

EPA/600/4-90/028
May 1991

**FIELD COMPARISON OF GROUND-WATER SAMPLING
DEVICES FOR HAZARDOUS WASTE SITES:
AN EVALUATION USING VOLATILE ORGANIC COMPOUNDS**

by

Karl F. Pohlmann
Ronald P. Blegen
John W. Hess
Water Resources Center
Desert Research Institute
Las Vegas, Nevada 89120

Cooperative Agreement
CR 812713-01

Technical Monitor

Jane E. Denne
Advanced Monitoring Systems Division
Environmental Monitoring Systems Laboratory
Las Vegas, Nevada 89193-3478

This study was conducted in cooperation with
Water Resources Center
Desert Research Institute
Las Vegas, Nevada 89120

**ENVIRONMENTAL MONITORING SYSTEMS LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
LAS VEGAS, NEVADA 89193-3478**

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

| | | | | | |
|---|--|--|--|---|--|
| 1. REPORT NO. EPA/600/4-90/028 | | 2. | | 3. PB91-181776 | |
| 4. TITLE AND SUBTITLE FIELD COMPARISON OF GROUND-WATER SAMPLING DEVICES FOR HAZARDOUS WASTE SITES: AN EVALUATION-USING VOLATILE ORGANIC COMPOUNDS | | | | 5. REPORT DATE May 1991 | |
| | | | | 6. PERFORMING ORGANIZATION CODE | |
| 7. AUTHOR(S) Karl F. Pohlmann, Ronald P. Blegen, and John W. Hess | | | | 8. PERFORMING ORGANIZATION REPORT NO. | |
| 9. PERFORMING ORGANIZATION NAME AND ADDRESS Water Resources Center, Desert Research Institute 2505 E. Chandler, Suite 1 Las Vegas, NV 89120 | | | | 10. PROGRAM ELEMENT NO. D109 (I15) | |
| | | | | 11. CONTRACT/GRANT NO. CR 812713-01 | |
| 12. SPONSORING AGENCY NAME AND ADDRESS Environmental Monitoring Systems Laboratory- LV, NV Office of Research and Development U.S. Environmental Protection Agency Las Vegas, NV 89114 | | | | 13. TYPE OF REPORT AND PERIOD COVERED Project Rpt. & Summary 1/87-9/90 | |
| | | | | 14. SPONSORING AGENCY CODE EPA/600/07 | |
| 15. SUPPLEMENTARY NOTES | | | | | |
| 16. ABSTRACT 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 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® devices, 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 results of this study indicate 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. | | | | | |
| 17. KEY WORDS AND DOCUMENT ANALYSIS | | | | | |
| a. DESCRIPTORS | | b. IDENTIFIERS/OPEN ENDED TERMS | | c. COSATI Field Group | |
| | | | | | |
| 18. DISTRIBUTION STATEMENT RELEASE TO PUBLIC | | 19. SECURITY CLASS (This Report) UNCLASSIFIED | | 21. NO. OF PAGES 113 | |
| | | 20. SECURITY CLASS (This page) UNCLASSIFIED | | 22. PRICE | |

NOTICE

The information in this document has been funded wholly or in part by the United States Environmental Protection Agency under Cooperative Agreement Number CR812713-01 to the Water Resources Center of the Desert Research Institute. It has been subjected to the Agency's peer and administrative review, and it has been approved for publication as an EPA document. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

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, the 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 a bladder pump, a bladder pump below an inflatable packer, a bailer, a bailer with a bottom-emptying device, a Westbay MP System, two *in situ* BAT® devices, and a 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 samples containing representative concentrations of the VOCs. The devices were installed on 6-m centers in a rectangular grid pattern, with the sampling zones of each installation placed at a depth of about 6 m. The well spacing was chosen to minimize geologic variability over the site while maintaining hydraulic isolation between installations. The first experimental phase consisted of eight sampling rounds over a 19-week period and involved seven of the devices. Results revealed considerable variation in the data between sampling devices and sample rounds. The second phase involved only the bladder pump, the bailer, one *in situ* BAT device, and the *in situ* Westbay MP System and was designed to reduce the possibility of temporal variability by collecting multiple replicate samples with each device during a single sampling event. Phase two results suggested that samples collected with either *in situ* device yielded VOC concentrations which were as accurate as those collected with the bladder pump. The bailer yielded the least accurate data. The final phase of the study was designed to study long-term VOC recovery patterns of six of the devices: the four devices used in the second phase, an additional *in situ* BAT device, and a bailer with a bottom-emptying device. Four sample rounds were conducted at 12-week intervals with the results suggesting that two of the *in situ* devices were as accurate and precise as the bladder pump. The two bailers utilized during this phase of the study were the least accurate and precise. No operational problems were encountered with any of the six devices tested during the final phase of the study. The results of this study indicate 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 report was submitted in fulfillment of Cooperative Agreement CR812713-01 by the Desert Research Institute under the partial sponsorship of the U.S. Environmental Protection Agency. It covers the period from July 1, 1986, through June 30, 1990, and work was completed as of September 30, 1990.

ACKNOWLEDGEMENTS

The authors wish to acknowledge the contributions of the U.S. EPA Environmental Monitoring Systems Laboratory (Las Vegas, Nevada) and the Desert Research Institute, Water Resources Center. Mr. Joseph J. DLugosz contributed to the project scope. Dr. Robert Kinnison and Dr. Forest Miller provided assistance in the experimental design and statistical evaluation of the results. Dr. Michael Whitbeck and Dr. Richard McArthur provided comments and assistance as the project progressed and critically reviewed the report. Ms. Debora Noack produced many of the figures and tables and put together the final document. We also wish to thank L'Eggs Products Inc. and Mrs. Vivian Carpin for their cooperation and willingness to allow these experiments to take place on their property.

CONTENTS

| | |
|--|--------|
| Abstract | iii |
| Acknowledgements | iv |
| Figures | vii |
| Tables | ix |
| 1. Introduction | 1 |
| Objectives and Approach | 2 |
| 2. Description of Sampling Devices | 4 |
| Bailers | 4 |
| Bladder Pumps | 6 |
| BAT Ground-Water Monitoring Systems | 9 |
| Westbay MP System | 12 |
| 3. Site Description | 16 |
| Site Location and History | 16 |
| Geology | 16 |
| Quaternary Alluvium | 18 |
| Muddy Creek Formation | 19 |
| Hydrogeology | 20 |
| Hydrochemistry | 23 |
| Monitoring Well Installation | 25 |
| 4. Experiment A | 28 |
| Experimental Design | 28 |
| Results | 31 |
| Benzene and Chlorobenzene | 32 |
| Total Organic Carbon | 34 |
| Week 19 Experiments | 35 |
| Discussion | 36 |
| 5. Experiment B | 38 |
| Experimental Design | 38 |
| Results | 38 |
| Discussion | 40 |
| 6. Experiment C | 43 |
| Experimental Design | 43 |
| Results | 44 |

| | |
|--|----|
| Discussion | 46 |
| 7. Summary and Conclusions | 50 |
| References | 52 |
| Appendices | |
| A. Well Construction Diagrams | 55 |
| B. Laboratory Analysis Methodology | 61 |
| C. Analytical Results | 63 |
| D. Data Plots and Statistical Analyses Results | 89 |

FIGURES

| <u>Number</u> | | <u>Page</u> |
|---------------|--|-------------|
| 1 | Typical bailer design | 5 |
| 2 | Typical bladder pump design | 7 |
| 3 | BAT filter tips | 10 |
| 4 | BAT in-line filter adapter | 11 |
| 5 | Westbay MP sampling probe operation | 13 |
| 6 | Westbay MP VOA bottle holder | 14 |
| 7 | Study site location, eastern Las Vegas Valley | 17 |
| 8 | Pittman Lateral study site | 18 |
| 9 | Configuration and altitude of the top of the Muddy Creek Formation, Henderson, Nevada | 19 |
| 10 | Hydrogeologic cross-section of the Pittman Lateral site | 20 |
| 11 | Water table elevation map, Henderson, Nevada | 22 |
| 12 | Contour map of total dissolved solids concentrations (mg/L) in ground water, Henderson, Nevada | 24 |
| 13 | Map of benzene concentrations (ppm) in ground water, Henderson, Nevada | 25 |
| 14 | Monitoring well layout, Pittman Lateral site | 26 |
| 15 | Plot of benzene concentration ($\mu\text{g/L}$) for each of five sample splits from wells 1, 4, and 6 | 29 |
| 16 | Plot of chlorobenzene concentration ($\mu\text{g/L}$) for each of five sample splits from wells 1, 4, and 6 | 29 |
| 17 | Plot of TOC concentration (mg/L) for each of five sample splits from wells 1, 4, and 6 | 30 |
| 18 | Benzene concentration ($\mu\text{g/L}$) recovered by each sampling device as a function of time | 33 |
| 19 | Chlorobenzene concentration ($\mu\text{g/L}$) recovered by each sampling device as a function of time | 33 |
| 20 | TOC concentration (mg/L) recovered by each sampling device as a function of time | 35 |
| A.1 | Well 1 construction diagram and lithologic log | 55 |
| A.2 | Well 2 construction diagram and lithologic log | 56 |
| A.3 | Well 3 construction diagram and lithologic log | 57 |

| | | |
|------|--|----|
| A.4 | Well 4 construction diagram and lithologic log | 58 |
| A.5 | Well 5 construction diagram and lithologic log | 59 |
| A.6 | Well 6 construction diagram and lithologic log | 60 |
| D.1 | Experiment B – Benzene data | 89 |
| D.2 | Experiment B – Chlorobenzene data | 89 |
| D.3 | Experiment B – 1,2-Dichlorobenzene data | 90 |
| D.4 | Experiment B – 1,3-Dichlorobenzene data | 90 |
| D.5 | Experiment B – 1,4-Dichlorobenzene data | 91 |
| D.6 | Experiment B – 1,1-Dichloroethane data | 91 |
| D.7 | Experiment B – 1,2-Dichloroethane data | 92 |
| D.8 | Experiment B – Ethylbenzene data | 92 |
| D.9 | Experiment B – Trichloroethene data | 93 |
| D.10 | Experiment C – Benzene data | 94 |
| D.11 | Experiment C – Chlorobenzene data | 94 |
| D.12 | Experiment C – 1,2-Dichlorobenzene data | 95 |
| D.13 | Experiment C – 1,3-Dichlorobenzene data | 95 |
| D.14 | Experiment C – 1,4-Dichlorobenzene data | 96 |
| D.15 | Experiment C – 1,1-Dichloroethane data | 96 |
| D.16 | Experiment C – 1,2-Dichloroethane data | 97 |
| D.17 | Experiment C – Ethylbenzene data | 97 |
| D.18 | Experiment C – Trichloroethene data | 98 |

