Zero-Purge Groundwater Sampling
At A Spent Purifier Media Disposal Site

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ABSTRACT

A quarterly ground water monitoring program utilizing low-flow sampling techniques is being implemented at a site formerly used for disposal of spent purifier media from a nearby manufactured gas plant. In association with this on-going monitoring program, split samples were collected from 4 monitoring wells using zero-purge sampling procedures during three consecutive quarterly monitoring events. Zero-purge samples were collected using a HydraSleeve™ sampler and analyzed for volatile organic compounds (VOC), total metals and dissolved metals.

A comparison of the data generated during this study indicates that VOC results for samples collected by zero-purge methods were, on average, 14% higher than the corresponding results for samples collected using low-flow techniques. Total metals (unfiltered) results for samples collected by zero-purge methods were, on average, 108% higher than the corresponding dissolved metals (unfiltered) results for samples collected using low-flow methods. Dissolved metals results for samples collected using zero-purge methods were, on average, 19% higher than the corresponding dissolved metals results for samples collected by low-flow methods. The metals results indicate that filtering is a necessary step in the acquisition of dissolved metals data using zero-purge sampling methods.

This study demonstrates that zero-purge sampling is a technically sound alternative to conventional ground water sampling procedures. VOC and dissolved metals results for samples collected using the HydraSleeve™ sampler are comparable to results for samples collected using low-flow methods.

Relative to low-flow sampling, zero-purge sampling offers the following advantages:

- The need for an electric power source and submersible pumps is eliminated;
- Sample acquisition requires less labor; and
- No purge water is generated, eliminating the cost for management and disposal.

Zero-purge ground water sampling yields accurate, valid analytical results at nearly half the cost relative to conventional methods for sample acquisition.

INTRODUCTION

An on-going quarterly ground water monitoring program is being implemented at a site formerly used for the disposal of spent purifier media from a nearby manufactured gas plant. Under the program, ground water samples are collected using low-flow techniques in accordance with state-approved methodologies. In association with the conventional monitoring program, duplicate ground water samples were collected for three consecutive quarterly events using zero-purge techniques. The duplicate sampling was conducted to generate data for determining if zero-purge sampling is a technically sound alternative to more costly conventional ground water sampling methods.

Site Description

The site is a partially-wooded, 5-acre parcel that was historically used as a quarry. From pre-1940 to the early 1960's, spent gas filtration media from a nearby manufactured gas plant was disposed in the former quarry. Much of the former quarry was filled, but a small portion remains as a steep depression with several feet of standing water.

In 1999, remedial investigations commenced at the site under Pennsylvania's Land Recycling and Environmental Standards Act (Act 2) program. The remedial investigations included the installation of a network of monitoring wells and commencement of a quarterly ground water monitoring program. Ground water is present at a depth of approximately 70 feet below ground surface, within a thick, highly-weathered bedrock unit. Ground water beneath the site contains volatile and semivolatile organic compounds typical of MGP operations (e.g. benzene and naphthalene) at concentrations above state standards. Several metals are also present in site ground water at concentrations above state standards.

Zero-Purge Sampling

Zero-purge sampling is a relatively new method for obtaining ground water samples that utilizes passive (i.e. non-pumping) procedures. Zero-purge sampling is based on the principal that ground water flow through a well screen is horizontal and the well is in constant equilibrium with the adjacent water-bearing unit. As such, representative ground water 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 relatively impermeable or impermeable to semivolatile organic compounds (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 VOCs and metals). 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 within the screened 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 ground water 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. The plastic straw method results in minimal sample agitation and minimal exposure to ambient air.

The length and diameter of the flexible chamber can be adjusted as necessary to collect the requisite sample volume.

TECHNICAL APPROACH

Nine wells at the site were sampled in March, June and September 2001 using low-flow techniques. A submersible pump was lowered to the mid-point of the screened interval and ground water 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 for:

- VOCs by Method 8260B; and
- Dissolved Metals by Method 200.7/6010.

Metals samples were filtered using a 40-micron in-line filter.

At least 2 weeks prior to the low-flow sampling events, HydraSleeve™ samplers were installed in four of the monitoring wells. Details regarding the construction of the four wells selected for zero-purge sampling are provided in Table 1.

Table 1. Zero-Purge Well Details

Well Identification	Diameter (in.)	Screened Interval (feet below grade)	Depth to Water (feet below datum)
MW-3	4	73-83	74
MW-6	4	74-84	77
MW-6D	2	124-144	79
MW-7	4	66-76	70

Historical sample results indicated that these wells contained VOCs at relatively high (MW-6), medium (MW-6D and MW-3) and low (MW-7) concentrations. Well MW-6D is screened approximately 47 to 67 feet below the water table. The other three wells are screened across the water table.

