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Evaluation of Micropurging Versus Traditional Groundwater Sampling at the Department of Energy's Kansas City Plant

Kansas City Division

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EVALUATION OF MICROPURGING VERSUS TRADITIONAL GROUNDWATER SAMPLING AT THE DEPARTMENT OF ENERGY'S KANSAS CITY PLANT

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85

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EVALUATION OF MICROPURGING vs. TRADITIONAL GROUNDWATER SAMPLING AT THE DEPARTMENT OF ENERGY'S KANSAS CITY PLANT

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ABSTRACT

A field trial comparing the micropurge and the traditional purge and sample method of groundwater sampling was conducted at the U.S. Department of Energy (DOE), Kansas City Plant (KCP) in 1993 and 1994. Duplicate groundwater samples were collected using traditional and micropurge methods, analyzed for selected organic and inorganic constituents, and the results compared statistically. Evaluation of the data using the Wilcoxon Sign Rank test indicates that within a 95% confidence interval, there was no significant difference between the two methods for the site contaminants and the majority of naturally occurring analytes. These analytical results were supported by visual observations with the colloidal borescope, which demonstrated impacts on the flow system in the well when using traditional sampling methods. Under selected circumstances, the results suggest replacing traditional sampling with micropurging based on reliability, cost, and waste minimization.

INTRODUCTION

Traditional sampling practices for groundwater monitoring wells commonly consist of purging three or more well volumes prior to sample collection. The rationale for purging wells is to remove stagnant water from the wellbore in order to permit representative water from the surrounding porous medium to enter the well.

The alternative sampling approach using micropurging is based on the premise that stagnant water in the well casing does not mix with groundwater flowing through the screen. Using tracer experiments, Robin and Gillham (1987) showed that groundwater moves through the screened portion of a well with little interaction or mixing with stagnant water in the

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overlying well casing. Similar studies by Powell and Puls (1993) supported this observation. These studies suggest that flow in the well screen is horizontal and laminar.

Using the colloidal borescope Kearl et al. (1992) suggested that water samples taken directly from the screened interval with a dedicated sample device were representative of groundwater in the surrounding formation and that purging several well volumes prior to sample collection is unnecessary. Mixing of the stagnant water with formation water in the screened interval of the well is avoided when the dedicated sample device is left in place such that flow in the screened interval is not disturbed. By using low pumping rates, only fresh formation water and only particles that are being advected by groundwater flow are sampled. Sampling at low flow rates without filtering, therefore, allows quantification of the total "mobile" pollutant load. In other words, both the contamination that is moving in the dissolved phase and contamination sorbed to mobile particles is being measured.

To determine whether groundwater samples collected by the micropurge methodology had application at the KCP, a site with very low flow rates and slightly reducing conditions, a comparison study was conducted. Consequently, samples were collected at low rates, (~ 100 ml/min); using a dedicated sampling pump to prevent disturbing the well. Only the sample tubing and pump are purged. The purging of three or more wellbore volumes associated with traditional sampling is eliminated, as are the large volumes of purge water requiring disposal. The two sampling methods were statistically compared to determine if differences exist.

Twelve sample events were conducted from February 1993 to March 1994 on six monitor wells. Wells were selected based on historical VOC concentrations to test the micropurge methodology on two predominantly clean wells (<100 ppb total VOCs); two moderately contaminated wells (100-1500 ppb VOCs); and a highly contaminated well (>1500 ppb VOCs). In addition, all selected wells had moderate to high values of inorganic compounds such as iron (5-45 mg/L), calcium (150-200 mg/L), magnesium (5-25 mg/L), and manganese (2-11 mg/L).

METHOD

Dedicated submersible pumps were installed in monitor wells with pump screens installed in the mid-portion of the well screen. Pumps were precalibrated to pump at 100 - 200 ml/min. The pumps were suspended in the middle portion of the screened interval by stainless steel wire rope fitted with 1/4" ID teflon discharge tubing and secured to a stainless steel quick connect mounted in a PVC well cap. The sample line discharge "pigtail" consisted of 1/4" ID Teflon tubing and was affixed to the quick connect in the PVC caps during sample events. The customized well caps were mounted snugly into the two inch PVC well casing preventing any unwanted motion of the pump when sampling.

Micropurge sampling was conducted initially followed by the traditional method of purging three bore volumes prior to sample collection. Data collected in the field (i.e., depth to water, pH, conductivity, temperature, volume of water prepumped, and pertinent well physical information) was recorded. For both, specific sampling methodology is described below.