TABLES

| <u>Number</u> | | <u>Page</u> |
|---------------|---|-------------|
| 1 | Sampling devices utilized in Experiment A | 31 |
| 2 | Tukey test results for Experiment A | 34 |
| 3 | Sampling Devices utilized in Experiment B | 39 |
| 4 | VOC concentration means and standard deviations of the four sampling devices utilized in Experiment B | 39 |
| 5 | Tukey test results for Experiment B | 41 |
| 6 | Sampling devices utilized in Experiment C | 43 |
| 7 | Test of effectiveness of bottom-emptying device, sample round 4 | 45 |
| 8 | Rankings of devices based on Tukey test results – highest VOC recovery | 47 |
| 9 | Rankings of devices based on Tukey test results – lowest VOC recovery | 47 |
| B.1 | Chemical species, referenced method analysis, and laboratory analysis equipment used | 62 |
| C.1 | Survey sampling results, well 1 | 63 |
| C.2 | Survey sampling results, well 4 | 64 |
| C.3 | Survey sampling results, well 6 | 65 |
| C.4 | Experiment A –Bladder pump sampling results | 66 |
| C.5 | Experiment A – Bailer sampling results | 67 |
| C.6 | Experiment A – PTFE filter tip sampling results | 68 |
| C.7 | Experiment A – Multi-port sampling results | 69 |
| C.8 | Experiment A – Well probe sampling results | 70 |
| C.9 | Experiment A – HDPE filter tip sampling results | 71 |
| C.10 | Experiment A – Bladder pump/packer sampling results | 72 |
| C.11 | Experiment A – LVVWD standard solutions | 73 |
| C.12 | Experiment A – EPA standard solutions | 74 |
| C.13 | Experiment A – Equipment blanks – bladder pump | 75 |
| C.14 | Experiment A – Equipment blanks – bailer | 76 |
| C.15 | Experiment A – Trip blanks | 77 |
| C.16 | Experiment A – Week 19 sampling results | 80 |
| C.17 | Experiment B – VOC analytical results for six replicate samples collected with each sampling device – November 8, 1988 | 81 |
| C.18 | Experiment B – Quality assurance samples | 82 |
| C.19 | Experiment C – VOC analytical results for sample round 1 | 83 |

| | | |
|------|--|-----|
| C.20 | Experiment C – VOC analytical results for sample round 2 | 84 |
| C.21 | Experiment C – VOC analytical results for sample round 3 | 85 |
| C.22 | Experiment C – VOC analytical results for sample round 4 | 86 |
| C.23 | Experiment C – Quality assurance blanks | 87 |
| C.24 | Duplicate analyses of random samples | 88 |
| D.1 | Experiment C – Tukey test results for round 1 | 99 |
| D.2 | Experiment C – Tukey test results for round 2 | 100 |
| D.3 | Experiment C – Tukey test results for round 3 | 101 |
| D.4 | Experiment C – Tukey test results for round 4 | 102 |

SECTION 1

INTRODUCTION

The ability to collect ground-water samples representative of aquifer hydrochemical conditions is a major concern in any ground-water investigation effort. Unfortunately, there are many factors in the sampling 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.

This Cooperative Agreement research was initiated to study the effectiveness of various elements of ground-water sampling procedures for hazardous waste sites. An early product of the study was a report (Blegen *et al.*, 1987) addressing concerns about well-purging, sample collection, and equipment decontamination at hazardous waste sites. The report outlined current methods and equipment and discussed their relative effectiveness. It also contained an annotated bibliography of important work on these subjects and a reference list of over 300 related documents. A matrix of ground-water sampling devices (Pohlmann and Hess, 1988) was also produced for this project. This report outlined the suitability of 12 categories of devices for sampling 14 types of ground-water parameters typically found at hazardous waste sites. Another element of the project was construction of a laboratory-based, simulated well environment for the purpose of providing a standardized basis for comparing ground-water samplers (Whitbeck and Williams, 1990). In addition, a laboratory-based study of the effects of purging techniques on volatile organic compound (VOC) concentrations in low-yield wells was conducted (Pohlmann *et al.*, 1990). Finally, this report focuses on a field comparison of ground-water sampling devices for sampling VOCs.

Of the many elements of the sampling process, 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 process. In addition, concern for obtaining representative samples of ground water containing VOCs has arisen because VOCs are common contaminants at hazardous waste sites (Plumb and Pitchford, 1985). To address these concerns, sampling devices and methods have been developed to minimize impact on sample quality.

Several published studies have focused on the effects sampling devices have on the physical and chemical integrity of the samples they are used to collect. Comparative studies, based either in the laboratory or in the field, are a common means of determining which sampling mechanisms or procedures function best under a given set of conditions. Laboratory studies by Unwin (1984), Barcelona *et al.* (1984), and Stolzenburg and Nichols (1985), and field studies by Houghton and Berger (1984), Muska *et al.* (1986), Imbrigiotta *et al.* (1986), Pearsall and

Eckhardt (1987), and Yeskis *et al.* (1988) compared some of the more commonly utilized ground-water sampling methodologies and devices.

In general, the devices tested during these studies are used in conventional monitoring wells and therefore require the removal of stagnant water from the well prior to sampling. While well purging is generally considered necessary in order to collect a representative ground-water sample, the purging process may also introduce considerable bias in the sampling. Gillham *et al.* (1985) note several potential problems associated with well purging, including:

- There is no assurance that all of the stagnant water has been removed from the well, or that the resulting samples have not been contaminated by stagnant water remaining in the well.
- A large drawdown, induced by the removal of large volumes of water during well purging, may alter ground-water chemistry (degassing, volatilization), or may draw into the well unrepresentative ground water from different hydrogeologic zones.
- Well purging can be time-consuming and require extra equipment, thereby increasing sampling costs.
- Waste water disposal may become a problem if the volume is large and/or if the water is contaminated.

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, so are often referred to as *in situ* systems. To date, few studies comparing these devices to the more conventional ground-water sampling methods have been published. However, the existence of these new devices raises three important questions:

- Do sampling methods exist which may eliminate the need for well purging prior to sample collection?
- How valid or representative is the resulting sample?
- Are the proposed *in situ* monitoring techniques inherently invalid because of the necessity of well purging?

This study was initiated to address the concerns expressed by these questions. In other words, can *in situ* monitoring techniques yield data representative of subsurface geochemical conditions, or will these data be biased due to the inherent need to purge the well bore prior to sampling?

OBJECTIVES AND APPROACH

The primary objective of this study was to conduct a field comparison between several ground-water sampling devices, including two *in situ* devices that require little or no pre-sample purging. Seven different sampling methods were evaluated to determine if the non-pumping methods yielded representative data, and to

compare the accuracy and precision of the various sampling devices. The comparison was based on the ability of each device to deliver a representative ground-water sample from the subsurface environment to the ground surface and into an appropriate sample container. Because VOCs are common contaminants at hazardous waste sites, emphasis was placed on the effect these devices had on the recovery of VOCs present in ground water at the study site.

The ideal approach to a study of this type would be to conduct the comparison in such a manner that each sampling device was subjected to identical sampling conditions. Under these conditions, the only sampling variable would be the device itself. However, the very nature of a field study implies variation in subsurface geologic and hydrochemical conditions. This problem was addressed by locating, designing, and constructing the wells in such a way that hydrogeologic and geochemical conditions were as similar as possible in a field setting.

The investigation was conducted in three separate phases (experiments A, B, and C) with the approach including the following major procedures:

- Six ground-water monitoring wells were installed close to each other at a site in southeastern Las Vegas Valley. Geologic and geophysical logs were utilized to delineate geologic variability at the site.
- An initial set of multiple replicate samples was collected from three wells to investigate variability in hydrochemistry between the sampling points. Laboratory results were also utilized to estimate expected laboratory error.
- Ground-water samples for experiment A were collected with each device on a regularly scheduled basis during nine sampling rounds over a 19-week period. Samples were analyzed in the laboratory for a variety of organic and inorganic chemical parameters.
- Laboratory results were subjected to statistical analysis, including a two-way analysis of variance designed to determine if significant chemical variations could be attributed to sampling device and/or sampling time. Emphasis was placed on sampling device effects on VOC concentration.
- A second experiment, experiment B, was developed based on the experiences and results of the first phase. Experiment B included replicate sampling during a single sampling period. Samples were analyzed for VOC concentration only.
- Statistical analysis of the new data included an analysis of variance and multiple comparison tests. Results of the analyses were evaluated to determine which sampling devices yielded the most accurate and precise VOC concentrations.
- Experiment C added the element of time by conducting four sample rounds over a one-year period. Patterns of VOC recovery over time and long-term device performance were of primary interest.

SECTION 2

DESCRIPTION OF SAMPLING DEVICES

Seven ground-water sampling devices were utilized in this comparative study, all of which are commercially available. 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 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 with the most chemically inert materials available from the manufacturers.

BAILERS

Bailers are perhaps the simplest of all ground-water sampling devices. They may be easily constructed from most tubular materials and are relatively inexpensive and simple to use. The basic design of most bailers consists of a long tube (usually of rigid PVC, Teflon®, or stainless steel) open at the upper end where a haul line is attached and with a simple ball-and-seat check valve at the bottom end (Figure 1).

