United States
Environmental Protection
Agency
Research and Development

Environmental Monitoring
Systems Laboratory
Las Vegas, NV 89193-3478
EPA/600/S4-90/028 July 1991

EPA

Project Summary

Field Comparison of Ground-Water Sampling Devices for Hazardous Waste Sites: An Evaluation Using Volatile Organic Compounds

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To determine whether ground-water contamination has occurred or remediation efforts have been effective, it is necessary to collect ground-water samples in such a way that the samples are representative of ground-water conditions. Unfortunately, formation of stagnant water within conventional monitoring wells requires that these wells be purged prior to sampling, a procedure that may introduce significant bias into the determination of concentrations of sensitive constituents such as volatile organic compounds (VOCs). The use of *in situ* ground-water sampling devices, which minimize or eliminate the need for well purging, may help alleviate some of the difficulties associated with sampling ground water at hazardous waste sites. In this study, several ground-water sampling devices, including two *in situ* systems, were field-tested to determine their capability for yielding representative VOC data.

Sampling devices included in the field study were a bladder pump, a bladder pump below an inflatable packer, a bailer, a bailer with a bottom-emptying device, an *in situ* Westbay MP System™*, two *in situ* BAT™* Ground-Water Monitoring Systems, and a prototype BAT well probe. The devices were field-tested at a site contaminated by a VOC plume, and the comparison was based on the ability of the devices to recover representative concentrations of the VOCs. The data show that, under these field conditions, the sample variability associated with the bladder pump and *in situ* samplers is of similar magnitude and that there is little difference in apparent accuracy and precision of these devices. In contrast, both bailers introduced significant variability into VOC determinations and were found to be less accurate and precise than the other devices tested. The study indicates that the tested *in situ* devices may eliminate the need for well purging prior to sample collection and that the resulting samples are at least as representative as those collected with a bladder pump in a conventional monitoring well.

This Project Summary was developed by EPA's Environmental Monitoring Systems Laboratory, Las Vegas, NV, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

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Introduction

The ability to collect ground-water samples representative of aquifer hydrochemical conditions is a major concern in any ground-water investigative effort. Unfortunately, there are many factors in the sampling and analysis process that can introduce variability into determinations of chemical constituent concentrations, greatly influencing the ability to obtain accurate results. Examples include well drilling method, well design, the materials used in well construction, well development and purging, sampling device, sample handling and preservation, and analytical technique. Of these, maintenance of sample integrity from the subsurface sampling point to the sample container has received considerable interest because of the great potential impact on sample representativeness possible during this phase of the sampling process.

Concern about obtaining representative samples of ground water containing volatile organic compounds (VOCs) has arisen because VOCs are common contaminants at hazardous waste sites and they are sensitive to sampling method. To address this concern, sampling devices have been developed to minimize impact on sample quality. These devices are generally used in conventional monitoring wells and therefore require removal of stagnant water from the well prior to sampling. While well purging is generally considered necessary to collect representative ground-water samples, the purging process itself may introduce considerable bias into the sampling results and may produce waste-water disposal problems and undesirable exposure of sampling personnel to potentially hazardous materials.

Among the newer commercially available sampling devices are two devices that need to have little or no water purged from the system prior to sampling. These devices are not used in conventional monitoring wells but are stand-alone systems installed directly into the subsurface, similar to conventional monitoring well installations. Because of the nature of their design and installation, these devices collect samples almost directly from the formation and so are often referred to as *in situ* systems. The existence of these devices raises three important questions:

- Do sampling methods exist that eliminate the need for well purging prior to sample collection?
- How valid or representative are the resulting samples?
- Are the proposed *in situ* sampling methods inherently invalid because of the necessity of well purging?

This study was initiated to address the concerns expressed by these questions. The primary objective of the study was to compare several conventional and *in situ* devices for their ability to collect representative VOC samples.

Descriptions of Sampling Devices

Seven ground-water sampling devices, all of which are commercially available, were utilized in this study. The devices may be categorized as grab samplers (bailers), positive displacement mechanisms (bladder pump, bladder pump below an inflatable packer), and *in situ* devices (Westbay MP System™, two BAT™ Ground-Water Monitoring Systems, and a prototype BAT well probe). To minimize the potential for bias resulting from contact with the materials of which the samplers were constructed, the devices were selected from the most chemically inert materials available from the manufacturer.

