ZERO-PURGE GROUNDWATER SAMPLING FOR SEMIVOLATILE ORGANIC COMPOUNDS

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ABSTRACT

Obtaining groundwater samples utilizing zero-purge (i.e. non-pumping) methods is gaining acceptance by various regulatory agencies. Zero-purge sampling is based on the principal that groundwater in a well maintains equilibrium with the adjacent water-bearing unit. As such, representative groundwater samples can be collected without performing the costly and time-consuming well purging activities utilized in many conventional well sampling methods.

Most studies of the zero-purge method have been limited to volatile organic compounds (VOC). The authors have been unable to identify any studies concerning the utility of zero-purge sampling for semivolatile organic compounds (SVOC), which are common constituents at MGP sites. This study presents a comparison of SVOC results for replicate groundwater samples collected at two MGP sites using conventional (low-flow) field sampling methods and zero-purge field sampling methods.

Groundwater samples were collected via zero-purge methods from 13 monitoring wells using a HydraSleeve™ sampler and analyzed for SVOCs. For the purpose of comparison, replicate samples were collected from 8 of the 13 wells by performing low-flow purging and collecting samples for SVOC analyses from the low-flow pump discharge. Replicate samples were also collected from 9 of the 13 wells by performing low-flow purging and collecting samples for SVOC analyses via bottom-loading bailer.

A comparison of the laboratory analytical results for SVOC generated by zero-purge sampling to those of the low-flow purging and sampling (pump discharge) indicates that:

- SVOC concentrations for the zero-purge samples were, on average, 122% higher than for the corresponding low-flow pump discharge samples;
- SVOC concentrations for one well varied by a factor of five for the two sampling methods (possibly attributable to LNAPL in the well contacting the outside of the HydraSleeve Sampler and becoming incorporated into the sample), which tended to exaggerate the difference between the two data sets;

- Excluding the results for the LNAPL-bearing well, SVOC concentrations for the zero-purge samples were, on average, 17% higher than for the corresponding low-flow pump discharge samples;
- Variability in the data sets shows no apparent correlation to well construction specifications (e.g. diameter, depth, screened interval).

A comparison of the SVOC concentrations generated by zero-purge sampling to concentrations generated by low-flow purging and sampling using a bottom-loading bailer indicates that:

- SVOC concentrations for the zero-purge samples were, on average, 161% higher than for the corresponding low-flow purge/bailer samples;
- Excluding the results for the LNAPL-bearing well, SVOC concentrations for the zero-purge samples were, on average, 150% higher than for the corresponding low-flow purge/bailer samples;
- The disparity between the concentrations for zero-purge samples and for low-flow purge/bailer samples may be attributable to difficulty accurately lowering the bailer to the depth of the pump intake during sample collection.

This study demonstrates that zero-purge sampling is a technically sound alternative to conventional groundwater sampling procedures. SVOC results for samples collected using the HydraSleeve™ sampler are comparable to results for samples collected using low-flow methods, provided the low-flow samples are collected from the pump discharge. HydraSleeve™ samplers may not be appropriate for use in wells with an LNAPL layer.

Relative to low-flow sampling, zero-purge sampling yields accurate, valid analytical results for SVOCs at nearly half the cost relative to conventional methods for sample acquisition. The savings are realized by reduced equipment, labor and purge water management/disposal costs.

TECHNICAL APPROACH

Groundwater monitoring was conducted at two sites as part of site assessment activities. Site #1 was used for the disposal of spent purifier media from a nearby manufactured gas plant. Site #2 is a former manufactured gas plant. Groundwater samples were collected using low-flow techniques, with slight variations as described below.

In association with the low-flow sampling activities, replicate samples were collected for semivolatile organic compounds (SVOC) analyses using zero-purge sampling methods. A comparison between the SVOC results generated by the two methods is presented to demonstrate that zero-purge sampling is an accurate and valid alternative to low-flow sampling procedures.

Low-Flow Sampling

At Site #1, samples were collected for SVOC analyses from four monitoring wells using low-flow techniques. A submersible pump was lowered to the mid-point of the screened interval and groundwater was pumped at a rate of 200 to 500 milliliters per minute (ml/min). Field parameters (pH, specific conductance, ORP, dissolved oxygen and turbidity) were monitored every 5 minutes until three consecutive stable readings were obtained. The discharge rate was then set at approximately 250 ml/min and samples were collected directly from the pump discharge.

