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ABSTRACT

The Savannah River Site has conducted a study to statistically quantify differences in metals concentrations as a function of sampling device and filter treatment. Twelve wells screened in unconsolidated coastal plain sediments were sampled for the study. All wells had histories of detectable toxic metals concentrations. Unfiltered and filtered (using 10 and 0.45 micron filters) samples were collected from all wells to evaluate the effects of filtering. To compare the effects of sampling device, the wells were sampled twice, once with a bladder pump and once with a centrifugal pump. An analysis of covariance (ANCOVA) method was used to assess the effects of sampling device and filtration on metals concentrations considering the variation in pH, conductivity, and turbidity among samples. This study demonstrates that when controlled sampling techniques are employed, differences in toxic metals concentrations between filtered and unfiltered samples are not statistically significant. However, variations in sampling devices yield samples with statistically different metals concentrations. The centrifugal pumps, which cause more agitation of the sample and the screened zone than bladder pumps, yield samples with statistically higher metals concentrations.

INTRODUCTION

Routine groundwater monitoring at the Savannah River Site (SRS) is performed quarterly by trained samplers using standardized site procedures [1] and centrifugal pumps. The wells sampled for this study were installed using mud rotary drilling and developed according to standardized procedures [1]. Installation procedures call for 3"-4" well casings, 0.125" slot size, and gravel pack. All monitoring wells are screened in unconsolidated sands, silts, and clays of the clastic Coastal Plain sediments, and many produce turbid samples. Therefore, as previously advisable under such conditions [2], samples for toxic metals analyses are filtered through 0.45 micron tortuous path filters prior to acid preservation (pH < 2).

Recent studies on sampling procedures [3, 4] suggest that the use of 0.45 micron filters may result in unrepresentative samples, prompting regulatory agency guidance prohibiting filtered samples. However, acid preservation of turbid samples may result in overestimation of mobile contaminants due to dissolution of immobile particulates, yielding apparent metals concentrations that do not comply with regulatory water quality standards. This concern is supported by a study on lead in water samples [5].

Sample collection using sampling devices with high flow rates may also bias detected contaminant concentrations. Recent research suggests that use of centrifugal pumps with flow rates of 10-20 liters/min may agitate the sample resulting in increased turbidity or formation of colloids [6] and volatilization of organic contaminants (VOCs) [2]. Thus, current regulatory agency guidance specifies sampling devices that produce less turbulence, such as bladder pumps [7], for sampling sites with VOCs or toxic metals.

Prior to altering groundwater sampling procedures to reflect these developments, SRS initiated a site-specific study to determine the effect of sampling changes on detected metals concentration. A statistically rigorous study was designed to detect differences in metals concentrations between unfiltered, 10 micron filtered, and 0.45 micron filtered samples, and to detect differences in metals concentrations in samples collected with bladder and centrifugal pumps. This paper presents a statistical analysis of the study data and the resulting improvements to SRS sampling procedures for collection of representative groundwater from aquifers located in unconsolidated, coastal plain sediments.

DISCUSSION

Experimental Design

Three filtration treatments and two sampling devices were examined in this study. Sampling devices were evaluated by sampling each well twice, once using a bladder pump and once by centrifugal pump. Two types of submersible centrifugal pumps were used: either 4" diameter Grundfos centrifugal pumps with stainless steel (SS) housings and impellers or 3" diameter Standard pumps with SS housings and plastic impellers. The bladder pumps used were submersible 1.5" diameter QED Well Wizards, with SS pump casings and Teflon bladders. Samples collected with each device were divided into three aliquots. The aliquots were either filtered with membranes of 10 µm pore size, 0.45 µm pore size, or not filtered. Filters used were Micron Separations nylon tortuous path filters, 142 mm in diameter. All aliquots were analyzed by the same laboratory to avoid interlaboratory variability.

Of approximately 1200 SRS monitoring wells, twelve were selected on the basis of detectable levels of toxic metals, sufficient water production, and a range of turbidity (0.5-350 NTU in unfiltered samples). During purging and sampling, the pH, conductivity, and temperature were monitored to ensure sufficient purging of the well. Turbidity, pH, and conductivity were included as covariates in all statistical analyses since these parameters may covary (or correlate) with the contaminant concentration. The method known as analysis of covariance (ANCOVA) [8] tested effects of sampling device and filtration treatment versus pH, conductivity, and turbidity.

