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by

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Abstract

Previous studies conducted under laboratory conditions demonstrated that the type of device used to sample ground water contaminated with volatile organic compounds can significantly influence the analytical results. The purpose of this study was to evaluate, under field conditions, both commercial and developmental ground water sampling devices as part of an ongoing ground water contamination investigation and remediation program at the Savannah River Plant (SRP). Ground water samples were collected using six types of sampling devices in monitoring wells of different depths and concentrations of volatile organic contaminants (primarily trichloroethylene and tetrachloroethylene). The study matrix was designed to statistically compare the results of each sampling device under the test conditions. Quantitative and qualitative evaluation criteria were used to determine the relative performance of each device.

Two categories of sampling devices were evaluated in this field study, positive displacement pumps and grab samplers. The positive displacement pumps consisted of a centrifugal (mechanical) pump and a bladder pump. The grab samplers tested were a syringe sampler, a dual-check valve bailer, a surface bomb sampler, and a pressurized bailer. The latter two devices (also called Chismar samplers) were developed at SRP specifically for this study. Preliminary studies were conducted to establish the analytical and sampling variability associated with each device. All six devices were then used to collect ground water samples in water table (unconfined), semi-confined aquifer, and confined aquifer monitoring wells. Results were evaluated against a set of criteria that included intrasampling device variability (precision), volatile organic concentration (accuracy), sampling and analytical logistics, and cost. The study showed that, by using careful and reproducible procedures, overall sampling variability is low regardless of sampling device. Depending on the situation, the study demonstrated that sampling logistics and cost criteria outweigh small quantitative differences in the selection of a sampling device.

Introduction

Obtaining sample that are representative of ground water quality is basic to any ground water investigative program. The accuracy and precision of the analytical techniques commonly used to characterize ground water are well known, and detailed protocols are available for many compounds. However, much less is known about the validity and reliability of the techniques that are used to obtain and deliver ground water samples to the analytical laboratory. This situation is not likely to change in the near future due to the many field variables that, unlike laboratory variables, cannot be systematically controlled and studied. However, site specific field studies can be conducted to determine which sampling variables are most likely to have the greatest affect on the final results obtained in the laboratory.

The Savannah River Plant (SRP) is currently remediating ground water contamination due to the degreaser solvents, trichloroethylene and tetrachloroethylene. To evaluate the effectiveness of the corrective action program and to further define the extent of contamination, an extensive and reliable ground water sampling effort is required. Approximately 200 wells are currently being monitored for the presence of degreaser solvents. Monitor well depths range from 70 to over 300 feet below the surface. Total chlorocarbon concentrations range from less than 1 part per billion (ppb), the detection limit, to over 200,000 ppb. This paper reports the results of a field study that evaluated the performance of different devices for sampling ground water from monitor wells of different depths and containing a range of volatile organic concentrations.

Experimental Design

Two categories of sampling devices were evaluated, positive displacement pumps and grab samplers. The study was divided into two phases. The primary objective of Phase I was to establish the analytical and sampling variability associated with each device. Secondary objectives were to evaluate the logistical problems in using the device and to eliminate devices for Phase II as appropriate.

Six devices were tested in Phase I in the same water table (unconfined) monitor well, which contained a moderate concentration of trichloroethylene (approximately 1000 ppb). Based on statistical criteria, a sample size of six was selected for each device. The within-sampler-variability was determined for each device. The objective of Phase II was to compare the between-sampler-variability in wells screened at different depths (unconfined, semi-confined, and confined) and containing a range of trichloroethylene concentrations (approximately 4 - 40,000 ppb). Four devices were tested during this phase. A set of evaluation criteria was established that included both quantitative and qualitative elements. These criteria included accuracy, precision, field logistics, analytical logistics, and cost. Analytical logistics were included because two of the devices, the Chismar samplers, required the development of special equipment for purging the samples prior to analysis by gas chromatograph. The selection of the

criteria and the final evaluations were based on the requirements of the ground water monitoring program at SRP.

Description of the Sampling Devices

Six samplers were field-evaluated in this study. Four of the devices are commercially available; two of the samplers were designed and built by the Savannah River Laboratory. Two categories of devices were tested; positive displacement pumps and grab samplers. The positive displacement pumps consisted of a submersible (centrifugal) pump and a bladder pump. The grab samplers tested were a syringe sampler, dual-check valve bailer, a surface bomb sampler, and a pressurized bailer. A description of each device follows.