Two bailers were utilized in the study. The first was a Teflon bailer with a Teflon-coated stainless steel haul line. The design of this bailer, with side ports and a closed top, was chosen to minimize the possibility of stagnant water entering the top of the device as it was retrieved from the well. The second bailer was similar in design but utilized a bottom emptying device (BED) to transfer the sample directly from the bottom of the bailer to the sample container.

Two Teflon bladder pumps were used in the study, one in conjunction with an inflatable packer mounted above the pump and the other without the packer. The packer is designed to reduce purge volumes by isolating stagnant well water above the pump and preventing that water from migrating downward to the pump intake. Each pump was dedicated to a single well, although the bladder pump without the packer was removed from its well after purging to allow for sampling with the bailers.

The BAT Ground-Water Monitoring System consists of sealed components with hydraulic interconnections between components accomplished through the use of hypodermic needles, flexible seals, and induced pressure gradients. The primary component of the system is the BAT filter tip which is threaded onto the bottom of standard 5.1-cm-diameter monitoring well casing and permanently installed at the desired depth. Ground-water samples are collected in sealed, evacuated glass vials contained in a sample container housing which is lowered down the casing to the filter tip. Contact between the container housing and the top of the filter tip causes a double-ended hypodermic needle to puncture septa in both the sample container and the filter tip cap, causing ground water to flow from the formation into the sample vial. When full, the sample is retrieved, and both septa are resealed as the syringe is withdrawn from the bottle and filter tip cap. The vials used fo sample collection may then be sent directl to the laboratory for analysis. Because onl the small volume of water contained withi and immediately outside the filter tip is i contact with the sampling device, the vol ume of stagnant water which needs purgin is significantly smaller than in conventiona monitoring wells. Two filter tips were utilize in this study, one with a filter consisting c polytetrafluoroethylene (PTFE), and on consisting of high-density polyethylen (HDPE). These devices are referred to i the report as the "PTFE filter tip" and th "HDPE filter tip," respectively.

A third BAT device used in this study wa a modified version of the PTFE filter ti which was installed in the screened interva of a conventional 5.1-cm-diameter monitor ing well. This device, referred to in the repo as the "well probe," utilizes two Viton™* O rings to seal off the well bore above an below the screened interval. With the we screen isolated, the well probe functions a a sampling port from which water containe within the screened interval alone is ex tracted, therefore, reducing the purge vol ume required. Sampling procedures ar identical to those for the *in situ* filter tips.

The Westbay MP System (referred to i the report as the "multi-port") allows dis crete samples or measurements to be take at multiple levels within a single borehol The system consists of various lengths c casing joined by regular or valved port cou plings and a variety of specialized tools an probes to access the ports and retrieve th samples or measurement data from th environment outside the sealed casin Sampling probes accessing a measure ment port draw the sample from directl outside the casing, so there is no exposur of the sample to fluids contained inside th casing. For this reason, there is no need t purge standing water inside the casing, an purge volume requirements are significantl reduced over the requirements of conven tional monitoring wells. The multi-port com ponents chosen for this study were con structed of stainless steel.

Procedure

The study was approached by conduct ing comparisons of seven ground-wate sampling devices, including two types of *i situ* devices, at a field site over a VOC

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contaminated shallow aquifer. The aquifer consisted of alluvial sands and gravels, with some silt and clay interbeds, overlying, at a depth of 9.5 m below ground surface, thick clay/silt beds containing thin, interbedded sands and some gravel. The water table depth was approximately 3 m below ground surface, resulting in a total unconfined aquifer thickness of 6.5 m.

Ground water at the site is contaminated by a variety of organic and inorganic compounds related to a major industrial site located approximately 3 km hydraulically upgradient. Much of the organic contamination is the result of an underground storage tank leak which released approximately 113,500 L of benzene into the ground water. Movement of the benzene plume downgradient has brought it into contact with a variety of other organic compounds, which may have been mobilized and transported away from their original disposal areas. The VOCs of highest concentration at the study site, benzene, chlorobenzene, 1,2-dichlorobenzene, and 1,4-dichlorobenzene, were each present at the initiation of the study in concentrations up to 1600 µg/L.