Potential sample variation caused by increased turbidity or changes in groundwater chemistry due to pump replacement was partitioned by a cross-over design feature [9] such that the 12 wells in this study were randomly divided into two groups of six wells. The order of the sampling devices used in each subset of wells differed (i.e. sampling first with a bladder pump followed by a centrifugal pump or *vice versa*) in order to partition variation in pump sequence from random sample measurements variation [9].

Sample Collection

Sampling occurred in October, 1990, according to standardized sampling procedures [2]. During purging, flow rates using centrifugal pumps ranged from 53 liters per minute to 15 liters per minute. Although the flow rate was manually reduced at the sampling port to achieve non-turbulent flow during sampling, the centrifugal device continued to pump at the same rate. Bladder pump flow rates ranged from 4 liters/minute to 0.5 liters/minute during purging and sampling.

All equipment was thoroughly rinsed with distilled water before sampling. For filtered samples, the first 100 mL of sample flushed through the filtering device was discarded. Immediately after collection, all samples were preserved with 50% nitric acid to pH < 2.

Field and Laboratory Measurements

Field pH measurements were obtained using a Microcomputer pH Vision Probe, Model 6077, manufactured by Markson Scientific. The pH meters were calibrated prior to each sampling event using pH 4 and pH 7 standard buffers. Conductivity measurements were obtained using an Amber Science, Inc. conductivity meter (Model 604) which was calibrated daily prior to sampling. Alkalinity titrations were performed using a Model 16900-01 HACH Digital Titrator. Turbidity measurements were completed by the Environmental Monitoring Section at SRS within 48 hours of sample collection using a HACH Turbidimeter, Model 2100. Turbidity analyses were conducted according to EPA Method 180.1 standard protocols. Other analytical measurements were completed by off-site, EPA certified laboratories, using EPA standard methods.

The off-site laboratory analyzed the samples for conductivity, pH, aluminum, barium, calcium, iron, lead, magnesium, manganese, zinc, chloride, tritium, and nonvolatile beta. Quality assurance samples included trip blanks consisting of deionized water transported in the field and sent to the laboratories, split samples collected in the field during the actual sampling event and sent to an alternate EPA laboratory, replicate samples collected similar to the split sample but sent to the primary EPA laboratory, and equipment blanks consisting of deionized water used to rinse field equipment.

Statistical Analysis

The data demonstrated two problems typical of environmental data: left censoring (concentrations reported as below detection limit) and skewness. Although most constituents showed largely 90% or greater quantifiable measurements, left censoring was addressed by replacing measurements below detection with half the detection limit. Skewness was demonstrated in the data by measurements which spanned several orders of magnitude for some constituents and was assessed using Box-Cox transformation [10]. To account for skewness and preserve the assumption of equal variances among the different levels of the treatment effects, subsequent data analysis was performed on logarithms of the data. Averages computed on this logarithmic scale of measurement were back-transformed to the original scale and are reported as geometric means.

The statistical test used is a repeated measures [11] ANCOVA with a cross-over design feature. To reduce the chance of falsely suggesting significant pump or filter effects, the Bonferroni method [9] was applied to identify relationships that are also meaningful within the group of statistically significant observations. Initial data analysis was completed with SAS® PROC GLM software using a VAX computer. Subsequent analyses used JMP® software on an Apple Macintosh.

RESULTS

The ANCOVA analysis indicates that decreasing sample pH correlates to increases in lead and magnesium concentrations, while increasing turbidity results in a significant and meaningful increase in iron concentrations. Filtration treatment had no significant and meaningful effect except for iron concentrations, which were reduced by filtration. On the other hand, the sampling device had a significant and meaningful effect on iron, lead, manganese, and zinc concentrations, which were increased in centrifugal pump samples. See Table 1 for details.

Table 2 gives the geometric means (GM, the least squares pump type means [8] back-transformed to the original scale) of constituent concentrations, as well as their upper (UCL) and lower (LCL) 95% confidence limits. In general, concentrations in centrifugal pump samples are higher than those from bladder pumps for all constituents except non-volatile beta and magnesium. In the latter two cases, centrifugal pump samples did not yield significantly lower concentrations than bladder pump samples. However, the intervals bounded by the confidence limits for lead, manganese and zinc do not overlap; this again suggests that variations in pump types influences these metals concentrations.