Positive Displacement Pumps

A 1/2-hp submersible pump with stainless steel impellers (Grundfos SP 1-16) was used to collect samples and to evacuate the well prior to using the other devices. For water table wells, the pump was set near the bottom of the 20-foot screen zone. For semi-confined and confined wells, the pump was set directly above the top of the 5- to 10-foot screen zone. The riser pipe supporting the pump was flush threaded PVC. During well evacuation, the flow rate was approximately 3 - 5 gpm depending on well depth. After four volumes were evacuated, the pump was throttled down prior to collecting the water sample.

The bladder pump evaluated in this study was an IEA Aquarius with a reported pumping rate of 0.25 - 0.75 gpm. This pump is air-actuated and contains a bladder that isolates the water sample from the air supply. The intake to the pump was set in the screen zone for each well tested. Although equipped with a packer, the packer was not used in these tests because all wells were evacuated with the submersible pump prior to sampling with the other devices. Ten gallons of water were pumped from each well with the bladder pump before samples were collected. Pumping rates ranged from approximately 300 to 2000 mL/min depending on well depth.

Grab Samplers

The syringe sampler was made by IEA. The sampler contains a Teflon™ piston that can be actuated at depth by applying either vacuum or pressure from the surface. The bailer was all Teflon™ with dual-check valves (Timco™ Mfg., Inc.). The bailer was lowered into the screen zone of each well on Teflon™-coated cable. The samples collected with these devices were from the screen zone.

The other grab samplers (Chismar samplers), surface bomb, and pressurized bailer, were developed at the Savannah River Laboratory. The design and operation of these devices are identical with modifications of the pressurized bailer to operate in the well, and of the bomb sampler to operate at the surface. The primary design requirement was for

a device that could sample for volatile organics, regardless of whether they were in the aqueous or gaseous phase. Also, the device had to maintain the integrity of the sample from the time of collection to the time of analysis, despite changes in temperature and pressure. The basic component of both devices is a stainless steel sample tube (approximately 12 inches long with a liquid capacity of 35 mL) with stainless steel ball valves at each end. The valves were both gas and liquid leak-proof. The tube is mounted on a frame that contains a lever arm connected to a pneumatic piston. The lever arm is attached to both valves. By actuating the piston with compressed air, the valves at each end of the sample tube can be quickly opened or closed simultaneously. The pressurized bailer was equipped with a protective stainless steel casing to facilitate lowering and raising in the well. The surface bomb contained an additional pneumatically operated valve upstream of the sampling tube. This valve could be opened after the valves for the sample tube were closed to relieve the resultant water pressure. Each sample tube was pressure tested to 150 psi. Extensive studies were conducted to ensure that the tubes could be cleaned/decontaminated after use.

Sampling Procedures

For Phase I, all six devices were tested in the same water table well. The trichloroethylene concentrations in this well were moderately high (1000 - 1200 ppb) and were known from previous analytical results. All sample devices and supports (i.e., riser pipe, cable, tubing) were thoroughly steam cleaned prior to lowering into the well. The completeness of steam cleaning was verified by filling the devices as appropriate (bailers, syringe, sample tubes) with deionized water and analyzing for the presence of degreaser solvents. No evidence of cross contamination was detected. The submersible pump was the first device installed in the well. The submersible pump was not only tested as a sampling device but was also used to fully evacuate the well casing between each of the other sampling devices tested.

After evacuating four well volumes with the submersible pump (at approximately 5 gpm) the pump was throttled down. A small sampling port was used to collect the water samples in precleaned 40 mL glass vials equipped with a Teflon™ lined silicone septum. These same types of vials were used for all sampling devices except the surface bomb and pressurized basiler. The steam cleaned stainless steel sampling tube served as the sample container for these devices. After collecting the samples for the submersible pump, it was removed from the well to make room for the down-the-well samplers. Approximately three hours were required for pump removal. The well was then sampled six times each with the dual check-valve bailer and syringe sampler. Standard field water quality measurements (pH, conductivity, temperature) were also made on the water collected by each device. After being steam cleaned, the submersible pump was reinstalled in the well and again four well volumes were evacuated. Each time the pump was reinstalled, an additional VOC sample was collected and field water quality measurements were made to check for any water quality changes that may have occurred in the time between the testing of different

devices. No significant water quality changes were observed. The surface bomb samples were collected next. After removing the submersible pump, the bladder pump was installed and samples were collected. Prior to testing the pressurized bailer, the submersible pump was reinstalled to evacuate the well, and then removed. Approximately three hours later, the pressurized bailer samples were collected.