Twelve test events were conducted over a 13-month period to account for seasonal variations. Previous investigations at the KCP have identified the presence of VOC contaminated groundwater. Metals contamination in site groundwater is not of concern and no inorganic plume development has been identified. Metals were sampled during this study as an additional basis of comparison, however.

Site soils are comprised of clayey silts with groundwater flow rates comparatively low (hydraulic conductivity 1.5 - 2.3 ft/day) which magnify the effect of colloids mobilized by high flow rate purging and sampling. Assuming proper well installation, water in this portion of the well is continuously exchanged with that of the surrounding aquifer. Samples collected at low flow rates with dedicated devices draw the sample from the screened portion of the well which is continuously replenished with water from the surrounding aquifer.

Dissolved phase transport is the primary migration component for VOCs. Therefore, minimal differences were expected in a head-to-head comparison of the two sample methodologies. Results of the two sample methodologies were not expected to be comparable for inorganics because the colloidal transport of inorganics is a major migration component and high concentrations of naturally occurring iron and manganese at the Kansas City Plant.

SAMPLING PROCEDURES - SPECIFIC

Micro-purge - The following steps were performed in the order and manner below:
A gas-powered generator powered the pump and controller box. Water discharge rates were slowly adjusted to achieve the desired 100-150 ml/minute discharge rate. Water was **continuously** extracted at ~100-150 ml/min during sampling. Two volumes of the sample discharge line were purged (~1 liter), VOC samples were collected, followed by collection of filtered and unfiltered inorganics.

Traditional Bailer Sample - The following steps were performed:
The well was purged at ~1 gal/min using the installed dedicated pump. Purging continued until temperature, conductivity, and pH stabilized, or three well bore volumes were extracted. The dedicated pump was then extracted and after the well had recovered a minimum of 95% of the initial static water elevation, sampling was initiated. Using a stainless steel bailer equipped with a bottom emptying device, VOC samples were collected followed by collection of filtered and unfiltered inorganics utilizing a peristaltic pump.

QA/QC

VOC trip and equipment blanks were collected and analyzed for each sample event. Since the micropurge sample methodology utilizes dedicated equipment, equipment blank contamination is not a concern. Other QA/QC steps specific to the lab included matrix spike/matrix spike duplicate (MS/MSD) analysis, laboratory control samples, method blanks, and surrogates.

DISCUSSION OF RESULTS

FIELD STABILIZATION RESULTS

Field stabilization readings of temperature pH and conductivity were collected and analyzed in a flow-through cell, and compared during the study. During the micropurge test, field sampling measurements were not measured immediately upon initiation of purging. The submersible pump and associated lines were purged, then VOCs and inorganics were collected in series. The flow through cell was then filled and approximately two cell volumes purged and stabilization parameters measured for micropurge. For a given well, approximately 4 liters were usually purged prior to obtaining the first field measurement during the micropurge sample event. Field stabilization readings were recorded after three bore volumes (~45 liters/well) had been purged during the traditional sample event.

Stabilization Parameter Comparisons

Comparison of pH, temperature, and conductivity values were compared from the first micropurge field measurement reading to the last reading collected after traditional purging. Values for pH were within plus or minus ten percent with two exceptions (DOE 1994). Temperature values were likewise comparable with the exception of one sampling event (DOE 1994). Freezing temperatures caused sample equipment to get progressively colder at a given well resulting in a lower value for the last reading. Conductivity values were not as comparable, however. Approximately half of the values did not satisfy the plus or minus ten percent criteria with one well (64L) consistently giving values beyond the ten percent stabilization criteria (DOE 1994). Elevated iron concentrations in this well and associated suspended solids during traditional purging accounted for this discrepancy.

Discounting the conductivity results determined in well 64L and temperature results from the March 1993 sample event, field stabilization tests are comparable between the two sample methodologies. Based on the above, results do not indicate the need to purge large volumes of water from the well prior to sample collection.