To minimize geologic and hydrochemical variability between the sampling devices it was necessary to install the wells close to each other. However, the wells also had to be spaced far enough apart so that the effects of pumping at one well would not impact the distribution of VOCs near adjacent wells. Based on site geology and capture zone calculations, a 6-m spacing was chosen. Six boreholes were drilled on a rectangular grid pattern by using a dual-tube percussion hammer drill rig. Two of the holes on opposite corners of the grid were logged by using magnetic induction and natural-gamma logging methods. These logs were used to study geologic variability across the site and to aid in locating the sampler intake depths. Results of the logging indicated that geologic conditions were similar at the two corners of the site and that well intake depths of 6 to 7 m would result in lower clay content and potentially better flow characteristics.

Five of the six wells were cased with 5.1-cm-diameter Teflon casing. Three of these wells were screened over a 0.3 m-interval (for installation of the bladder pump, bladder pump/packer, and well probe), while the other two had HDPE and PTFE filter tips installed. The sixth well consisted of the stainless steel multi-port. The well screens, filter tips, and the deepest multi-port measurement port were all installed at depths of about 6 m.

The sampling devices were evaluated to compare their relative accuracy and precision and to determine if the non-pumping *in situ* methods yielded representative data. The comparison was based on the ability of each device to deliver representative samples from the subsurface environment to the ground surface and into an appropriate sample container. Because VOCs are common contaminants at hazardous waste sites, the effects the tested devices had on VOC recovery were of primary importance. As virtually all field sampling techniques introduce bias into VOC determinations, a true assessment of accuracy, and therefore representativeness of ground-water conditions, is not possible in a field study. However, because of the physical and chemical properties of most VOCs, losses of VOCs from a sample are much more likely than increases. Therefore, a relative approximation of accuracy was based on the concentrations of VOCs recovered during the sampling process (i.e., those devices which recovered the highest VOC concentrations were considered the most accurate).

Because the sampling devices were the source of variability of most interest to this study, all other sources of variability present in the study were minimized. In addition, it was necessary to make the assumption that geologic and hydrochemical conditions at each of the six well sites were identical. However, despite the assumption to the contrary, the natural variability in lithology and stratigraphy of alluvial materials suggests that geologic conditions were certainly not identical at each of the six wells. The variability in geologic conditions may be an important element of the total variability observed in this study but could not be adequately quantified in a way that would relate to effects on VOC concentration variability. Likewise, the assumption that hydrochemical conditions were the same at each of the six well sites was made in order to form a basis for the sampler comparison. To test this assumption a "survey" sampling round was conducted in which an initial set of samples was collected from three of the wells. These wells were utilized for the survey sampling because they were the only wells that could be sampled with the same device, a Teflon bladder pump, and because their locations represented a fairly complete coverage of the study site. Because of their design, the other three wells could not be sampled with the bladder pump and, therefore, were not included in the survey sampling. The results indicated that mean concentrations at each of the three sampled wells were within one standard deviation of each other and within laboratory error. However, some variability in VOC concentrations was evident in the survey sampling, and the possible contribution of this small variability to the overall variability observed in the sampling results was kept in mind during the analysis.

The VOC concentration data resulting from the comparisons were statistically analyzed by means of a two-way analysis of variance to determine if the sampling devices and/or sampling time introduced a significant source of variability to the data. Univariate analyses of variance were then used to determine if significant differences existed between device sample means, based on recovery of each individual compound. Finally, Tukey multiple comparison tests were conducted to identify which individual pairs of sample means during each sampling event were significantly different at the 5 percent level. The devices were then grouped accordingly by bracketing those devices whose mean concentrations showed no significant differences.

The comparisons in this study were divided into three experiments: A, B, and C. Experiment A consisted of eight sample rounds over a 19-week period and involved all of the devices except the BED bailer. Experiment B, which utilized only the bladder pump, bailer, PTFE filter tip, and multi-port, consisted of multiple replicate samples collected with each device during a single sampling event. Experiment C included the four devices used in Experiment B, with the addition of the HDPE filter tip and BED bailer. Four sample rounds were conducted at 12-week intervals during this experiment.