During Phase II, four devices were evaluated. A statistical analysis of the Phase I data showed that three samples with each device would provide an adequate basis for statistical comparison. Each of the Phase II devices were tested in five monitor wells; one water table, two semi-confined, and two confined. For each well, samples were collected by all four devices within a six-hour period. As in Phase I, the submersible pump was installed first to evacuate the well. After collecting three submersible pump samples, the surface bomb was connected to the discharge pipe and three samples were collected while the submersible pump was operating. The submersible pump was then removed and the syringe and bladder pump samples were taken. This process was repeated for the remaining four wells. As in Phase I, field water quality measurements were made on each sample. All samples collected for VOC analysis during Phase I and II were immediately transported to on onsite laboratory following Chain-of-Custody/quality assurance procedures. The procedures used to analyze the samples for VOC's, specifically trichloroethylene, are described in the following sections.

Analytical Procedures

All well water samples and field blanks were analyzed for trichloroethylene following EPA method 601 for "Purgeable Halocarbons." Water samples collected with the submersible pump, bladder pump, syringe, and bailer were purged at atmospheric pressure with conventional purge and trap instrumentation. Samples from the surface bomb and pressurized bailer were purged in a pressurized system designed to capture volatile organics from both the liquid and gaseous phases of the sample. A detailed description of each procedure is presented below.

Single-Phase Purge and Trap System

Water samples (5 mL) were injected into a Tekmar Model LSC-2 purge and trap instrument. The halocarbons were desorbed onto a gas chromatographic column. The gas chromatograph used was a Tractor Instruments 565 GC with 700A Hall detector. The standard detection limit of this system is 1 ppb. Quality control was maintained through daily calibrations using external standards. Field and laboratory blanks were routinely analyzed. Also, 10% duplicate and spiked samples were run to confirm results and to determine percent recovery. The accuracy and the precision of the method is $\pm 4\%$ at the 95% confidence level.

Two-Phase Closed Purge System

The pressurized bailer and surface bomb samplers were designed to capture volatile organic compounds in both the liquid and gas phase. the standard purge and trap system used with the other sampling devices was not adequate to maintain sample integrity. Therefore, a system was developed at SRP to quantitatively purge the entire contents of the sampler into a secondary container without loss of any volatile organics. The gas mixture from the secondary container could then be subsampled for analysis. A diagram of this purge system is presented in Figure 1.

Helium gas is bubbled for a minimum 10 minutes at 100 cc/min through the entire water sample (approximately 35 mL) and any gaseous head space contained in the sample tube. The volatile compounds are collected into an attached gas sampling bag (BGI, Incorporated, 1.5 l), which is equipped with a twist-open valve and a septum. The bag is then subsampled through the septum with a gas-tight syringe. Aliquot sizes ranged from 1 - 100 cc depending upon volatile organic concentrations in the water sample and the volume in the bag.

A Tekmar Model 4000 Dynamic Head Concentrator was modified for gas analyses by the addition of an injection port. This port was placed between the water sample purge chamber and the halocarbon sorbent tube. From this point on, the analytical procedure is identical to the single-phase purge and trap method. The halocarbon trap is heated and backflushed onto a column in a Hewlett-Packard 5890A GC equipped with a Tracor 700A Hall detector. The standard detection limit of this system is also 1 ppb.

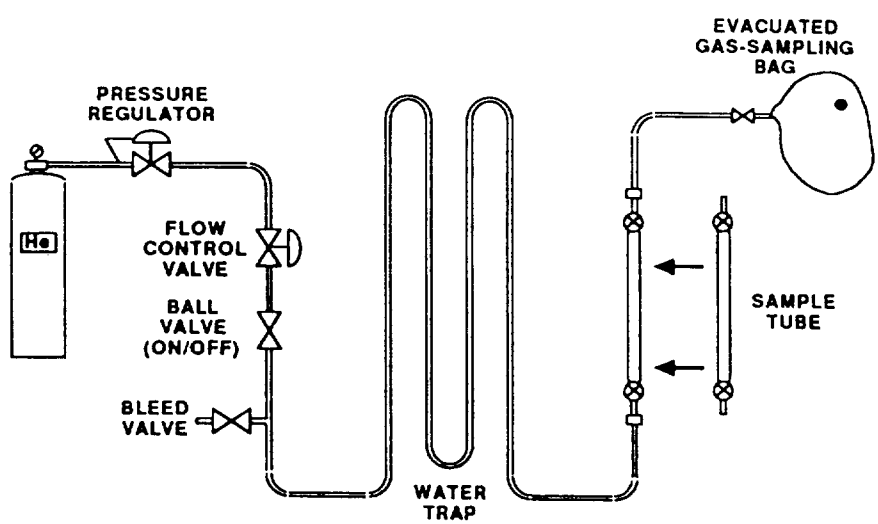

FIGURE 1. Two-Phase Closed Purge System for Sample Tubes from the Pressurized Bailer and Surface Bomb Samplers