DATA ANALYSIS

Before presenting the data comparison and statistical review of results from the two sampling methods, two issues must be emphasized. The first is that the contaminants of interest, and the ones for which monitoring is required by EPA at all but one location at the KCP, are the organic compounds. Considerable data exist to demonstrate that there is no inorganic contaminant plume development at the KCP. The second issue of importance is the site's physical characteristics: site soils are clayey-silts, groundwater flow rate is slow, and subsurface conditions are reducing. Slow flow rates and reducing conditions are obviously the circumstances under which it is most difficult to demonstrate the acceptability of micropurging for inorganic constituents primarily because of the redox-sensitive elements (iron and manganese). Redox sensitive elements are prone to significant fluctuations in concentration when redox conditions change such as when a sample from a slightly reducing environment is brought to the oxygenated surface environment (Kearl et al. 1994).

VOCs and 23 metals were analyzed with each sampling event, however, only those constituents detected are discussed. Following is a well by well discussion of results for organics and total and filtered inorganics. A statistical review of the data follows the well by well comparison.

Data Discussion

Well KC97-58U

Organics - This well was sampled 8 times during the comparison study from February to August 1993. Traditional sampling detected a cumulative total of 544 ppb of organics from the eight sampling events consisting of chloroethene, methylene chloride, 1,2 dichloroethylene (1,2 DCE), trichloroethylene (TCE) and methyl isobutyl ketone (MIBK). Micropurge sampling detected a total of 431 ppb (total) of the same organics.

Inorganics - The following elements were detected: Aluminum (Al), Arsenic (As), Barium (Ba), Cadmium (Cd), Calcium (Ca), Copper (Cu), Iron (Fe), Lead (Pb), Magnesium (Mg), Manganese (Mn), Potassium (K), Sodium (Na) and Zinc (Zn). Aluminum was effectively removed by filtering in all but two samples. Similar concentrations were noted for all other analytes from this well.

Well KC87-64L

Organics - This well was sampled 8 times between February and August 1993 with contaminants consisting of vinyl chloride, 1,1 dichloroethylene (1,1, DCE), 1,2 DCE and TCE. Total VOC results for the 8 sampling events for micropurge totaled 49,373 ppb with traditional sampling totaling 44,380 ppb.

Inorganics - Al, As, Antimony (An), Ba, Cd, Ca, Fe, Pb, Mg, Mn, K, Se, Na, and Zn were detected in this well. Micropurge samples were slightly but consistently higher than traditional sample results for Ba, Ca, Fe, Mg, Mn, and Na. All other compounds exhibited good correlation between sampling methods. Aluminum was effectively filtered out in both sampling methods in all but one case.

Well KC87-76L

Organics - This low level contaminated well was also sampled 8 times between February and August 1993. Micropurge sampling detected organics totaling 273 ppb with traditional sampling from the eight events totaling 237 ppb. Contaminants consisted of vinyl chloride, 1,2 DCE and TCE.

Inorganics - Al, As, Ba, Cd, Ca, Fe, Mg, Mn, K, Na and Zn were detected in this well. Filtering effectively removed Al in all but one sample. Good agreement existed between all other compounds during sampling.

Well KC91-168L

Organics - This contaminated well was sampled four times between March and April 1994 with contamination consisting primarily of 1,2 DCE with one detection of methyl bromide during the first test event. During four sample events total VOCs for the micropurge method equaled 16,370 ppb with the traditional sampling method totaling 7700.

Inorganics - Al, As, An, Ba, Cd, Ca, Cr, Cu, Fe, Mg, Mn, K, Na, and Zn were detected in this well. Traditional sampling produced higher sodium results on average while manganese results for micropurge were slightly higher on average.

Well KC85-34L

Organics - This contaminated well was sampled four times between March and April 1994. Contaminants included only TCE and 1,2 DCE. Total organics for the four sampling events for the micropurge method totaled 23,570 ppb while traditional sampling totaled 21,480 ppb.

Inorganics - Al, As, An, Ba, Cd, Ca, Fe, Mg, Mn, K, and Zn were detected from this well. An overall good agreement was noted between all compounds sampled.

Well KC85-39U

This low level contaminated well was sampled between March and April 1994 and exhibited contamination only by 1,2 DCE. Micropurge sampling from the four sampling events totaled 666 ppb with the traditional method totaling 680 ppb.

Inorganics - Al, As, An, Ba, Cd, Ca, Fe, Mg, Mn, K, Na, and Zn were detected in this well. An overall good agreement was noted among all elements detected. A few sporadic detections of inorganics were noted but no pattern existed as the scattered detections were noted from traditional sampling for some elements and from micropurge for others.