The bailer is lowered into a well by the haul line. Contact with the water surface dislodges the check valve ball, which allows water to flow through the main body of the bailer as it is lowered through the water column. When the descent of the bailer is stopped at the desired sampling depth, the weight of the overlying water column closes the check valve, thus trapping a sample inside the bailer. The bailer is then withdrawn from the well and the sample transferred to appropriate sample containers.

Nielsen and Yeates (1985) and Scalf *et al.* (1981) list several advantages and disadvantages of using bailers to sample ground water from wells. Advantages include:

- Bailers may be constructed from a wide variety of materials and in virtually any dimensions to accommodate any well diameter and desired sample volume.
- Bailers are mechanically simple, easily operated, portable, and require no external power source.
- Bailers are relatively inexpensive, making it possible to dedicate a separate bailer to each well.
- Samples may be taken from virtually any depth.

Disadvantages of bailers include:

- Purging a well of stagnant water with a bailer is often impractical, particularly with deeper wells. Other devices are often needed to purge the well prior to sampling with the bailer.

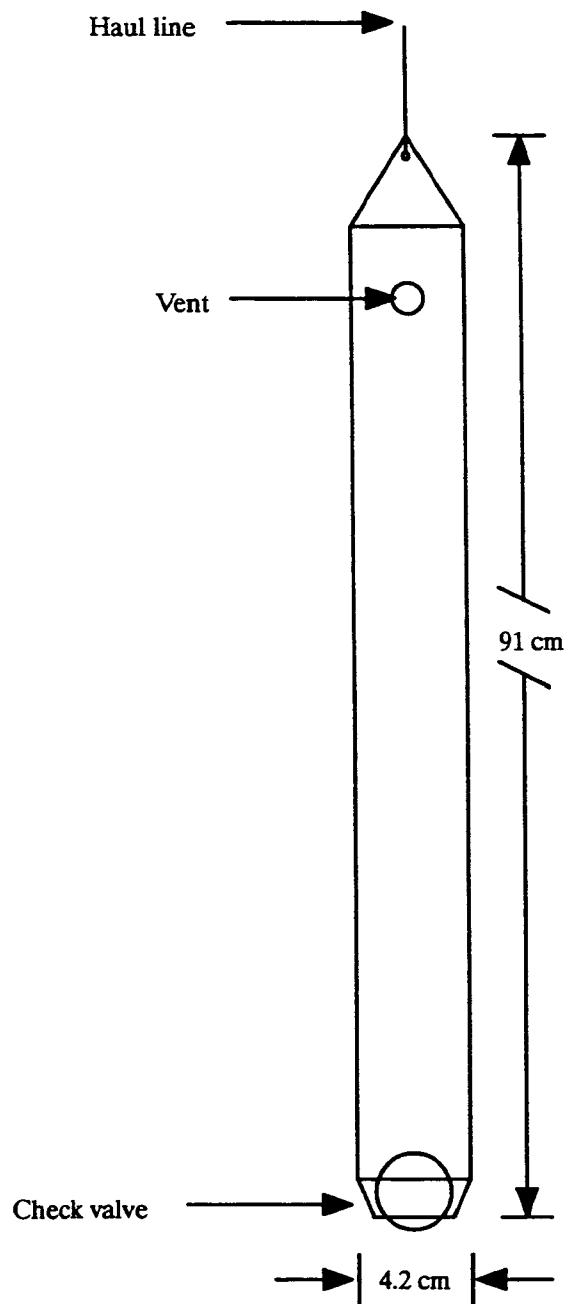


Figure 1. - Typical bailer design.

- Haul lines must be of a noncontaminating material, adequately cleaned, and dedicated to a single well to prevent cross-contamination.
- Aeration, degassing and turbulence may occur while lowering and raising the bailer through the water column and while transferring the sample to appropriate containers.
- Sampling personnel may be exposed to any contaminants in the sample.
- The sample may not be representative of a specific point within the water column.
- Movement of the bailer may dislodge particulate matter from the casing wall, resulting in a turbid and unrepresentative sample.

One bailer utilized in this project was an all-Teflon closed-top bailer produced by the Galtex® Corporation. The closed top with side ports design was chosen to minimize the possibility of stagnant water entering the device as it was retrieved from the well. A Teflon-coated stainless steel haul line was used to lower and raise the bailer. Sample water was discharged into clean glass beakers by carefully dislodging the check valve ball against the bottom of the beaker. This bailer will be denoted as the “standard bailer” or “bailer” in this report.

The second bailer utilized in this project was similar in operating principle but used a controlled flow bottom-emptying device (BED) to transfer the sample directly from the bottom of the bailer to a volatile organic analysis (VOA) vial. This feature was designed by the manufacturer to minimize agitation of the sample that may occur during transfer to the sample container by decanting from the bailer top or by discharging into a beaker from the bailer bottom and then pouring into a VOA vial. This bailer, denoted as the “BED Bailer” in this report, was manufactured by Norton Performance Plastics. A closed top and “V”-notched orifices on the side of the bailer at the top were designed to prevent the contents from mixing with well water during retrieval.

The bailers were cleaned in the laboratory before being used in the field. The cleaning procedure involved careful scrubbing with a nonphosphate detergent/tap water solution, followed by rinsing with a 10 percent acetone solution and distilled water. Equipment blanks were collected following the distilled water rinse. The haul lines were subjected to the same cleaning process. When not in use, the bailers were stored in clean polyethylene bags.

BLADDER PUMPS

Bladder pumps, also known as gas-squeeze pumps, are classified as positive-displacement sampling devices due to the utilization of positive gas pressure to “push” water samples from depth to the ground surface for collection. While specific designs may vary somewhat, most bladder pumps consist of a flexible membrane (the “bladder”) housed in a long rigid tube, a water intake check valve, a discharge check valve, a tubing line which allows for gas pressurization of the annular space between the membrane and the pump housing, and another tube for sample discharge (Figure 2). Bladder pumps require a supply of compressed gas and an automated control system which controls gas pressure and gas flow rates to the pump, which in turn dictate water sample discharge rates (Nielsen and Yeates, 1985).

Bladder pump operation is relatively simple. When the pump is lowered into the well and submerged, water may enter the pump by passing through the intake check valve and into the bladder. Gas pressure applied to the annular space between the bladder and the rigid outer wall of the pump compresses the bladder. This causes the intake check valve to close and forces the water sample through the discharge check valve and up the sample discharge tube. When this “pump phase” is complete, pressure inside the pump is released and vented at the ground surface by the control system. The discharge check valve closes under the weight of the overlying water column within the discharge tube and prevents water in the tube from flowing back into the pump. With the bladder now fully relaxed, water may again enter the pump and fill the bladder. The process is repeated to cycle water to the ground surface. Adjustments to the automated control system regulate applied pressure and control

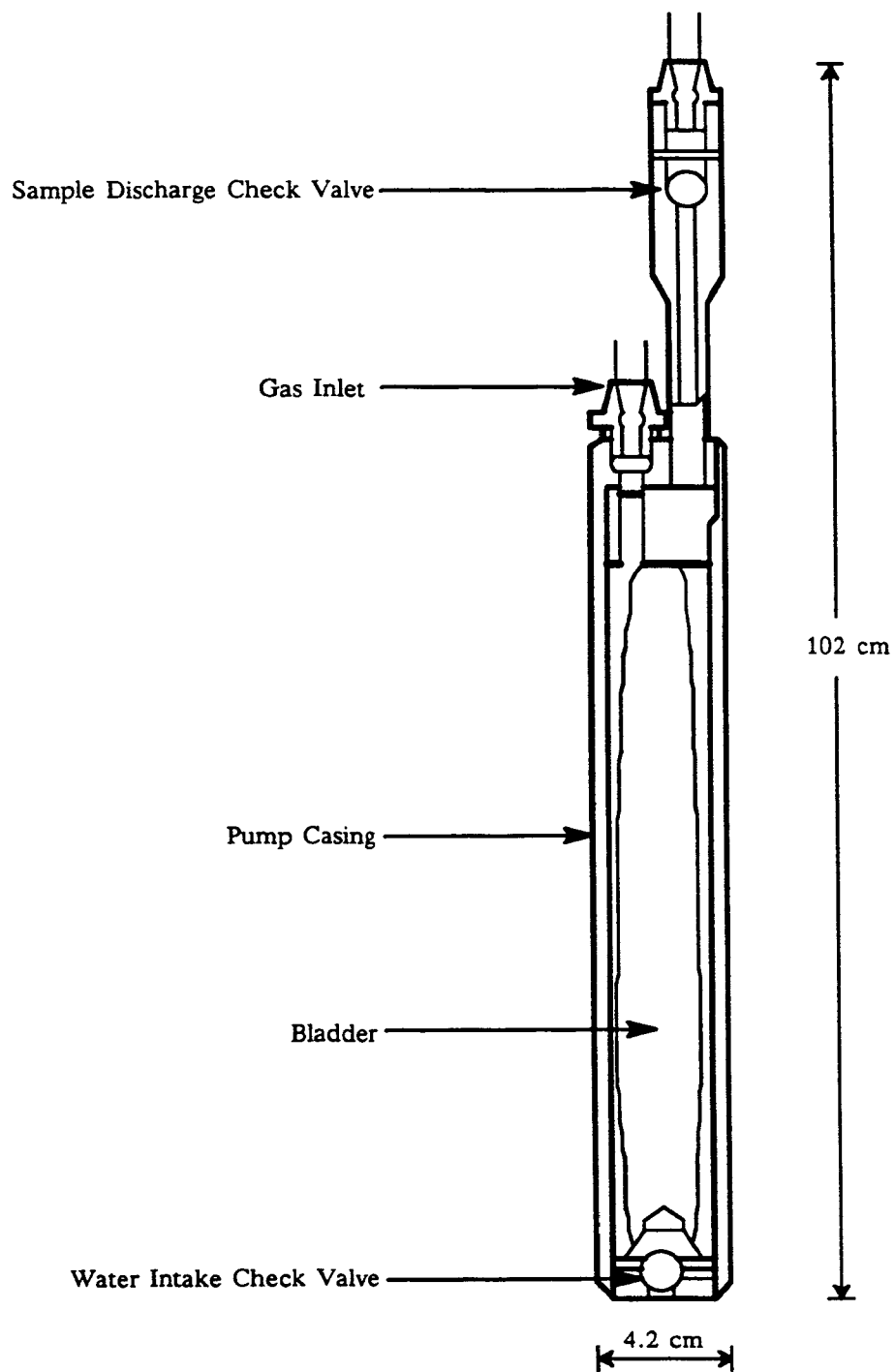


Figure 2. - Typical bladder pump design.

the frequency with which pressure is applied to and released from the pump, thus controlling sample flow rates and lift capability as well as optimizing pumping efficiency (Nielsen and Yeates, 1985).