At Site #2, samples were collected from four wells using these same procedures (i.e. low-flow sampling via pump discharge). In addition, samples were collected from 9 wells by purging as described above, then removing the submersible pump and collecting samples using a bottom-loading bailer. The bailer was lowered to a depth that coincided with the depth of the pump intake during purging, then retrieved for sample collection.

Details regarding the construction of the monitoring wells utilized in this study are provided in Table 1.

Table 1. Monitoring Well Details

Well Identification	Diameter (in.)	Screened Interval (feet below grade)	Depth to Water (feet below datum)
Site #1			
MW-3	4	73-83	74
MW-6	4	74-84	77
MW-6D	2	124-144	79
MW-7	4	66-76	70
Site #2			
MW-1	2	15-25	17
MW-2	2	17-27	21
MW-3	2	12-22	17
MW-4xD	6	125-160	21
MW-4xxD	6	250-275	20
MW-6DD	2	58-68	15
MW-6xxD	6	239-270	16
MW-7D	2	34-44	17
MW-7xxD	6	250-270	14

Zero-Purge Sampling

Zero-purge sampling is a relatively new method for obtaining groundwater samples that utilizes passive (i.e. non-pumping) procedures. Zero-purge sampling is based on the principal that groundwater flow through a well screen is horizontal and the well is in constant equilibrium with the adjacent water-bearing unit. As such, representative groundwater samples can be collected without performing the costly and time-consuming well purging activities utilized in more conventional well sampling methods.

Most zero-purge sampling studies performed to date have utilized polyethylene-based passive diffusion bag (PDB) samplers. The PDB samplers are filled with deionized water and suspended in a well for approximately two weeks. During that time, volatile organic compounds (VOCs) diffuse through the PDB sampler and equilibrium conditions are established wherein VOC concentrations in the PDB sampler are equal to concentrations in the well and surrounding formation. The PDB samplers are then retrieved and samples are collected for laboratory analysis.

The PDB samplers are semi-permeable or impermeable to SVOCs and metals. This limitation has precluded the use of zero-purge sampling methods at MGP sites where monitoring is often required for SVOCs and metals.

This study utilizes a new zero-purge sampling tool, the HydraSleeve™ sampler, that is amenable to sampling for VOCs, SVOCs and metals (though the current study is limited to SVOCs). The HydraSleeve™ sampler consists of a flexible polyethylene chamber that is closed at the bottom and fitted with a spring-loaded check valve at the top

(Figure 1). The HydraSleeve™ sampler is suspended at the mid-point of the screened or open interval of a well with the flexible chamber in a collapsed position. The sampler remains undisturbed for approximately 2 weeks to allow any disturbance (e.g. turbidity) from placement of the sampler to dissipate.