The HydraSleeve™ samplers were suspended approximately 1 foot off the bottom in the three water table wells (MW-3, MW-6 and MW-7) and at the mid-point of the screened interval in the deep well (MW-6D). Within 4 hours prior to sampling via low-flow techniques, the HydraSleeve™ samplers were filled and retrieved as described above. A rigid plastic straw was inserted through the flexible chamber wall and containers were filled (Figure 2) for the following analyses:

- VOCs by Method 8260B;
- Dissolved Metals by Method 200.7/6010; and
- Total Metals by Method 200.7/6010.

Dissolved metals samples were passed through a 40-micron filter prior to adding preservative.

Figure 2. Zero-Purge Sample Collection

COMPARISON OF RESULTS

Volatile Organic Compounds

Results of analyses for benzene, toluene, ethylbenzene and total xylenes (BTEX) are summarized in Table 2. Other VOCs, including some chlorinated compounds, were detected in the samples, but their occurrence was sporadic relative to the BTEX results. For the sake of simplicity, the comparison is limited to BTEX compounds. Similar trends (as discussed below for BTEX compounds) were observed for the other VOCs detected.

On average, the BTEX results for samples collected using zero-purge techniques were 14% higher than the corresponding results for samples collected using low-flow techniques. The variations between the data sets were sample-specific and not compound-specific. The variation may be attributable to the loss of BTEX compounds through volatilization during sample collection using a submersible pump.

Figure 3 presents scatter plots of the data in Table 2, with the zero-purge concentrations on the x-axis and the corresponding low-flow concentrations on the y-axis. The two data sets show similar results, particularly at concentrations below approximately 1,000 ug/l. At concentrations above 1,000 ug/l, the zero-purge results were generally higher than the corresponding low-flow results.

Table 2. Comparison of BTEX Results (ug/l)

	Benzene		Toluene		Ethylbenzene		Xylenes	
	0-Purge	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**
MW-3								
March	750	580	680	580	55	44	320	360
June	600	580	630	570	55	45	440	360
September	580	580	600	550	55	44	450	370
MW-6								
March	3,300	2,100	6,500	3,900	630	370	2,400	1,440
June	2,100	2,300	4,900	3,800	550	430	2,140	1,690
September	1,400	1,600	3,300	2,700	420	300	1,700	1,180
MW-6D								
March	230	200	170	150	<20	12	86	99
June	170	190	130	150	12	13	98	109
September	170	160	140	110	12	10	114	78
MW-7								
March	30	29	34	37	8	12	64	72
June	37	32	54	41	14	12	94	73
September	26	31	38	39	6	9	77	73

Figure 4 presents scatter plots of zero-purge data versus low-flow data for results exclusive of monitoring well MW-6, which exhibited the maximum impacts.

On average, the zero-purge results for the lower concentration data set were 10% higher than the corresponding low-flow results.

As a practical matter, the two data sets showed 100% correlation with regard to state ground water standards. That is, all results reported in excess of state ground water standards for samples collected via low-flow techniques were also reported above the corresponding standards for samples collected via zero-purge techniques. The converse was also true in that all results below state standards for samples collected via low-flow techniques were also below state standards for the zero-purge data set.