As noted by Nielsen and Yeates (1985), Scalf *et al.* (1981) and Gillham *et al.* (1983), advantages of the bladder pump include:

- No direct contact occurs between the driving gas and the water sample, thereby minimizing concerns about gas stripping.
- The pumps may be constructed of a wide range of materials, including stainless steel and Teflon.
- A wide range of pumping rates is possible and the rate may be controlled relatively easily. This allows the bladder pump to be used for well evacuation at high pumping rates as well as for sampling at low flow rates.
- Depth capability is controlled primarily by the operating pressure of the pump. Many bladder pumps are capable of pumping lifts of over 60 m.
- The pumps are easily disassembled for cleaning and repair.
- The pumps are commercially available in a variety of lengths and diameters, although most are designed for use in 5.1 cm diameter monitoring wells.

Disadvantages include:

- Large gas volumes and long cycles are necessary when pumping from deeper wells. This increases operating time and expense.
- Although adjustable, pump discharge is intermittent.
- The pump may subject the sample to turbulent flow and large pressure changes.
- Minimum pumping rates may be higher than ideal for sampling ground water contaminated with VOCs.
- Check valves may fail in water with a high suspended solids content.
- Commercially available pump units may be relatively expensive.

Two all-Teflon Well Wizard® bladder pumps (produced by Q.E.D. Environmental Systems, Inc.) were utilized for this project. The gas-supply and sample discharge tubes and all fittings are also made of Teflon.

One of the two bladder pumps was used in conjunction with an inflatable packer mounted above the pump. The packer serves to reduce purge volumes by isolating stagnant well water above the pump and preventing that water from migrating downward to the pump intake. The Purge Miser® inflatable packer (manufactured by Q.E.D. Environmental Systems, Inc.) consists of a stainless steel body and fittings and a Viton® bellows. The pump/packer combination was dedicated to a single well, and after installation it remained downhole for the duration of the sampling period. The other bladder pump was also dedicated to a single well, but it was necessary to remove it from the well after purging and sampling to allow for sampling with the bailer.

The pumps were cleaned in a manner similar to that described for the bailer. Prior to installation in a well the pumps were placed in cleaning tubes which contained the cleaning solutions. The pump was activated and allowed to pump approximately 19 L of each solution through the pump and discharge lines. The solutions used were (a) a nonphosphate detergent/tap water solution, (b) a 10 percent acetone solution, and (c) distilled water. Equipment blanks were collected during the final distilled water rinse.

BAT GROUND-WATER MONITORING SYSTEMS

The BAT Ground-Water Monitoring System is a relatively new type of ground-water monitoring system developed in Sweden by BAT Envitech, Inc. Each component of the system is sealed, and hydraulic interconnections between components are accomplished through the use of hypodermic needles, flexible seals, and induced pressure gradients. Ground-water samples are collected in sealed, evacuated glass vials which may be sent directly to the laboratory. Therefore, the system makes it possible to collect pressurized water and gas samples without purging large amounts of well water or transferring samples to other containers, a procedure which often results in a loss of VOCs or external contamination (Torstensson and Petsonk, 1986).

The primary feature of the system is the BAT filter tip (Figure 3a), the standard configuration of which consists of a thermoplastic body and a filter of high-density polyethylene. The filter tips can be produced from a variety of materials and in several design configurations to meet expected installation and sampling conditions. The filter tip is reinforced with a core of Teflon-coated stainless steel and sealed with a flexible septum of a resilient material (fluororubber septa were used for this project). The filter tip is threaded onto the bottom of an extension pipe and additional lengths of pipe are added as needed. Normal installation procedures call for the filter tip to be pushed into the ground to the desired sampling depth under a static load, although the installation may be completed in pre-drilled holes (Torstensson and Petsonk, 1986); the latter was done during this study.

Ground-water samples are obtained by inserting the pre-sterilized, pre-evacuated sample vial into a sample container housing, which is then lowered down the extension pipe. At the lower end of the housing, a "guide sleeve" assembly contains a double-ended hypodermic needle. The glass sample vials contain a flexible septum similar to those in the filter tips. Contact between the guide sleeve and the filter tip cap causes the needle to puncture the septa in both the cap and the sample vial. The vacuum in the vial may then draw ground water from the formation, through the filter tip and into the vial. When the sample housing is withdrawn, the hypodermic needle withdraws from both the sample vial and the filter tip. The guide sleeve mechanism causes the needle to withdraw from the sample vial first, thus preventing a loss of sample fluid and/or gas (Torstensson and Petsonk, 1986). The septa in both the filter tip and the vial automatically reseal as the needle is withdrawn. Pressurized samples may be obtained if the sample vial remains connected to the filter tip long enough for the pressure inside the vial to equalize with formation water pressure. When the vial is disconnected from the filter tip, formation pressure is preserved inside the sample vial (Torstensson, 1984). Filtered samples may be obtained through the use of an in-line filter adapter (Figure 4).

The *in situ* design of the BAT system means that the volume of water which needs purging is considerably less than that in conventional monitoring wells. Theoretically, only the small volume of water contained within and immediately outside the filter tip itself would need to be removed prior to sample collection, because this water is in contact with the sampling device and could be considered stagnant water. The manufacturer suggests that one 250 to 500-mL sample volume, collected and discarded before collection of samples, may be sufficient to purge the system. As discussed previously, this small purge volume feature is of primary interest in this investigation. Other advantages or disadvantages of *in situ* systems observed during the investigation will be discussed in subsequent sections of this report.

The two *in situ* filter tips used for this study were designed to be threaded onto a 5.1-cm-diameter Teflon extension pipe, which allows sample sizes of up to 500 mL to be obtained. Both of the *in situ* filter tips are modified versions of the standard BAT Mk II filter tip. One of the tips has a body of polytetrafluoroethylene (PTFE, or Teflon) with a porous PTFE filter (hereafter referred to as the "PTFE filter tip"), while the other tip has a polyacetal body with a filter of high-density polyethylene (hereafter referred to as the "HDPE filter tip"). Both *in situ* filter tips were installed in pre-drilled boreholes, with the installations completed by backfilling with gravel pack and cement-bentonite slurry surface seals.

A third BAT device used for this project is a major modification of the *in situ* tip and requires completely different assembly and installation procedures. However, once installed, it is functionally identical to a standard

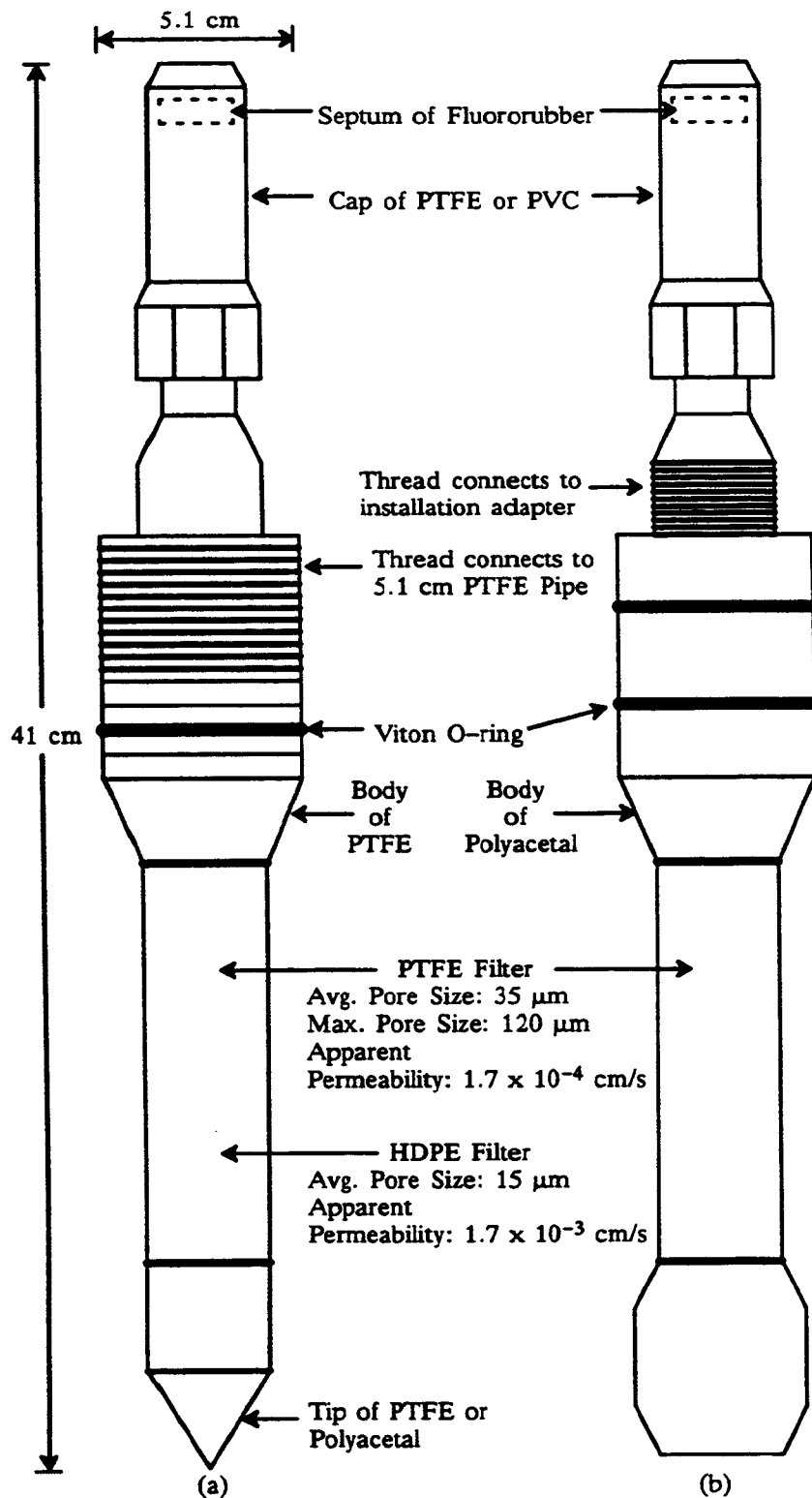


Figure 3. - BAT filter tips: (a) *In situ* BAT filter tip, (b) BAT well probe (adapted from BAT Envitech, Inc., 1987).