This method was validated through routine calibration using external trichloroethylene standards and determining percent recovery and precision from replicate analyses of known standards purged from laboratory spiked sample tubes. Based on five replicate tube analyses for trichloroethylene, the mean recovery was 99% and the accuracy and precision of the procedure was within 6% at the 95% confidence level (i.e., 6% of the variability of the actual data could attributed to the analytical procedure).

Phase I Results

The Phase I results are summarized in Table I. Average trichloroethylene concentrations for each device ranged from a low of 861 ppb for the bladder pump to 1277 ppb for the surface bomb. A statistical analysis of the data showed that the average concentration for the bladder pump was significantly different from the other devices at the 95% confidence limit. No significant differences were determined between the remaining five devices.

Within sampling device variability ranged from 2.5% for the submersible pump to 13.7% for the dual-check valve bailer. All devices performed remarkably well. However, the dual-check valve bailer was eliminated from Phase II due to its relatively high variability. The pressurized bailer was also dropped from the study. This device, although exhibiting the second lowest variability in Phase I, proved to be difficult to handle in the field.

TAble I. Comparison of Phase I Well Sampling Devices Based on Trichloroethylene Analyses (n = 6)

Sampling Device	Average Trichloroethylene Concentrations, ppb + S.D.*	% Variability
Submersible Pump	1164 ± 29	2.5
Pressurized Bailer	1016 ± 40	3.9
Syringe	1090 ± 94	8.6
Bladder Pump**	861 ± 77	8.9
Surface Bomb	1277 ± 147	11.5
Dual-Check Valve Bailer	1032 ± 142	13.7

*Average parts per billion ± standard deviation
**Significantly different at P=05 level

Phase II Results

The results from Phase II are presented in Table II. Results for the submersible pump, surface bomb, syringe, and bladder pump (n = 6) from Phase I are also included in the table for comparative purposes. In wells containing moderate to high trichloroethylene concentrations,

the submersible pump and surface bomb produced similar results and the measured concentrations tended to be higher than the levels found in the samples collected by the syringe and bladder pump. At these same concentrations, the trichloroethylene concentrations found in the bladder pump samples tended to be the lowest; however, the precision of the bladder pump as reflected by the small standard deviations was very good.

TABLE II. Comparison of Phase I and Phase II Well Sampling Devices Based on Trichloroethylene Analyses

Sampling Device	Well Description	Sample Size	Average Trichloroethylene Concentration, ppb + S.D.*
Submersible Pump	Unconfined	3	38,933 ± 950
Surface Bomb		2	39,600 ± 707
Syringe		3	22,100 ± 400
Bladder Pump		3	27,300 ± 1752
Submersible Pump	Unconfined	6	1,164 ± 29
Surface Bomb		6	1,277 ± 147
Syringe		6	1,090 ± 94
Bladder Pump		6	861 ± 77
Submersible Pump	Semi-confined	3	919 ± 149
Surface Bomb		2	908 ± 26
Syringe		3	777 ± 40
Bladder Pump		3	567 ± 36
Submersible Pump	Semi-confined	3	642 ± 104
Surface Bomb		2	790 ± 19
Syringe		3	547 ± 69
Bladder Pump		3	385 ± 47
Submersible Pump	Confined	3	445 ± 5
Surface Bomb		3	514 ± 29
Syringe		3	337 ± 34
Bladder Pump		3	233 ± 2
Submersible Pump	Confined	3	0.2 ± 0.1
Surface Bomb		3	4.5 ± 0.6
Syringe		3	2.5 ± 0.2
Bladder Pump		3	5.8 ± 0.1

*Average parts per billion ± standard deviation

In the confined aquifer monitor well, which contained low trichloroethylene concentrations, the pattern between sampling devices was considerably different. Trichloroethylene was barely detected in the submersible pump samples (0.2 ppb), whereas, the concentration detected in samples from the other devices ranged from 2.5 ppb for the syringe to 5.8 ppb for the bladder pump. Additional studies would be required

to determine if this pattern is a function of the well sampled (a deep confined well) or is a characteristic of this sampling device in wells containing low VOC levels.