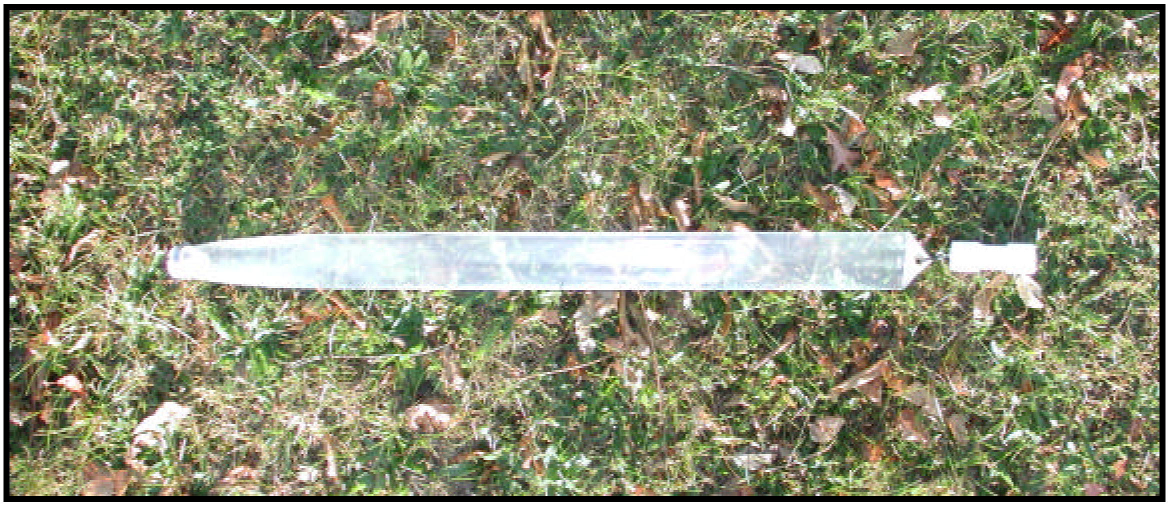

Figure 1. HydraSleeve™ Sampler

A sample is collected by pulling the HydraSleeve™ sampler up 6 to 12 inches and allowing it to drop back down to the initial position. During the up-stroke, the spring-loaded check valve opens and groundwater enters the flexible chamber. This process is repeated until the sampler is full. As the sampler is brought to the surface, a floating ball in the check valve prevents stagnant water above the screened interval from entering the sampler. Samples are collected by manually releasing the check valve and pouring the water into containers or by inserting a rigid plastic straw through the flexible chamber wall and directing the water into the sample containers (Figure 2). The plastic straw method results in minimal sample agitation and minimal exposure to ambient air.

At Site #1, the HydraSleeve™ samplers were installed in four monitoring wells approximately 1 week after low-flow sampling was performed. The HydraSleeve™ samplers were retrieved two weeks after installation, or approximately 3 weeks following sampling using low-flow methods. The timing of the zero-purge sampling relative to the low-flow sampling at Site #1 was due to scheduling issues unrelated to this study. Samples were analyzed for base/neutral extractable organic compounds by Method 8270C.

At Site #2, the HydraSleeve™ samplers were installed in 9 wells approximately 2 weeks prior to being retrieved. The low-flow replicate samples (both pump and bailer samples) were collected within 24 hours following zero-purge sampling. Samples were analyzed for polycyclic aromatic hydrocarbons by Method 8270C.

Figure 2. Zero-Purge Sample Collection

COMPARISON OF RESULTS

Results of analyses for fluorene, acenaphthylene, acenaphthene and naphthalene are presented in the tables and figures below. Other SVOCs were detected in the samples, but their occurrence was sporadic relative to these four compounds. For the sake of simplicity, the comparison is limited to these four commonly-detected compounds. Trends similar to those discussed below were observed for the other SVOCs detected.

Zero-Purge Versus Low-Flow Pump Discharge Samples

Results of analyses for fluorene, acenaphthylene, acenaphthene and naphthalene for samples collected using a HydraSleeve™ sampler and from the low-flow pump discharge are summarized in Table 2. On average, the SVOC concentrations for samples collected using zero-purge techniques were 122% higher than the corresponding concentrations for samples collected from the low-flow pump discharge. This comparison includes all compounds that were detected in at least one sample. In instances where a compound was reported in a sample collected using one sampling method, but not in the corresponding sample collected using the other method, one-half the reporting limit was used for the comparison.

Table 2. Comparison of SVOC Results (ug/l)
Zero-Purge vs. Low-Flow Pump

	Fluorene		Acenaphthylene		Acenaphthene		Naphthalene	
Well	**0-Purge**	**L-F/Pump**	**0-Purge**	**L-F/Pump**	**0-Purge**	**L-F/Pump**	**0-Purge**	**L-F/Bailer**
MW-3	8	7	5	<11	<11	<11	2200	1200
MW-6S	26	24	120	97	55	35	2700	2700
MW-6D	<10	<10	<10	<10	<10	<10	510	320
MW-7	<11	<10	<11	15	<11	<10	15	180
MW-1	4100	800	630	150	12000	2300	25000	10000
MW-6DD	590	580	1200	1100	140	130	14000	9600
MW-6xxD	10	7	50	29	23	15	2100	1200
MW-7xxD	<11	5	<11	6	32	31	430	340

On an individual well basis, 7 of the 8 wells in this data set had average zero-purge concentrations that were higher than the corresponding low-flow sample concentrations. The ratio ranged from a high of 4.96 (zero-purge results relative to low-flow results) for well MW-1 to a low of 0.54 (zero-purge results relative to low-flow results) for well MW-7. There was no discernable relationship between well construction specifications (e.g. depth, screened/open interval, diameter, etc.) and the ratio of zero-purge sample concentrations to low-flow sample concentrations.

The ratio of zero-purge sample concentrations to low-flow sample concentrations was markedly higher for well MW-1 than for the other 7 wells. Well MW-1 has exhibited a layer of light nonaqueous-phase liquid (LNAPL) during previous sampling events. A review of field notes recorded during zero-purge sampling activities indicates that the sample collected at well MW-1 was collected "from beneath an LNAPL layer. Small bit of LNAPL incorporated into sample." As such, it is likely that the LNAPL in the zero-purge sample from well MW-1 skewed the SVOC concentrations high relative to the corresponding low-flow sample concentrations.