Statistical Review

Table 1 is a statistical comparison of micropurge versus traditional sampling for organic compounds. Table 2 is a statistical comparison of micropurge non-filtered versus traditional filtered inorganic samples. The logic behind this comparison is that the micropurge methodology does not mobilize colloidal sized particles and the traditionally collected filtered sample removes mobilized colloids when a 0.45 micron filter is used.

The objective of the statistical analysis was to evaluate the equivalence of the micropurge sample methodology to the traditional bailer method. Equivalence of the methods was assumed to be that, from a given well on a given day, the values obtained from the two sampling methods have the same distribution. If the two methods are not equivalent, the difference was assumed to be due to sampling heterogeneity. The data collected was intended to compare the methods on this basis. The samples are paired in that they were collected from the same well on the same date and were analyzed on the same date.

The expected results of this study were to observe no significant change in VOC analysis when comparing the two sampling methods as it was assumed that the traditional sampling

TABLE 1

STATISTCAL COMPARISON OF MICROPURGE vs TRADITIONAL ORGANIC SAMPLES WILCOXOX RANK

VINYL CHLORIDE ORDERED DIFFERENCE	RANK	1,2 DCE ORDERED DIFFERENCE	RANK	TCE ORDERED DIFFERENCES
-1	2.5	-1	1	-3.5
-1	2.5	2	2	-50
-1	2.5	-3	3	-100
-1	2.5	-4	4.5	-355
-2	5.5	-4	4.5	500
-2	5.5	-5	6	600
-5	7.5	-7	7.5	700
-5	7.5	7	7.5	-840
-6	9	10	9	-1140
7	10.5	-20	10	-1175
7	10.5	-50	11	-2475
-9	12.5	100	13	WSR calc.
9	12.5	100	13	NUM +'s
10	14	-100	13	sign prob
11	15	120	15	WSR (.01)
-17	16	170	16	
80	17	500	17	
150	18	700	18	
220	19	1100	19	
220	20	1700	20	
-460	21	2100	21	
700	22	3100	22	
WSR calc.	-34	-3500	23.5	
NUM +'s	10	3500	23.5	
SIGN PROB	0.588	3600	25	
WSR (.01)	-77.5	5900	26	
		WSR calc.	91.5	
		NUM -'s	10	
		sign prob	0.1634	
		WSR (.01)	99.5	

TABLE 2

STATISTICAL COMPARISON OF MICROPURGE vs TRADITIONAL FILTERED INORGANIC SAMPLES

ELEMENT	N	MEAN	STD	T	PROBT	MSIGN	PROBM	SIGNRANK	PROBS	NORM	PR_N	UCL975	LCL975
Al	31	0.4431	0.7165	3.44317	0.0017	12.5	0	215	0	0.85402	0.0004	0.7059	0.1803
As	29	0.0388	0.096	2.17757	0.038	8	0.0037	125.5	0.0025	0.65689	0.0	0.0753	0.0023
Ba	36	0.1334	0.2062	3.88024	0.0004	11	0.0003	241.5	0	0.81406	0	0.2031	0.0636
Ca	36	7.8389	16.7067	2.81523	0.008	8	0.0113	158	0.0109	0.93026	0.0318	13.492	2.1861
Fe	36	10.069	14.1612	4.26597	0.0001	15	0	294	0	0.78062	0	14.86	5.2771
Mg	36	1.8336	3.5246	3.12136	0.0036	8	0.0113	167	0.0068	0.86892	0.0003	3.0262	0.6410
Mn	36	2.0652	3.1335	3.95437	0.0004	10.5	0.0005	218	0.0001	0.82075	0	3.1254	1.0049
Na	36	-2.119	7.9606	-1.59746	0.1192	-4	0.2153	-54	0.3203	0.78222	0	0.574	-4.811
Zn	30	-0.002	0.0194	-0.679	0.5025	-5	0.0987	-65.5	0.1822	0.94088	0.113	0.0048	-0.0096

Legend:

Mean = Sample mean

STD = Sample standard deviation

T = t statistic

PROBT = Significance value of T

MSIGN = Centered sign test statistic

SIGNRANK = WSR statistic

PROBS = SIGNRANK significance value

NORM = Test statistic for mormality

PR_N = Significance value of NORM

PROBM = Significance value of MSIGN

UCL 975 = Upper limit of the 95% confidence interval for the mean difference

LCL 975 = Lower limit of the 95% confidence interval for the mean difference

WSR = Wilcoxon signed rank

methodology produced representative results. VOCs, the contaminants of concern at the KCP do not sorb onto aquifer materials, therefore, influences caused by the mobilization of colloids were expected to be minimal. Additionally, utilizing micropurge sampling techniques assumes that no mixing of water occurs between the screened portion of the well bore and groundwater lying stagnant in the well casing. Indeed, results of the statistical comparison between traditionally collected VOC samples and samples collected by the micropurge technique do not show statistically significant variations (Table 1).