Although elevated turbidity did not generally covary with elevated metals concentrations, Figure 1 indicates that the use of centrifugal pumps results in a broad range of turbidity values as well as values that are higher than turbidity measured in samples collected with bladder pumps. While no meaningful and significant relationship is apparent between the two orderings of sampling devices, a comparison between metals concentrations obtained with different pump types and metals concentrations when varying filtration treatment suggests these two variables are highly independent.

CONCLUSIONS

This study indicates that carefully collected samples that are filtered with membranes of 0.45 µm pore sizes or larger prior to acid preservation yield toxic metals concentrations equivalent to similarly collected unfiltered samples, with the exception of iron. On the other hand, samples collected with centrifugal pumps are more turbid, and result in higher concentrations of iron, lead, manganese and zinc than samples collected with bladder pumps. Since metals concentrations are affected by sampling devices and not filter treatment and both variables are independent, the higher metals concentrations resulting in samples collected with centrifugal pumps most likely result from dissolution of particulates smaller than 0.45 µm.

It is important to note that the differences in metals concentrations resulting from varying pump types most likely arises from the difference in the pumping rates of the two devices. The flow rates of the bladder pumps used in this study were approximately one-tenth the flow rates of the centrifugal pumps. Therefore, decreasing the flow rate of any pumping device should minimize collection of minute particulates in groundwater samples.

SUMMARY

Based on the results of this research, SRS plans to discontinue sample filtration in all groundwater samples and use low flow rate sampling devices in areas of toxic metals contamination. While this work indicates that future results obtained with unfiltered samples should not be statistically different from historical results obtained from filtered samples, a follow-up study is planned to determine if metals concentration variance increase will result from unfiltered groundwater samples. If variance does increase, the sensitivity of statistical significance tests will be reduced, and the frequency of future false negative results will increase. Such a trend may reduce the probability of early detection of slight contamination problems.

TABLE 1

Significance test results for a repeated measures ANCOVA to determine the effects of sample filtration and pump type on contaminant concentration estimates - homogeneous slopes for all covariates is assumed.

				COVARIATES		
ANALYTE	PUMP TYPE EFFECTS	FILTER EFFECTS	ORDER EFFECTS	pH	Conductivity	Turbidity
Aluminum	+	-	-	-	-	+
Barium	-	-	-	-	-	+
Calcium	-	-	+	+	-	-
Chloride	-	+	0	-	-	-
Iron	++	++	-	+	-	++
Lead[a]	++	-	0	++	+	-
Magnesium	0	-	+	++	+	-
Manganese[a]	++	-	-	-	-	-
Nonvolatile Beta	-	-	-	-	-	-
Tritium	-	-	-	-	0	-
Zinc	++	-	-	-	-	-

Legend:

- **0:** Differences in concentration marginal ($.05 < p \leq .10$)
- **+:** Differences in concentration are significant. ($p \leq .05$)
- **-:** Differences in concentration are not significant. ($p > .10$)
- **++:** Also significant at the Bonferroni multiple comparison criteria ($p < .0045$)

Footnotes:

[a] This analyte was found to have heterogeneous slopes for concentration vs each covariate for each pump type in subsequent analyses.

TABLE 2

Least squares[a] geometric[b] mean concentrations and confidence limits of five metals from 12 groundwater monitoring wells showing the concentration disparity from using two pump types to sample water from the same wells.

PUMP TYPES[c]