Excluding the results for MW-1, the zero-purge SVOC sample concentrations were, on average, 17% higher than the corresponding low-flow pump sample concentrations. Figure 3 presents scatter plots of the data in Table 2, exclusive of the results for well MW-1. The zero-purge concentrations are plotted on the x-axis and the corresponding low-flow pump discharge concentrations are plotted on the y-axis.

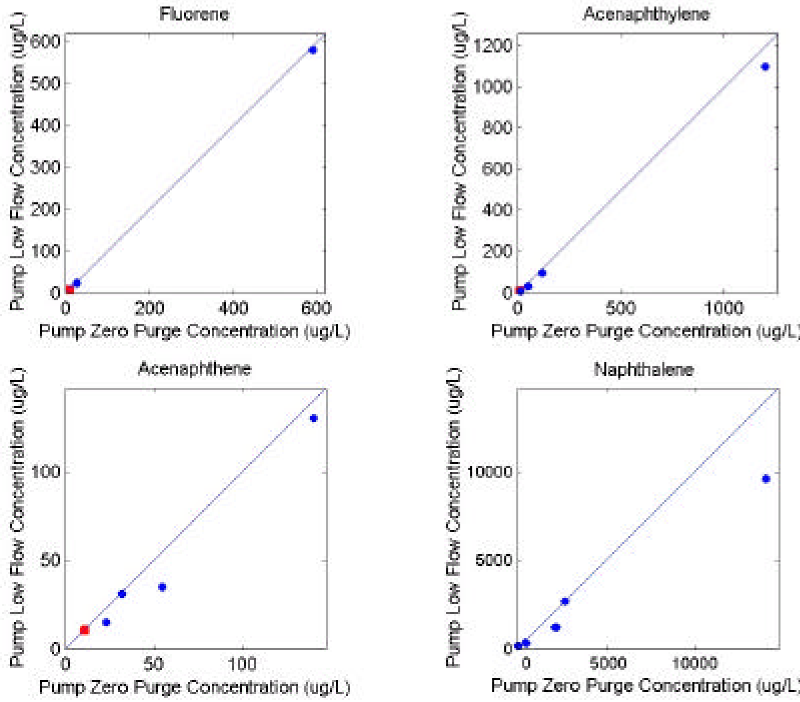

Figure 3. Zero-Purge (x-axis) Versus Low-Flow (y-axis) Results Excluding Well MW-1 Low-flow samples collected from pump discharge.

Zero-Purge Versus Low-Flow Bailer Samples

Results of analyses for fluorene, acenaphthylene, acenaphthene and naphthalene for samples collected using a HydraSleeve^{TM} sampler and from a bottom-loading bailer following low-flow purging are summarized in Table 3. On average, the SVOC concentrations (for all detected compounds) for samples collected using zero-purge techniques were 161% higher than the corresponding concentrations for low-flow bailer samples. Again, one-half the reporting limit was used for the comparison in cases where a compound was detected in a sample collected using one method, but not in the corresponding sample collected by the other method.

On an individual well basis, all wells in which SVOCs were detected produced higher concentrations via zero-purge sampling than via low-flow bailer sampling. The ratio for individual wells ranged from a high of 14.75 (zero-purge results relative to low-flow results) for well MW-7xxD to a low of 1.33 (zero-purge results relative to low-flow results) for well MW-7.

Table 3. Comparison of SVOC Results (ug/l)
Zero-Purge vs. Low-Flow Bailer

	Fluorene		Acenaphthylene		Acenaphthene		Naphthalene	
Well	**0-Purge**	**L-F/Bailer**	**0-Purge**	**L-F/Bailer**	**0-Purge**	**L-F/Bailer**	**0-Purge**	**L-F/Bailer**
MW-1	4100	1400	630	280	12000	3900	25000	10000
MW-2	<10	<1	<10	<1	<10	<1	<10	<1
MW-3	250	210	110	68	460	450	360	620
MW-4xD	30	4	150	21	32	15	2800	380
MW-4xxD	<11	<1	<11	<1	<11	3	54	40
MW-6DD	590	500	1200	1100	140	110	14000	9000
MW-6xxD	10	8	50	38	23	18	2100	970
MW-7D	<6	<0.9	<6	<0.9	<6	<0.9	<6	<0.9
MW-7xxD	<11	<1	<11	<1	32	4	430	20

Excluding well MW-1 (for which LNAPL was incorporated into the zero-purge sample), the zero-purge sample concentrations were, on average, 150% higher than the corresponding low-flow bailer samples. Figure 4 presents scatter plots of the data in Table 3, exclusive of results for monitoring well MW-1.