Results from the comparison of metals data collected by each methodology were not expected to be comparable. It has been previously established by numerous authors (Puls and Powell, 1992, Kearl et al., 1992) that purging the well at high rates mobilizes colloidal particles, transporting otherwise immobile inorganic species. For comparison purposes, however, filtered and unfiltered metal's samples collected by traditional methods and micropurged methods were statistically compared.

A test of normality of the differences across all wells and dates was performed to determine the applicability of parametric or nonparametric tests. The tests for normality conclude that the data for both inorganic and organic compounds are not normal (at the five percent level of significance). Therefore, a nonparametric test, the Wilcoxon signed rank (WSR) test was applied. Monitor wells identified for this study were chosen with relatively low, medium, and high concentrations of VOCs, thus biasing the distribution of data non-normally.

A minimum of six valid data pairs were required for statistical comparison. Tables 1 and 2 summarize results of statistical comparisons of organic and inorganic data. Table 1 lists the summary statistics for organic compounds. Two columns are provided for each organic compound on Table 1, the first is the ranked differences of the raw data and the second is the rank. If the smallest sum of positive ranks less $n(n+1)/4$ is within the upper and lower critical value, the result in not rejected (i.e., no statistical difference). This is determined on Table 1 by comparison of the absolute value of the WSR(.01) value to the WSR calc. value. No statistical difference is determined if the WSR(.01) value is greater than the WSR calc. value. Results of the study determined no significant difference between analysis of samples collected by micropurge versus traditional methodologies for VOCs.

Table 2 lists summary statistics for comparison of inorganic constituents collected by micropurging and those collected "traditionally" and filtered with a 0.45μm filter. The column of most interest on this table is PROBS. Values greater than 0.05 are not significant at the five percent level meaning comparison of values determined by analysis of samples collected by the two methodologies are not statistically different. Sodium and zinc were not significant at the five percent level. Comparison of results for aluminum, arsenic, barium, calcium, iron, manganese, magnesium, and zinc were determined statistically different. As stated above, these results are not unusual. For example, it is difficult to obtain accurate values for trace levels of iron in groundwater (Urasa and Mavura, 1992). The difficulties are due to the complexity of irons' aqueous chemistry, which is greatly affected by redox conditions. The principal problem is the sampling and analysis of colloidal iron (Kennedy et al. 1974). Neither samples collected by traditional or micropurge methodology were consistently higher for inorganic analytes.

BENEFITS

Dedicated Systems

Dedicated systems eliminate the need to collect samples to assess the effectiveness of decontamination efforts. With conventional sampling equipment, a sample blank is collected every 10 samples. With dedicated samples, the potential for cross contamination is eliminated. Monitoring wells do not have to be re-sampled to prove that the analytical results are not affected by ineffective decontamination.

Waste Minimization

As a part of waste minimization efforts at the KCP, the process of sampling groundwater was characterized and evaluated with alternatives that would minimize the generation of both hazardous and non hazardous waste. As a result of implementing the micropurge sampling technique in 60 well completions a savings of almost 21,000 pounds of waste and $7200.00 in waste disposal costs are realized on an annual basis.

Sampling Time

Sampling times were evaluated as a part of the project. Sampling times for wells sampled for VOCs were reduced by 75% while times for wells sampled for both metals and VOCs were reduced by 50% . Sample costs were estimated by an outside vendor to be 50% cheaper using this method.

CONCLUSIONS

The micropurge sampling methodology was found to be a more time efficient, cheaper, and, in the case of organics analysis, statistically similar to the traditional bailer method of sampling. It was also found to produce less waste than the traditional method. Samples for the analysis of metals should also be collected by micropurge sampling methodology without filtration. Numerous researchers, as referenced in this paper, have noted that sampling without filtration at low flow rates produces samples most representative of aquifer conditions.

Based on the study outlined in this paper, the KCP solicited Missouri Department of Natural Resources and EPA approval to sample groundwater utilizing the micropurge process. Regulatory approval has been obtained and dedicated sample systems will be installed in 1995 to facilitate the micropurge sampling process.

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