Evaluation of Sampling Devices

A comparison of the devices using the evaluation criteria previously discussed is presented in Table III. No attempt was made to develop a numerical scale for the criteria or to rank the devices based on an overall score. Instead, descriptive terms were used to provide a qualitative comparison. Clearly each device offers certain advantages and disadvantages relative to the evaluation criteria selected for this study.

The accuracy and precision evaluations were based on the Phase I and II results. The submersible pump and surface bomb were, in most cases, the most accurate devices but demonstrated no consistent pattern relative to precision. For the well with a low trichloroethylene concentration, the submersible pump produced samples with low VOC levels relative to the other devices. Although additional testing is required to confirm this pattern, these data indicate that the use of submersible pumps may have disadvantages for sampling wells with low VOC concentrations.

Table III. Qualitative Comparison of the Sampling Devices Based on the Evaluation Criteria Selected for this Study

Evaluation Criteria	Submersible Pump	Surface Bomb	Bladder Pump	Syringe	Bailer*	Pressurized* Bailer
Accuracy	Excellent	Excellent	Moderate	Moderate	Good	Good
Precision	Good	Good	Excellent	Moderate	Low	Excellent
Field Logistics	Easy	Easy	Acceptable	Acceptable	Acceptable	Difficult
Lab Logistics	Easy	Difficult	Easy	Easy	Easy	Difficult
Cost	Moderate	High	High	Moderate	Low	High

*Only tested in Phase 1

Although the results for samples collected by the bladder pump consistently showed the greatest precision, the concentration levels measured relative to the other devices were generally lower. No explanation for this pattern has been developed. The syringe sampler also tended to provide water samples whose trichloroethylene concentrations

were low relative to some of the other devices. Its accuracy and precision were judged to be moderate. The bailer and pressurized bailer were only tested in Phase I. The bailer was clearly the least precise device tested. The pressurized bailer was ranked high in both accuracy and precision but was eliminated from Phase II for logistical reasons.

A comparison of the devices based on field logistics is difficult because of the obvious advantages that a dedicated submersible pump has for rapid well evacuation. The field personnel that conducted this study were interviewed as to the reliability and general field operation of the devices. Except for the pressurized bailer, all devices exhibited acceptable performance, with the submersible pump and surface bomb demonstrating the best performance. Based on Laboratory logistics and cost, the surface bomb and pressurized bailer were predictably difficult to work with and costly due to their developmental status. The cost ranking of the other devices from low to high is: bailer, syringe, submersible pump, and bladder pump.

Conclusions

As part of an ongoing remedial action and ground water assessment program at the Savannah River Plant, there is a need for an accurate, reliable, and cost effective method to sample ground water for the presence of volatile organic compounds. This study was conducted to evaluate different sampling devices to fulfill SRP needs. Ground water investigative programs with different objectives and sampling needs may have selected different sampling devices and evaluation criteria. The results of this study show that all devices have their advantages and disadvantages. The final selection should be based on site-specific criteria.

For SRP purposes, the submersible pump was selected because of its high accuracy and precision, its reliability and ease of field operation, its ability to rapidly evacuate a well, and its moderate cost. The only shortcoming of a submersible pump, based on the results of this study, is the sampling of wells with VOC concentrations near analytical detection limits (1 - 10 ppb). Loss of VOC's may be due to pump agitation that could change the physical and chemical composition of the ground water prior to its collection at the surface. In SRP ground water, this effect is only significant in monitoring wells containing low VOC concentrations.

Although at the developmental stage, the results from the Chismar samplers, particularly the surface bomb, are encouraging. As demonstrated by its high accuracy and relative ease of use in the field, the surface bomb has potential as a volatile organic sampling device. Further developmental studies are planned in the field and the laboratory to make the device more practical for routine use.

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Biographical Sketches

Carl F. Muska received a Ph.D. in Environmental Toxicology from Oregon State University. For the past two years he has worked as a Staff Engineer on a project to assess and remediate a volatile organic ground water contamination problem at the Savannah River Plant. Prior to his current position, he worked for five years as a Research Toxicologist at Du Pont's Haskell Laboratory for Toxicology and Industrial Medicine in Newark, DE. Areas of specialization include hazardous waste management and environmental regulatory issues with an emphasis on water quality standards and criteria. E. I. du Pont de Nemours & Co., Savannah River Plant, 320-4M, Aiken, SC 29808.

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