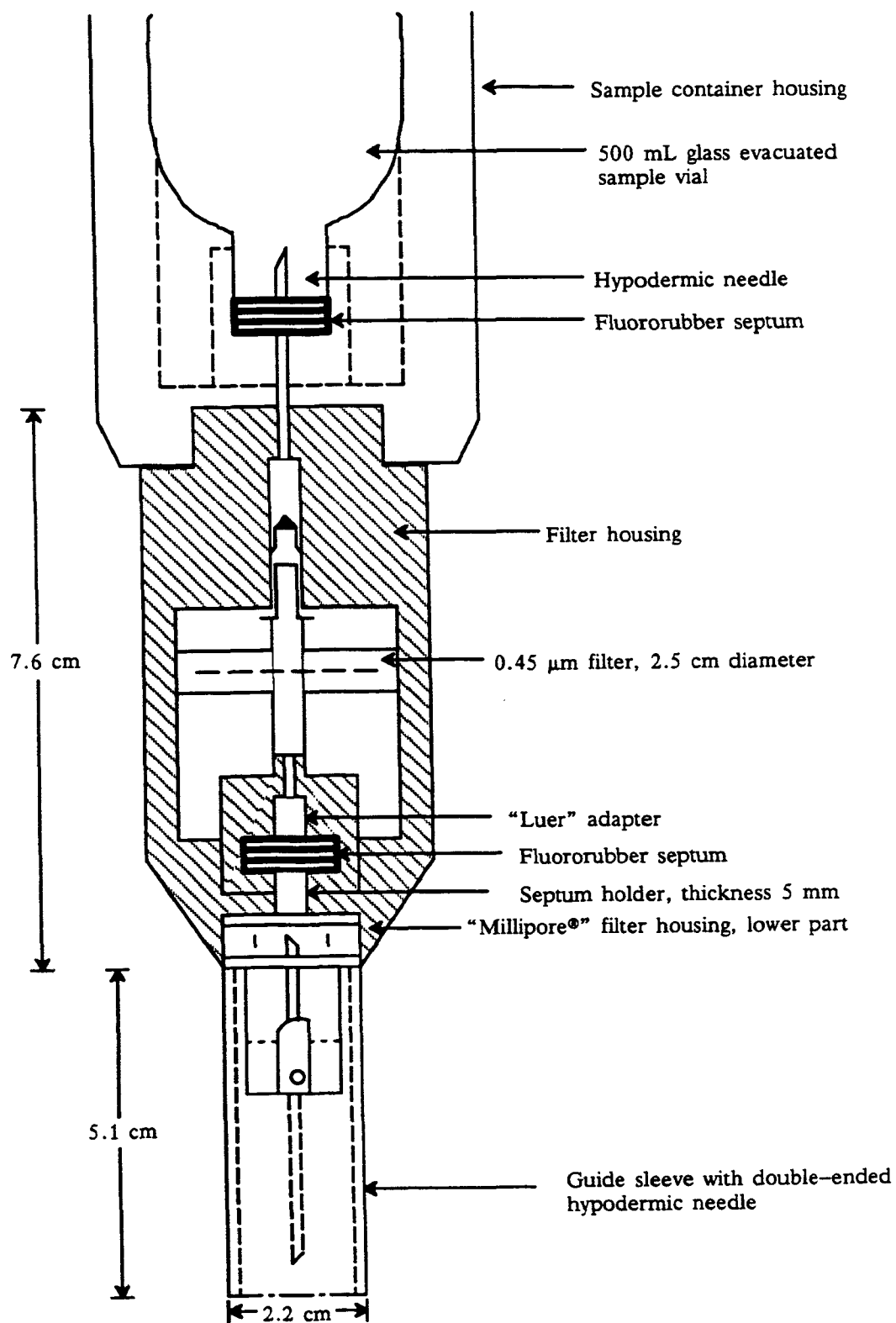


Figure 4. - BAT in-line filter adapter (adapted from BAT Envitech, Inc., 1987).

filter tip. Developed by BAT Envitech, Inc., for the Desert Research Institute (DRI), the BAT "well probe" (shown in Figure 3b) is designed to be pushed down the inside of an existing 5.1-cm-diameter well. The two Viton O-rings on the probe function as a packer to seal off the well screen from the environment in the casing above. With the well screen sealed off, the probe functions as a sampling port from which samples from the screened interval may be extracted. The well probe was installed in a conventionally designed monitoring well following well development. The well was purged of stagnant water prior to insertion and placement of the probe within the screened interval.

WESTBAY MP SYSTEM

The Westbay MP System, designed and distributed by Westbay Instruments, Ltd., is a ground-water monitoring device which allows discrete samples or measurements to be taken at multiple levels within a single borehole. The system consists of various lengths of casing joined by regular or valved port couplings, and a variety of specialized tools and probes designed to access the ports and retrieve samples or measurement data from the environment outside the sealed casing. The modular design allows for the establishment of as many monitoring zones as desired, and the well design may easily be altered at the time of installation to adjust to unexpected subsurface conditions. The valved nature of the ports does not allow formation water to enter the MP casing, thus eliminating the need to purge stagnant water from inside the casing prior to sampling. Sampling probes accessing a measurement port draw the sample from directly outside the casing (Black *et al.*, 1986).

The standard Westbay MP casing has an inside diameter of 3.7 cm and is available in several different lengths. All couplings and end caps are connected to the casing with a flexible shear rod, and O-rings provide a tight hydraulic seal which prevents water from entering the casing. Regular couplings are used where valved ports are not required. Pumping ports are used at intervals where it may be desirable to remove large quantities of water. The port may be opened and closed with a specially designed tool by moving an internal sleeve which exposes (or covers) slots that allow water to flow into the casing. Opening this port makes it possible to develop a desired monitoring zone, and positioning a pumping port just below a measurement (sampling) port allows for the development of the region around that port as well. A measurement port coupling is essentially a regular coupling with a check valve in the coupling wall through which fluid samples may be extracted. Normally closed, the valve may be accessed and opened with a sampling probe (Black *et al.*, 1986).

The procedure for obtaining a fluid sample is depicted in Figure 5. A sample container is attached to the sampling probe and lowered down the casing to a point below the desired measurement port. The backing shoe is briefly activated (pneumatically activated, nitrogen-gas driven), releasing the location arm. The probe and sample bottle are then raised above, then lowered down to, the measurement port where they automatically position themselves with respect to the port valve. Activating the backing shoe pushes the probe to the wall of the coupling and simultaneously forces the port valve to open as the face seal of the probe seals around the valve. Opening the probe sampling valve creates a hydraulic connection between the formation water outside of the port and the sample bottle. After allowing enough time for the sample container to fill, the sampling valve is closed, the backing shoe deactivated, and the probe returned to the surface. The port valve automatically closes as the backing shoe is deactivated (Black *et al.*, 1986).

Several sample container configurations are available. The container used to collect VOA samples is shown schematically in Figure 6. The container holds a standard 40-mL glass VOA bottle. Two hypodermic needles penetrate the bottle septum, one of which is hydraulically connected to the sampler probe through a 0.32-cm-diameter Teflon tube. When the sampler valve is opened, water flows through the tube and needle and into the bottle. As the bottle fills, the second needle vents gas and excess water into the container housing. This design allows the bottle to be thoroughly flushed with formation water with only the last 40 mL kept as a sample (Black *et al.*, 1986).

