) fluctuations and yields little insight on the longer-term trends (see figure). Annual or even less frequent sampling may be appropriate for some sites where stable groundwater plumes have been demonstrated, losing little information regarding long-term trends while reducing costs considerably. Project ER-201209 has shown that simplified low flow sampling procedures and passive sampling may improve cost structures without compromising data quality. The key point in these recently developed findings is that for some methods (e.g., modified low flow) and equipment (e.g., Snap Samplers), time, equipment, and waste generation can be reduced while maintaining data low relative sampling variability.

Project ER-1704 was designed to better understand the relationships between contaminant concentrations measured in a well using either passive samplers (Snap Samplers) or in situ sensors, and the concentrations present in the surrounding formation. The central hypothesis is that many wells are in fact "naturally purged" due to the natural groundwater flow regime, and that passive sampling (or sensor monitoring) in fact provides the ideal sample - a single, inexpensive, representative sample collected directly from the screened interval. Results indicate many wells can be monitored successfully using passive samplers or sensors, at lower costs than conventional sampling. Further, many wells mix contaminants within the well to the point that the stratification that occurs within the aquifer cannot be measured adequately in many screened monitoring wells.

SUMMARY

Passive samplers can provide valid samples for many analytes of concern, under a wide range of conditions. Credible technical and regulatory guidance is now available for using passive samplers. The results indicate that these devices can greatly reduce monitoring costs, without sacrificing data quality. In addition, a better understanding of the causes for variability in groundwater monitoring results has led to improvements in sampling strategies. At many sites, monitoring events can be less frequent than the typical quarterly to yearly schedules, while still providing the data needed to quantify long-term trends and ensure environmental protection. These improvements promise to further reduce long-term monitoring costs, and therefore, overall management costs, especially for sites undergoing MNA.

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REPRESENTATIVE RESULTS FOR PASSIVE SAMPLERS

A. SNAP SAMPLER™ -

Performance Objective	Data Requirements	Success Criteria	Results
Quantitative			
1. Ability to sample a range of contaminants at site	Adequate sample volume for all analyses	Similar detection capabilities (as with low-flow sampling)	Yes
2. Reproducible data	Analyte data for replicate samples	Among replicate samples, a %RSD of 25% or less, or equal to or better than that for low-flow samples	Yes for VOCs, dissolved inorganics, and total non-metal ions. Testing problems occurred for some total metals analyses for both Snap Sampler and low-flow sampling
3. Agreement between sampling methods for analytes of interest	Analyte concentrations for each sampling method for all wells	Lack of statistically significant differences Lack of bias	Yes, except total Fe and total Mn, where testing problems limited determinations
4. Reduced sampling time	Field records of activities at each well	Less time needed to sample a well	Yes
5. Less costly sampling method	Records of the costs for equipment and supplies Field record of technician's time	Cost savings of at least 25%	Yes, 46%-67% cost savings
Qualitative			
1. Ease of use	Field records of activities at each well	Technician able to learn the procedure with relative ease	Yes
2. Ease of use	Field records of activities at each well	Few problems requiring second attempt to sample the well	Yes (providing manufacturer's directions were followed)
3. Ease of use	Feedback from field technician	Operator acceptance	Yes

B. REGENERATED CELLULOSE DIALYSIS MEMBRANE (RCDM) SAMPLER

Performance Objective	Data Requirements	Success Criteria	Results
Qualitative Performance Objectives			
Determine if RCDM samplers recover same chemical parameters as PDB samplers and LF.	Identify chemical parameters recovered by RCDM samplers, PDB samplers, and LF.	Chemical parameters detected in PDB and LF are the same detected by RCDM samplers.	Criteria met
Determine if RCDM membrane integrity is maintained over the course of equilibration.	Observe sampler membranes for perforations.	No perforations noted during the course of the test.	Criteria met
Quantitative Performance Objectives			
Determine if RCDM samplers recover the same concentrations as LF.	Measure inorganic and organic compound concentrations recovered by RCDM samplers and LF.	NSD at $p<0.05$ between chemical concentrations recovered by the RCDM samplers and LF.	Criteria met for 96% of all chemicals tested
Determine if RCDM samplers recover the same concentrations as PDB samplers.	Measure VOC concentrations recovered by RCDM samplers and PDB samplers.	NSD at $p<0.05$ between VOC concentrations recovered by the RCDM sampler and the PDB sampler.	Criteria met for 100% of all chemicals tested
Determine if RCDM samplers can sample low concentrations.	Measure concentrations of chemicals near detection limits.	Concentrations within 2-5 times the detection limit can be detected.	Criteria met
Determine if RCDM samplers take significantly less field time to collect samples than LF.	Measure time needed t › collect samples using RCDM samplers and LF.	Comparison of field time required to sample RCDM samplers versus LF should be 5 times shorter.	Criteria met

C. AGI UNIVERSAL SAMPLER

Performance Objective	Data Requirements	Success Criteria	Results
1. Equivalent analyte detection limits	Detection levels for all AGI and low-flow samples.	Detection levels near or below EPA's MCL values for all contaminants tested.	APG site: The MDL for AGI sampler was below the MCLs. However, it was ~20x > low-flow MCL. Pease site: For most analytes, MDLs equivalent to low-flow. MDLs were 10x < MCLs.
2. Equivalent analyte concentrations to low-flow sampling	Analyte concentrations for each sampling method for all wells	Lack of statistically significant differences at $p < 0.05$	APG site: Significant differences for several analytes. Pease site: Generally no significant differences; poorest agreement for benzene and xylenes
3. Comparable concentrations across the entire range of analyte concentrations present	Analyte concentrations for each sampling method for all wells	Linear least fit model shows linear relationship with a slope that is not significantly different from 1.0	Both sites: Significant linear relationships between the AGI and low-flow data, with a slope = 1.0, for all analytes except TCA and CF at APG and toluene at Pease.
4. Ability to measure vertical profiles within wells	AGI results from all depth intervals tested.	Vertical profile of wells with AGI Sampler	Vertical profiles revealed. Pronounced concentration gradients in wells near plume epicenters, even in a well with a 5 ft screen.
5. Cost savings	Records of the costs for equipment and supplies Field record of field crew's time	Cost savings of at least 25%	APG site: Cost savings of 18% to 35%, depending upon the size of field crew. Pease site: Cost savings of 10% to 25%, depending on size of field crew. Both sites: Cost savings of 30% to 40% using recent price quote for samplers.