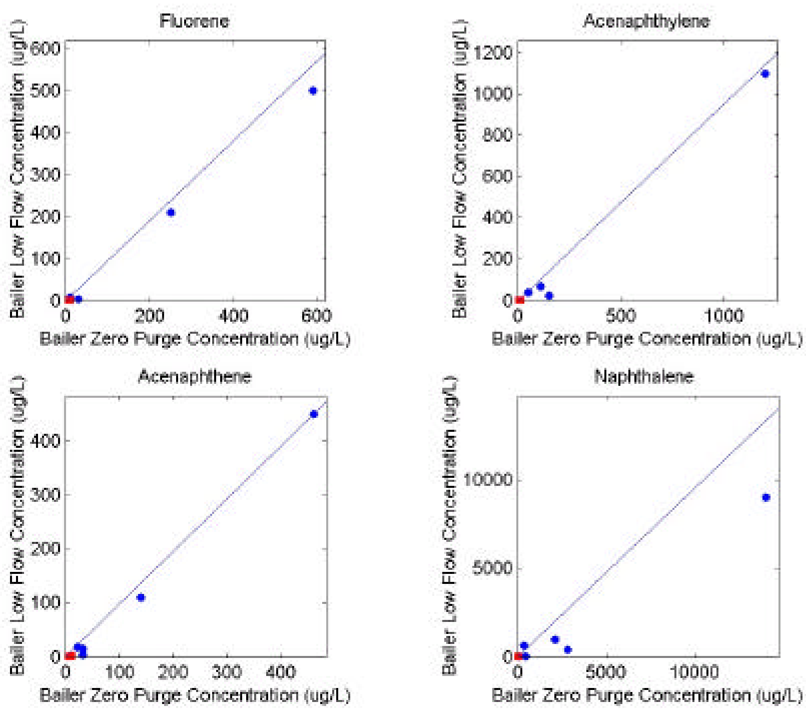

Figure 4. Zero-Purge (x-axis) Versus Low-Flow (y-axis) Results Excluding Well MW-1
Low-flow samples collected via bottom-loading bailer.

SUMMARY AND CONCLUSIONS

In this study, the zero-purge method was evaluated as a potential alternative to conventional low-flow techniques for the collection of groundwater samples for SVOC analyses. Groundwater samples for SVOC analyses were collected from monitoring wells at two MGP sites using a zero-purge HydraSleeve™ sampler. Replicate samples were collected using two variations on the low-flow sampling method, including: 1) low-flow purging and sample collected from the pump discharge; and 2) low-flow purging and sample collection via bottom-loading bailer. A comparison of the data generated by the zero-purge and low-flow methods yields the following observations:

- The presence of LNAPL precludes the effective use of HydraSleeve™ samplers.
- In the absence of an LNAPL layer, zero-purge SVOC sample concentrations were, on average, 17% higher than the concentrations reported for corresponding low-flow samples collected from the pump discharge.
- Zero-purge SVOC sample concentrations were significantly higher (150% higher, on average) than the corresponding concentrations reported for samples collected via bottom-loading bailer following purging using low-flow methods. The disparity between these two data sets may be attributable to inaccuracies in the low-flow bailer sampling methodology, particularly with regard to the depth at which purging is conducted via submersible pump and the depth at which the sample is subsequently collected via bailer.

The results of this study indicate that the zero-purge method is a technically sound alternative to conventional low-flow methods for collecting groundwater samples for SVOC analyses. The principles behind zero-purge sampling have already been accepted by various regulatory bodies, including the Interstate Technology Regulatory Cooperation Work Group (ITRC) and the Federal Remediation Technologies Roundtable (EPA, DOE, DOD, Department of Interior, Navy, Air Force, etc.). However, these groups have focused their studies on PDB samplers that are appropriate for VOC sampling, but are not amenable to SVOC sampling. On the basis of the data presented above, zero-purge sampling using the HydraSleeve™ sampler warrants consideration as an acceptable sampling procedure for SVOCs.

Zero-purge sampling offers a number of distinct advantages relative to more conventional sample collection techniques (e.g. low-flow sampling and purging of 3 to 5 well volumes). Advantages offered by the zero-purge sampling method include:

- The method does not require an electric power source and submersible pumps.
- Less labor is required relative to conventional methods. Zero-purge sampling, requires approximately 20 minutes per well as compared to approximately 45 minutes per well for low-flow sampling.
- Zero-purge sampling does not generate purge water that requires costly management and disposal.

Relative to low-flow sampling methods, zero-purge sampling can reduce groundwater sample acquisition costs by 30 to 50 percent.