The Westbay MP System components chosen for this study were made of stainless steel. Three measurement ports were installed at various depths, but only data from the lowermost port were used in the

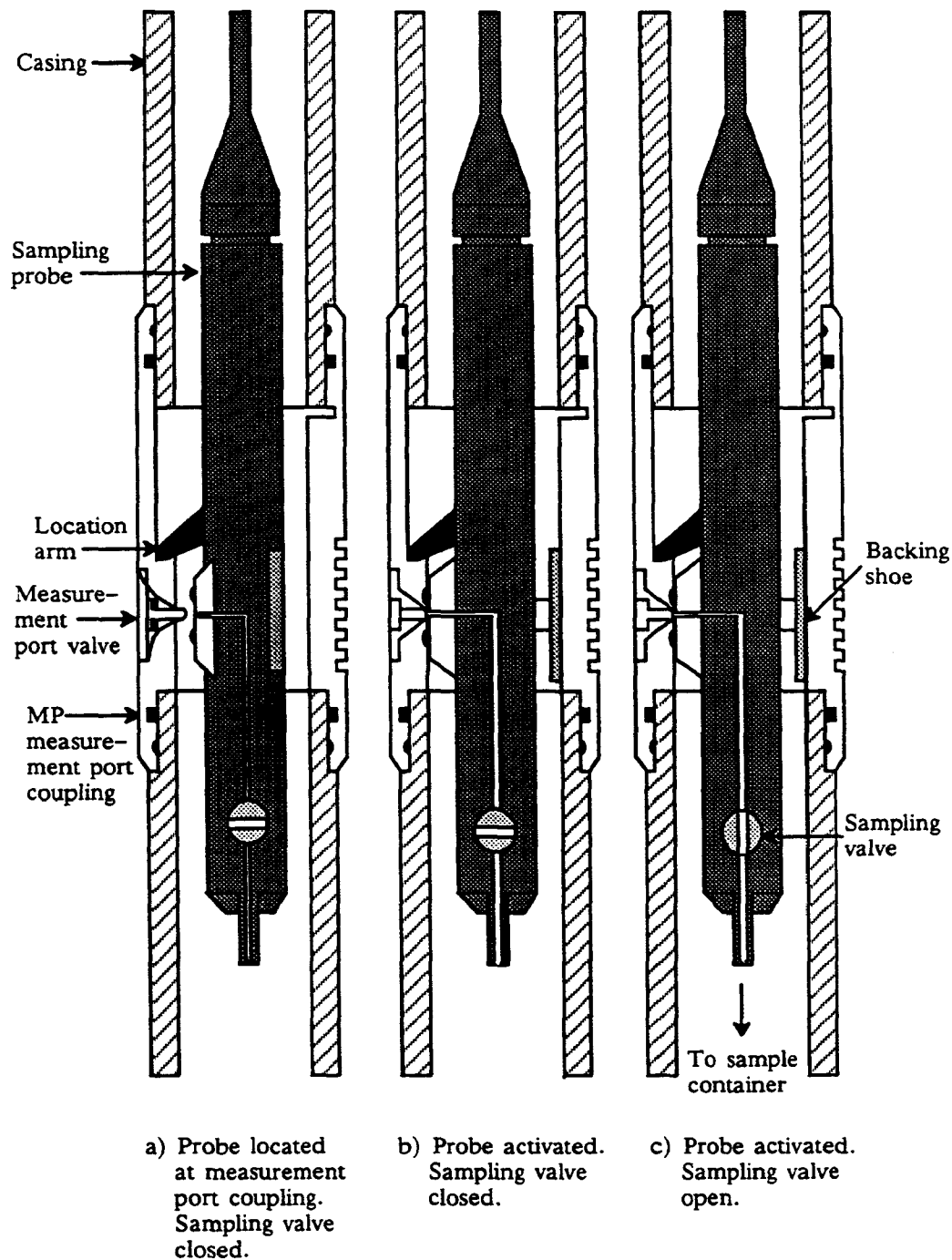


Figure 5. - Westbay MP sampling probe operation (adapted from Black *et al.*, 1986).

comparative work. A pumping port was installed 0.6 m below the lower measurement port to allow development of the monitoring zone and a 0.9-m section of screen (0.025-cm slots) was placed around both ports. The well construction was completed by backfilling with gravel pack around the monitoring zones, separated by bentonite seals. A standard method of development for Westbay installations, and the method used for this installation, is

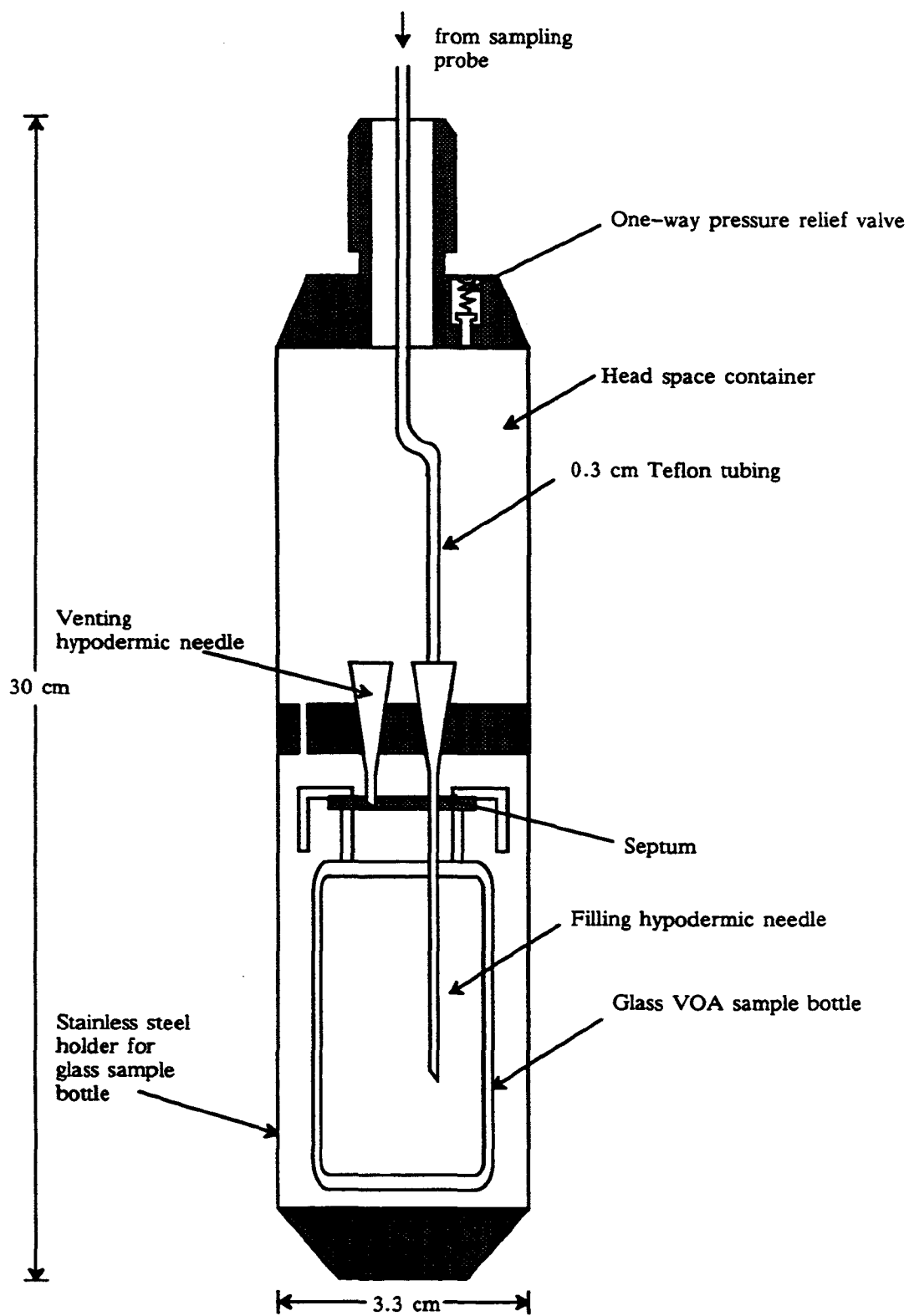


Figure 6. – Westbay MP VOA bottle holder (adapted from Black *et al.*, 1986).

to open a pumping port and airlift the water from the inside of the casing. The Westbay MP System will be denoted as the “multi-port” in this report.

As with the *in situ* BAT devices, the design of the Westbay MP system is significant in that the volume of water needing purging from the installation is considerably less than that required in conventional monitoring wells. Theoretically, only the small volume of water in contact with the casing outside the measurement port should need removal before a sample is collected. The manufacturer suggests that, depending on conditions at the individual site, a 250 mL volume collected and discarded prior to sample collection may be sufficient to purge the installation. Again, this small purge volume is a feature that is of primary interest in this study, and other advantages or disadvantages of *in situ* devices observed during the investigation will be discussed in subsequent sections of this report.

SECTION 3

SITE DESCRIPTION

SITE LOCATION AND HISTORY

The site chosen for this field study is in the southeastern part of Las Vegas Valley, within the city limits of Henderson, Nevada, and approximately 3 km north of the Basic Management, Inc., (BMI) Complex, a large facility which houses several major chemical production companies (Figure 7). Directly adjacent to the site is the Pittman Lateral, a major water conduit supplying Colorado River water to the Las Vegas metropolitan area (Figure 8). Also adjacent to the study area is a series of 23 ground-water monitoring wells, collectively known as the Pittman Lateral Transect, which are situated roughly perpendicular to the northward flow of ground water. The site chosen for installation and testing of the ground-water sampling equipment is near the center of the Pittman Lateral Transect.

In the early 1940s, the Federal Government, in response to an increased wartime need for magnesium, constructed the Basic Magnesium facility in Henderson. After the war, the facility was sold to several private corporations. BMI was created in 1952 by several of these corporations to manage certain portions of the complex (JRB Associates, Inc., 1981).

From the early 1940s to the late 1970s, unknown quantities and types of liquid and solid wastes were routinely disposed of in leach beds and unlined evaporation ponds on BMI property. Increased recharge due to leakage from the unlined ponds had an almost immediate effect on the local shallow ground-water system as water levels rose rapidly. Flooded basements and cesspools in the community of Pittman, 3 km north of the BMI complex, were reported as early as 1942 (Geraghty and Miller, Inc., 1980).

At least one organic plume has been determined to have originated from beneath property within the BMI complex. An accidental spill from an underground storage tank in 1976 released approximately 113,500 L of benzene, contributing to the extensive organic contamination which exists today (Geraghty and Miller, Inc., 1980). The downgradient movement of the benzene plume 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.

In the spring of 1983, 23 monitoring wells were installed along the Pittman Lateral Transect by the DRI, Lockheed Engineering and Sciences Company, and the EPA. The primary purpose of the Pittman Lateral wells was to define the local hydrogeology as well as the chemical character of the contaminant plumes. Since that time, the site has been used for a number of soil gas studies, fiber optics experiments, and surface and borehole geophysics experiments.