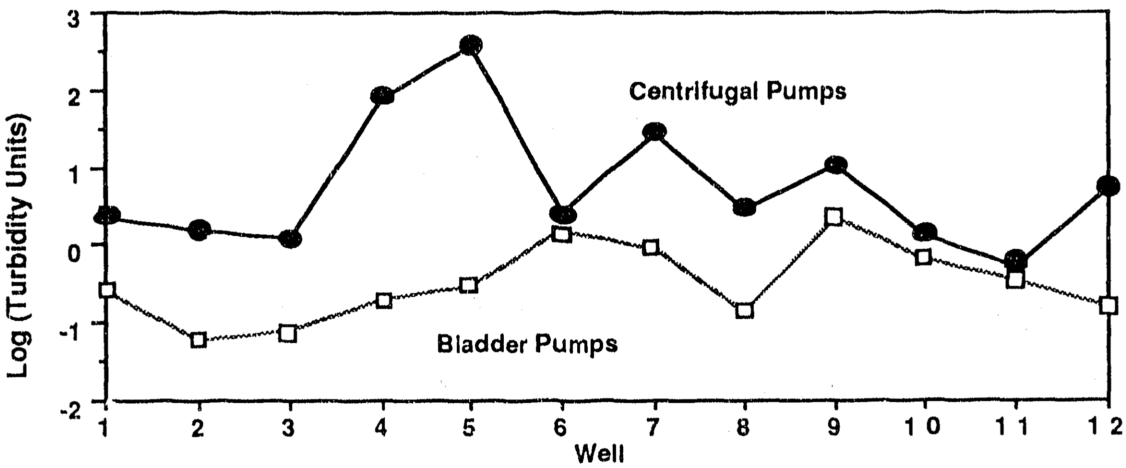
ANALYTE	BLADDER (ppb) LCL_{95}	BLADDER (ppb) GM	BLADDER (ppb) UCL_{95}	CENTRIFUGAL (ppb) LCL_{95}	CENTRIFUGAL (ppb) GM	CENTRIFUGAL (ppb) UCL_{95}
Aluminum	108	156	225	160	232	337
Barium	11.0	12.7	14.6	12.1	14.00	16.2
Nonvolatile Beta	3.85	4.66	5.65	3.59	4.34	5.26
Calcium	1,580	1,650	1,720	1,610	1,670	1,750
Chloride	4.02	4.44	4.90	4.34	4.80	5.30
Iron	29.1	49.3	83.4	80.1	135.6	229.6
Lead	3.02	3.81	4.82	8.76	11.07	14.00
Magnesium	1,300	1,360	1,430	1,240	1,300	1,360
Manganese	15.2	18.7	23.1	23.5	29.0	35.7
Tritium	18.1	19.9	21.9	19.0	20.9	23.0
Zinc	19.1	22.9	27.5	29.5	35.3	42.4

(a) Least squares means are in this case, the predicted arithmetic averages of the natural logarithms of well sample concentrations back-transformed to the original scale and based on the repeated measures ANCOVA model. These means are calculated at the average values of the covariates pH, conductivity and turbidity.

(b) The least squares means have been back-transformed to their original scale (i.e. exponentially) and are thus reported as geometric means.

(c) Most values rounded to three significant figures.

FIGURE 1: Turbidity values in unfiltered samples collected using centrifugal and bladder pumps.



AKNOWLEDGEMENT

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June 14, 1991

Ms. Natalie M. Park
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Dear Ms. Park:

I am pleased to inform you that your paper entitled "Effects of sample collection device and filter pore size on concentrations of metals in groundwater samples" has been accepted for presentation at the 1991 Annual Meeting and 10th Anniversary of the American Institute of Hydrology, Orlando, Florida. I apologize for taking so long to notify you of the acceptance of your paper. We had a larger that expected number of abstracts submitted.

Your paper is scheduled to be presented on Monday, November 4, 1991 at 2:30 PM in a session titled New Technologies: Water Quality. A 35mm slide projector and an overhead transparency projector will be available for your use. The paper is scheduled for 20 minutes (15 minutes for the presentation and 5 minutes for questions). Since we will have three concurrent sessions that are simultaneously scheduled, it is important that you stay within the allotted time.

As the original meeting announcement explained, it is our hope that we can do much of the manuscript preparation electronically. If you have not already done so, it will assist us tremendously it you will mail me a copy of your abstract on a floppy disk no later than July 15. The disk can be either density, 3.5 or 5.25" format. I use Word Perfect, but text can be either WP, Wordstar, or ASCII. The formats of the abstracts as submitted are fine.

If you choose to submit a paper for publication, I also ask that you submit the papers by August 30 in the same format. Papers should be limited to seven (7) pages (8.5x11 inch, 1 inch margins, equivalent to 10 pitch type, single spaced), including illustrations and references. Indicate in the papers where illustrations should be inserted. The proceedings will be edited by John Moore and myself. We will put the manuscripts into a common font and format. Illustrations should be sent to me in camera-ready form.

If you have any questions, please call me at (813) 974-2237 or contact me by FAX ((813) 974-5243). See you in Orlando!

Sincerely yours,

Sam B. Upchurch
Technical-Program Chairman

END

DATE
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5/08/92