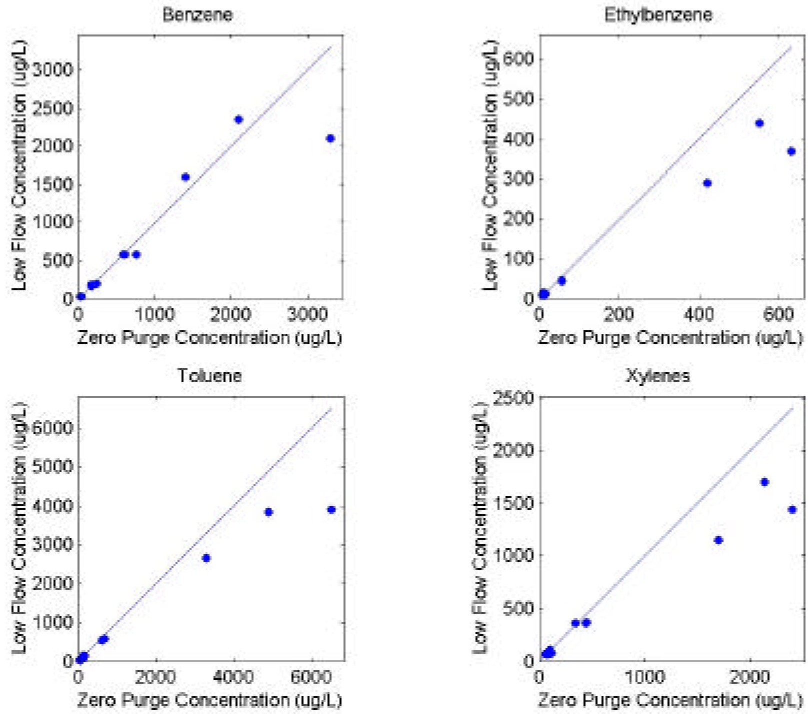

Figure 3. Zero-Purge Results (x-axis) Versus Low-Flow Results (y-axis). All data.

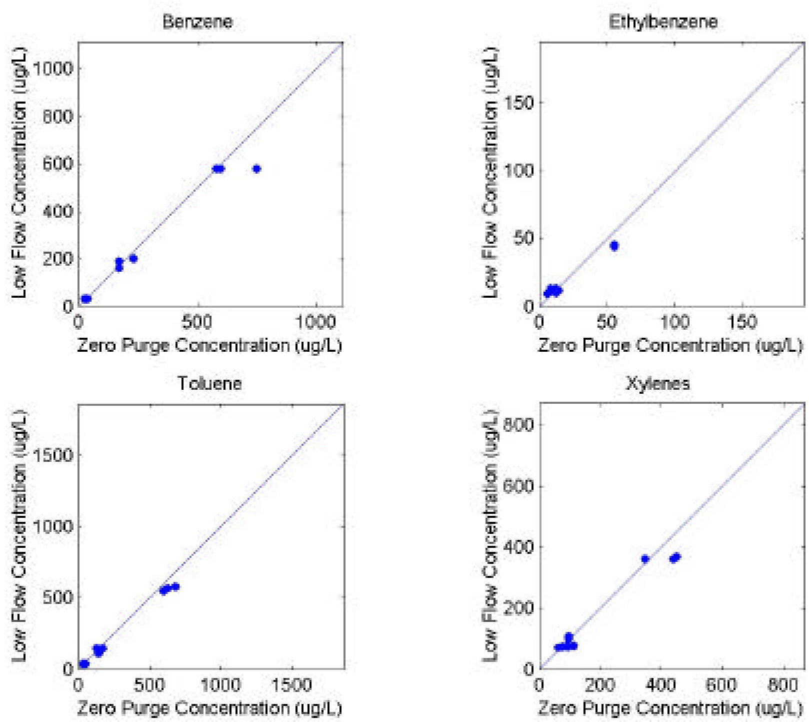

Figure 4. Zero-Purge Results (x-axis) Versus Low-Flow Results (y-axis). Exclusive of well MW-6.

Metals

Analyses were performed for 13 metals. The data base consisted of total and dissolved metals concentrations for samples collected using zero-purge techniques and dissolved metals concentrations for samples collected via low-flow techniques. Tables 3 and 4 summarize the results for cadmium, copper, lead and zinc. These four metals were detected most frequently and comparisons based on these metals are representative of the metals results not presented herein.

Zero-Purge Total Metals Versus Low-Flow Dissolved Metals. Table 3 presents a comparison of the total (unfiltered) metals results for samples collected via zero-purge methods and dissolved (filtered) metals results for samples collected via low-flow techniques.

Table 3. Comparison of Metals Results (ug/l)
Zero-Purge Total (unfiltered) Versus Low-Flow Dissolved (filtered)

	Cadmium		**Copper**		**Lead**		**Zinc**	
	0-Purge	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**
MW-3								
March	0.09	0.08	0.04	0.04	0.057	0.059	1.20	1.20
June	0.05	0.05	<0.1	<0.1	<0.02	0.03	1.10	0.94
September	0.05	<0.05	<0.10	<0.2	0.05	<0.05	1.10	1.00
MW-6								
March	1.10	1.10	0.82	0.83	0.14	0.13	13.0	12.0
June	1.20	0.22	1.50	0.30	0.04	0.09	14.0	6.1
September	1.20	0.90	3.00	1.80	0.09	0.08	18.0	14.0
MW-6D								
March	0.10	0.089	0.10	0.02	0.51	0.091	9.90	7.90
June	1.10	0.04	1.40	<0.10	0.04	0.06	14.00	5.70
September	0.06	0.04	<0.10	0.03	0.20	0.07	7.60	7.30
MW-7								
March	0.005	<0.004	<0.02	<0.02	<0.005	<0.005	0.08	0.03
June	<0.005	<0.005	0.02	<0.02	<0.005	<0.005	0.12	0.03
September	<0.005	<0.005	<0.02	<0.02	<0.005	<0.005	0.07	0.04

In general, the two data sets compare favorably. However, there are several instances where the zero-purge total metals concentrations exceed the corresponding low-flow dissolved metals concentrations by an order of magnitude. Examples include the June cadmium results for MW-6D, the June copper results for MW-6, the September lead results for MW-6D and the June zinc results for MW-7. These spurious results may indicate that metals-bearing particulates were incorporated into the unfiltered samples collected via the zero-purge technique.