GEOLOGY

The near-surface geology of the site is composed of two major geologic units: the unconsolidated sands, gravels and cobbles of the Quaternary alluvial fan deposits, and the underlying Muddy Creek Formation, here composed primarily of clays, silts and fine sands.

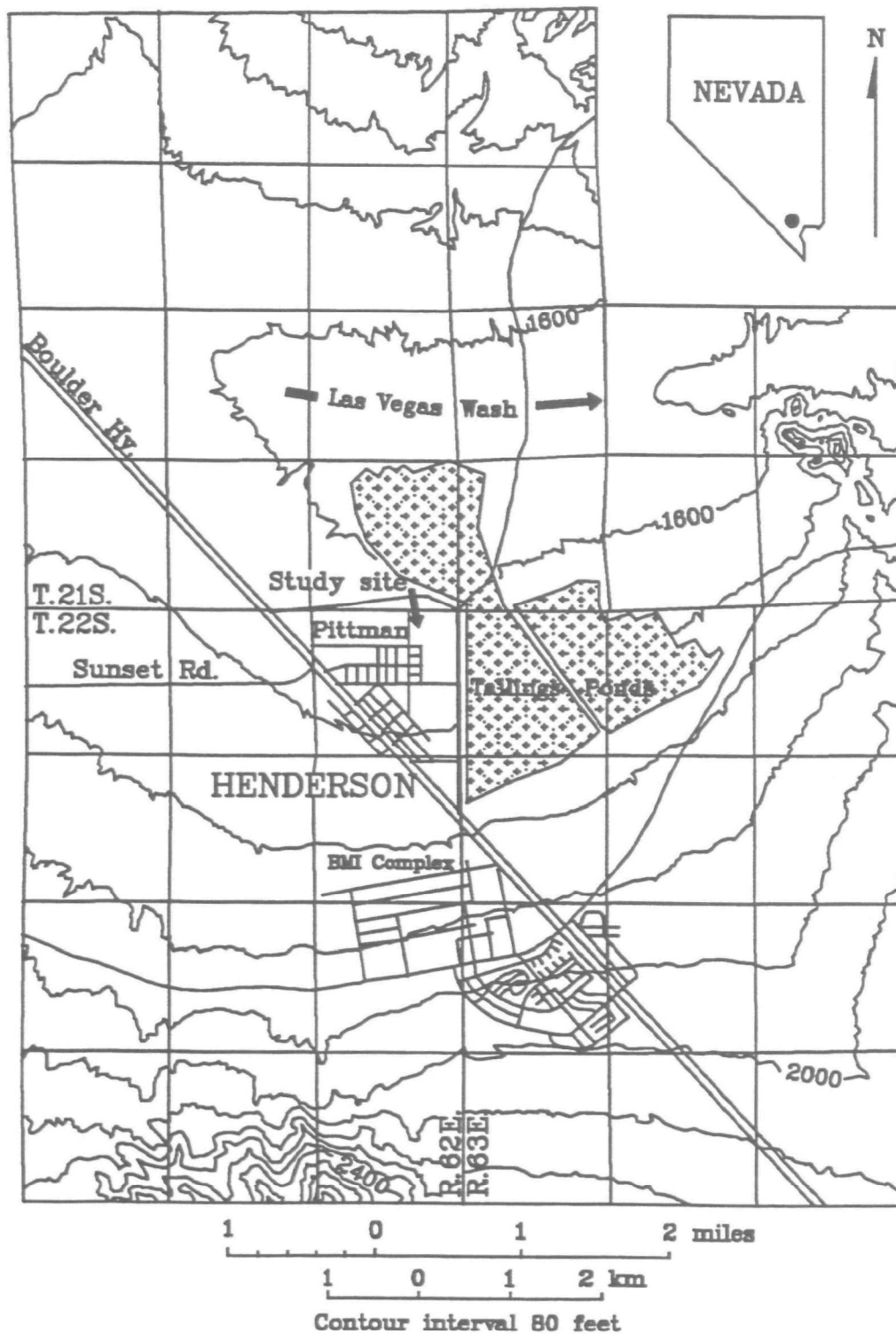


Figure 7. – Study site location, eastern Las Vegas Valley (adapted from U.S. Bureau of Reclamation, 1984).

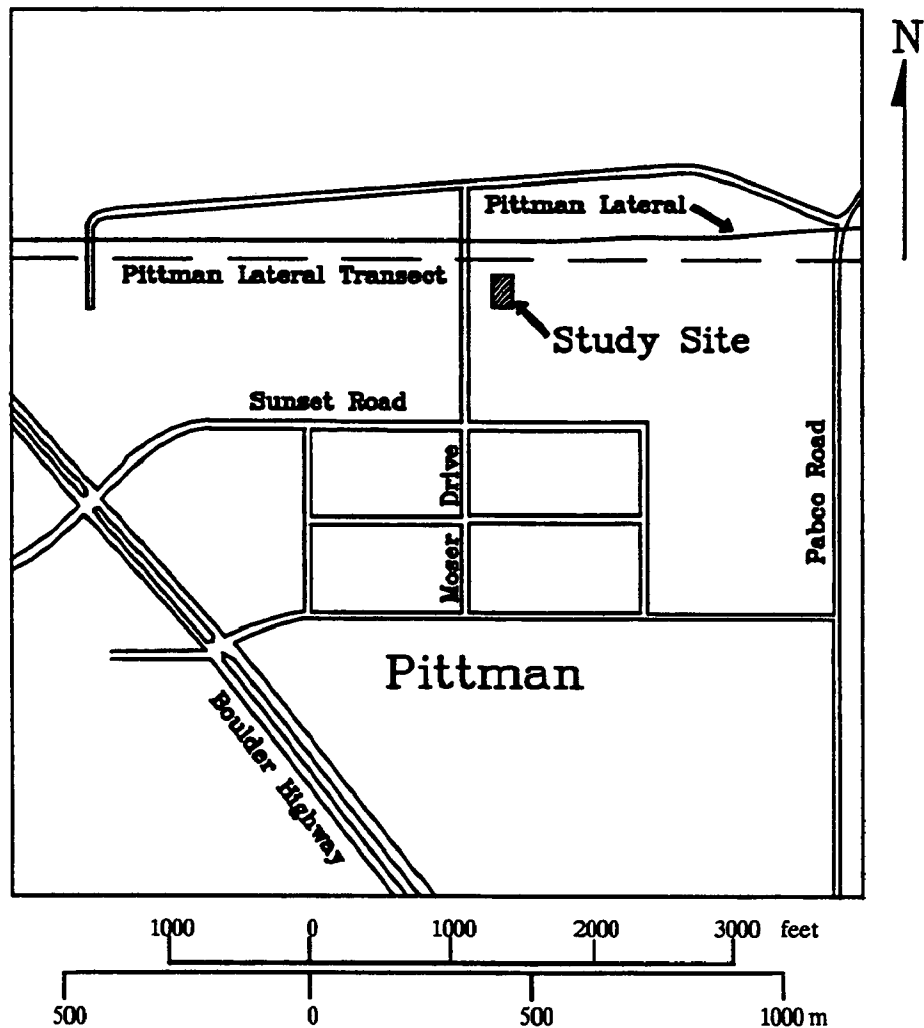


Figure 8. – Pittman Lateral Study Site (adapted from U.S. Bureau of Reclamation, 1984).

Quaternary Alluvium

Quaternary alluvial fan and valley-fill deposits originating in the McCullough Range and River Mountains directly overlie the Tertiary Muddy Creek Formation at the study site. The U.S. Bureau of Reclamation (1982) describes two distinct alluvial deposits near the site. An older fan deposit, consisting of poorly stratified, weakly indurated, light brown to buff, gravelly sand and cobbles, is usually found as a layer 3-m to 6-m-thick overlying the Muddy Creek Formation. This unit tends to average 40 to 60 percent sand, 20 to 50 percent igneous gravel and cobbles, and 10 to 20 percent non-plastic fines (U.S. Bureau of Reclamation, 1982; Fordham *et al.*, 1984). Thickness of these deposits is controlled by the shape of the erosional surface of the Muddy Creek Formation, with a maximum thickness of 78 m being recorded in a well east of Henderson. Hall (1986) and U.S. Bureau of Reclamation (1982) report local strongly caliche-cemented sands and gravels above the Muddy Creek Formation-alluvium contact.

Younger alluvial fan and valley-fill deposits are also described by U.S. Bureau of Reclamation (1982) as poorly sorted, unconsolidated sands and gravels, consisting of 50 to 60 percent sands, 40 to 50 percent fine

subangular gravels, and traces of non-plastic fines. Maximum thickness of these deposits near the study site is approximately 9 m.