Results and Discussion

The results of Experiment A suggest that both of the filter tip devices and the well probe recovered benzene and chlorobenzene with an accuracy greater than that of the bailer and at levels rivaling those obtained with the bladder pump. Before determining the source of the anomalously low concentrations, the multi-port produced VOC samples which were much less accurate than those collected with the bladder pumps, filter tip, and well probe devices. Additional experiments with the multi-port have shown that replacement of the perforated VOA bottle septum with a new septum can prevent sample degradation and allow this system to extract accurate samples which can be preserved until the time of analysis.

Experiment B, the design of which was based on the results and problems noted during the first experiment, confirmed many of the original findings. The statistical analysis indicated that for eight of the nine detected VOCs, concentrations recovered by the PTFE filter tip were significantly higher than, or not significantly different from, concentrations recovered by the bladder pump. Although the multi-port was slightly less accurate than the bladder pump and filter tip, precision was comparable for all three. Samples collected with the bailer appeared to be less accurate than those collected with all other devices. However, the bailer sampling procedures used did not allow for the collection of true replicate samples, and, therefore, complete assessments of the accuracy and precision of the bailer could not be made. Experiment B also confirmed the ability of the multi-port to collect more accurate samples when the perforated sample vial septum is replaced.

The results of Experiment C followed several of the trends established during the previous two experiments, but provided longer-term information. This experiment suggested that the bladder pump and the filter tips were the most accurate of the devices tested and that the bailers were the least accurate. The multi-port was found to be somewhat less accurate than the bladder pumps and filter tips. The multi-port, bladder pump, and HDPE filter tip provided the most precise samples, while the bailers, the BED bailer in particular, provided the least precise samples.

Conclusions and Recommendations

The variability observed in the survey sampling, although less than the stated analytical error, indicates that some spatial variability may exist at the site and that the assumption of identical conditions between devices may not have been strictly valid. Because of the nature of this study, a complete understanding of the hydrochemical variation between the well installations could not be determined independently of the tested devices. As a result, the possibility of spatial variability contributing to the overall observed variability cannot be discounted. If spatial variability typical of many field sites is included in the final analyses, these experiments suggest that the variability associated with the bladder pump and *in situ* samplers is of similar magnitude and that there may be little difference in the accuracy and precision of these devices. The bailers, on the other hand, which sampled the same well as the bladder pump, were not subjected to the uncertainty of varying spatial conditions, so the samplers were the primary source of variability.

This study shows that, under field conditions, *in situ* devices may provide samples with essentially the same precision and accuracy as bladder pumps and greater precision and accuracy than bailers. It appears that the designs of the two types of *in situ* devices tested virtually eliminate the need for well purging prior to sample collection and can provide representative VOC samples in sand and gravel aquifers.

In addition to collecting representative samples and minimizing purging volumes, the *in situ* devices allow samples to be collected quickly, while reducing both exposure of sampling personnel to potentially hazardous materials and the volume of purge water to be disposed of. Furthermore, these sampling systems are relatively easy to operate and maintain, the standardized sampling methodology reduces variability potentially introduced by sample handling, and fewer sampling personnel are required to obtain samples. The few operational difficulties experienced with the two *in situ* devices are described fully in the report.

To obtain a more accurate evaluation of these sampling devices, it is suggested that additional studies be developed and implemented, such as application in various hydrogeologic conditions, including low permeability environments, or areas with different contaminants. Other installation methods and devices at varied depths also should be investigated. Further studies performed at a variety of sites and involving these and other commercially available *in situ* sampling devices, are needed to improve understanding of the applicability of these devices to a variety of monitoring situations.

☆U.S. GOVERNMENT PRINTING OFFICE: 1991 - 548-028/40020

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The complete report, entitled "Field Comparison of Ground-Water Sampling Devices for Hazardous Waste Sites: An Evaluation Using Volatile Organic Compounds," (Order No. PB91-181 776/AS; Cost: $23.00, subject to change) will be available only from:

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