On average, the zero-purge total metals results were 108% greater than the corresponding low-flow dissolved metals results.

Zero-Purge Dissolved Metals Versus Low-Flow Dissolved Metals. Table 4 presents a comparison between dissolved (filtered) metals results for samples collected by zero-purge and low-flow techniques.

Table 4. Comparison of Metals Results (ug/l)
Zero-Purge Dissolved (filtered) Versus Low-Flow Dissolved (filtered)

	Cadmium		Copper		Lead		Zinc	
	0-Purge	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**	**0-Purge**	**Low-Flow**
MW-3								
March	0.08	0.08	0.04	0.04	0.060	0.059	1.10	1.20
June	0.05	0.05	<0.1	<0.1	<0.02	0.03	1.20	0.94
September	0.05	<0.05	<0.10	<0.2	0.05	<0.05	1.00	1.00
MW-6								
March	1.10	1.10	0.84	0.83	0.16	0.13	12.0	12.0
June	0.05	0.22	<0.10	0.30	0.18	0.09	7.3	6.1
September	1.00	0.90	2.40	1.80	0.09	0.08	15.0	14.0
MW-6D								
March	0.07	0.089	0.04	0.02	0.13	0.091	7.80	7.90
June	0.04	0.04	0.14	<0.10	0.08	0.06	7.20	5.70
September	0.05	0.04	<0.10	0.03	0.09	0.07	6.80	7.30
MW-7								
March	0.004	<0.004	<0.02	<0.02	<0.005	<0.005	0.04	0.03
June	<0.005	<0.005	<0.02	<0.02	<0.005	<0.005	0.05	0.03
September	<0.005	<0.005	<0.02	<0.02	<0.005	<0.005	0.05	0.04

The two data sets for dissolved metals compare favorably. On average, the zero-purge dissolved metals results were 19% higher than the corresponding low-flow dissolved metals results.

There is greater consistency between the dissolved metals data sets than between the total and dissolved data sets discussed above. This suggests that filtering is a necessary step for obtaining accurate dissolved metals results using the zero-purge sampling method.

With regard to state ground water standards, results for the two sampling techniques were generally consistent. In most cases, concentrations reported above the corresponding state standard for low-flow samples were also reported above the standard for zero-purge samples. Exceptions to this rule typically involved results near the standard or instances of suspected calculation errors on the part of the analytical laboratory.

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 ground water samples for VOC and metals analyses. On the basis of the data generated, the following observations are made:

- VOC results for samples collected using zero-purge techniques were, on average, 14% higher than corresponding results for samples collected by low-flow methods.
- Zero-purge and low-flow samples are in agreement with respect to state ground water standards for VOCs.
- Total (unfiltered) metals results for samples collected via zero-purge methods are not comparable to dissolved (filtered) metals results for samples collected via the low-flow method. The disparity between the two data sets is apparent in a number of instances where the zero-purge total metals results exceed the corresponding low-flow dissolved metals results by an order of magnitude.
- On average, zero-purge total metals results exceed the corresponding low-flow dissolved metals results by 108%. This suggests that sample filtering is necessary to generate dissolved metals results for samples collected via zero-purge methods.
- Dissolved (filtered) metals results for samples collected by the zero-purge and low-flow methods compare favorably. On average, the zero-purge dissolved metals results were 19% higher than the corresponding results for samples collected via low-flow methods.

The results of this study indicate that the zero-purge method is a technically sound alternative to conventional low-flow methods for collecting ground water samples for VOC and dissolved metals analyses. Zero-purge sampling using PDB samplers has 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.). On the basis of the data presented above, zero-purge sampling using the HydraSleeve™ sampler also warrants consideration as an acceptable sampling procedure.

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). Zero-purge sampling eliminates the need for an electric power source and submersible pumps. Zero-purge sampling requires less labor than conventional methods, requiring approximately 20 minutes per well as compared to approximately 45 minutes per well for low-flow sampling. Finally, 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 ground water sample acquisition costs by 30 to 50 percent.

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