Lithologic logs from observation and monitoring wells drilled in the area reveal several deep and narrow channels eroded into the top of the Muddy Creek Formation (Figure 9). Geraghty and Miller, Inc., (1980) report

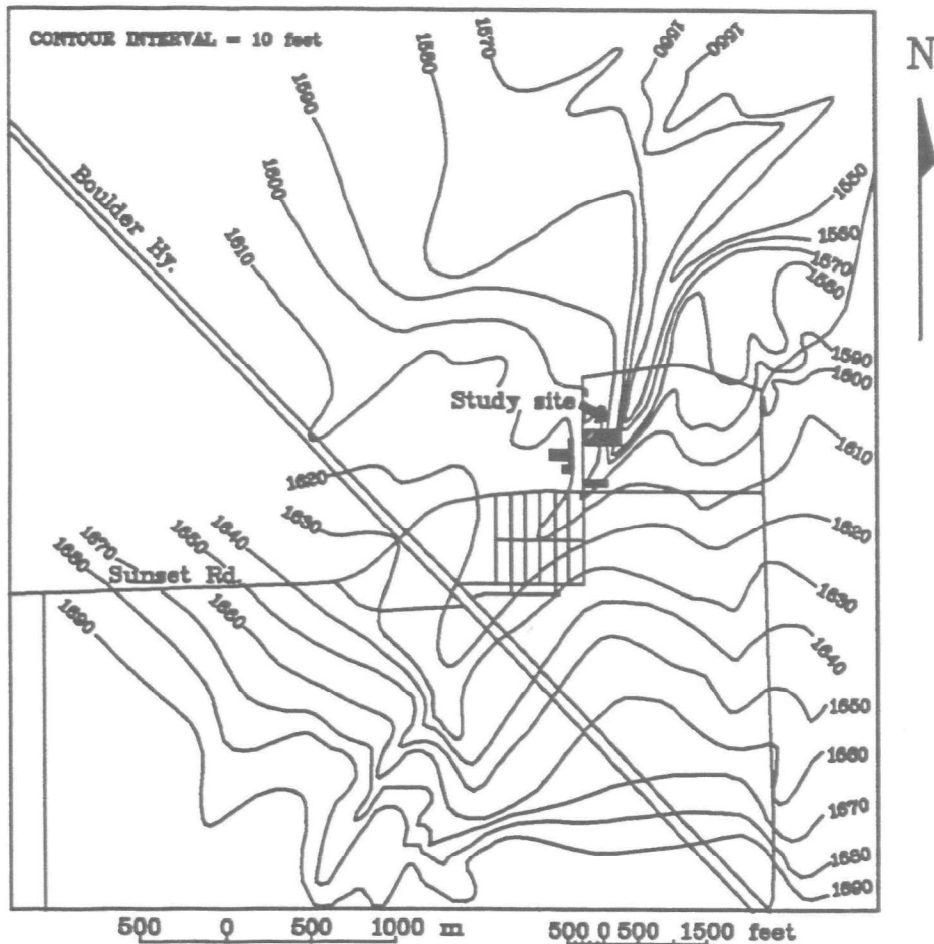


Figure 9. – Configuration and altitude of the top of the Muddy Creek Formation, Henderson, Nevada (elevation contours in feet above mean sea level) (adapted from U.S. Bureau of Reclamation, 1984).

that these channels are often filled with moderately well-sorted deposits of sand and gravel resembling “gravel trains,” which have been buried by subsequent alluvial fan deposits. Near the study site, U.S. Bureau of Reclamation (1982) labels these deposits as the younger Quaternary alluvial fan and valley-fill mixtures described above.

Muddy Creek Formation

Most, if not all, of the Las Vegas Valley is believed to be underlain by the Tertiary Muddy Creek Formation, described by Longwell *et al.* (1965) as valley-fill deposits consisting of several facies which intergrade laterally from coarse-grained deposits near mountain fronts to progressively finer-grained deposits in basin lowlands. It is believed to have been deposited in an interiorly drained basin, or basins, prior to development of the present Colorado River drainage system. The formation is characterized lithologically as clays, sandy clays,

silty clays, gypsiferous sandy clays, clayey sands and conglomerates (Fordham *et al.*, 1984). Malmberg (1965) and Geraghty and Miller, Inc. (1980) describe the formation as consisting of thin layers of sand with some gravel, interbedded with thick beds of clay. Finer-grained facies are typically light-colored, ranging from reddish-tan to light green or white (Geraghty and Miller, Inc., 1980). Exposures of Muddy Creek Formation within the eastern portion of the Las Vegas Valley are rare, occurring only along the southern edge of Frenchman Mountain and near Whitney Mesa, west of Henderson, where exposed sediments consist of a sequence of reddish to pink clays and silts up to 6 m thick (Kaufman, 1978).

Lithologic logs from wells installed along the Pittman Lateral reveal a sharp delineation between the white to brown clays and silts of the Muddy Creek Formation and the overlying coarse sands and gravels of the alluvial fan deposits (Figure 10). The sharp contrast allows for easy determination of the top of the Muddy Creek Formation at depths ranging from approximately 3 m to 20 m below ground surface (Fordham *et al.*, 1984). However, U.S. Bureau of Reclamation (1984) notes that the top of the “first clay formation” may be a more recent deposit than the Muddy Creek Formation and may or may not be contiguous with it.

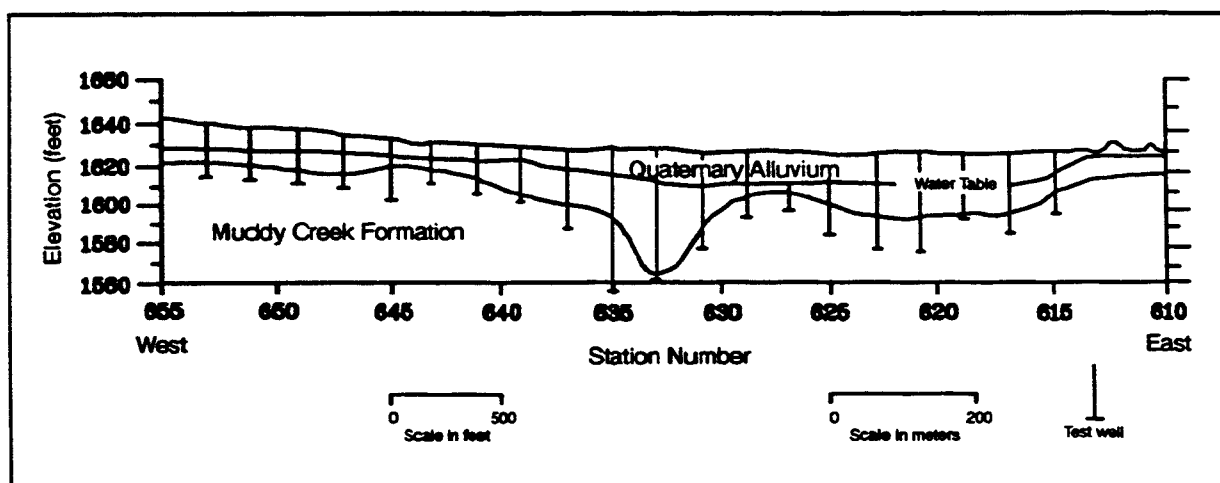


Figure 10. - Hydrogeologic cross-section of the Pittman Lateral site (adapted from U.S. Bureau of Reclamation, 1984).

The thickness of the Muddy Creek Formation is largely unknown, but probably varies greatly throughout most of the valley. Malmberg (1965) reported approximately 930 m of sediments logged as Muddy Creek Formation from an oil test well near Whitney Mesa. Another deep exploration well, drilled within the BMI complex by the Stauffer Geology Department, contained 660 m of Muddy Creek sediments.

HYDROGEOLOGY

The aquifer system within the Las Vegas Valley is complex, consisting of coarse-grained alluvial sands and gravels interbedded with finer-grained valley fill deposits. These interfingering units of the fine-grained Muddy Creek Formation have led to the development of artesian, semi-artesian and unconfined ground-water conditions throughout the valley. Maxey and Jameson (1948) identified four principal aquifer zones in the Las Vegas Valley. Three artesian aquifers, designated as shallow, middle and deep, are penetrated by wells at 60 m to 140 m, 150 m to 215 m, and over 215 m. Fault zones and semi-confining materials provide hydraulic connections which allow for generally upward leakage between aquifer zones. A fourth major zone, the so-called “near-surface” aquifer, is generally found overlying the Muddy Creek Formation within the Quaternary alluvial fan and valley-fill deposits. Ground water in the near-surface aquifer occurs primarily under water-table

(unconfined) conditions although small areas of artesian conditions may exist where ground water has been confined by caliche layers or by lenses of low-permeability sediments (Kaufman, 1978; Fordham *et al.*, 1984).

Prior to extensive development of the ground-water resources in the valley, virtually all recharge to the near-surface aquifer was by upward leakage from deeper, artesian aquifers. Recharge due to precipitation is generally considered to be negligible (Malmberg, 1965). Natural discharge was primarily to springs, direct evaporation (where the water table was near the ground surface), and phreatophyte evapotranspiration, with little or no water discharging to Las Vegas Wash (Malmberg, 1965; U.S. Bureau of Reclamation, 1982).

In recent years, however, recharge to the near-surface aquifer, particularly in the lower Las Vegas Valley (the "lower" valley is defined here as that portion of the valley which lies to the east of Whitney Mesa and south of Frenchman Mountain), has changed considerably. Urbanization of the valley has increased recharge to the near-surface aquifer by increasing irrigation infiltration and by removing phreatophyte vegetation near the washes. Primary sources of recharge to the shallow system in the Henderson area now include infiltrating irrigation water, sewage-treatment-plant effluent, industrial effluent, and the upward leakage of ground water from deeper aquifers (Kaufman, 1978).

From the early 1940s to 1977, it was the policy of several of the companies within the BMI complex to discharge industrial waste water into unlined ditches and evaporation ponds north and east of Henderson. Malmberg (1965) noted that the ensuing recharge caused ground-water levels in the Pittman area to rise to within a few meters of land surface. As noted earlier, rising ground-water levels flooded basements in Pittman as early as 1942. To alleviate this flooding, waste-disposal ponds south of Pittman were abandoned, and over the ensuing two years, the water table near the center of Pittman dropped up to 3.5 m (U.S. Bureau of Reclamation, 1984).

Discharge from the near-surface aquifer in the lower Las Vegas Valley area is by seepage into Las Vegas Wash and by evapotranspiration. No large production wells tap the near-surface aquifer in this area, primarily because of poor water quality (Geraghty and Miller, Inc., 1980).

Geraghty and Miller, Inc. (1980), in their ground-water investigation of the nearby Stauffer Chemical Company property, noted three primary geologic factors which govern the occurrence and movement of ground water at that site. It may be assumed that these factors also play a major role at the current study site, approximately 3 km north of the Stauffer site. These factors are:

- The configuration and slope of the top surface of the Muddy Creek Formation,
- The lithology of the Muddy Creek Formation, and
- The presence of deep erosional channels in the surface of the Muddy Creek Formation that contain relatively high-permeability gravel train deposits.

Although the Muddy Creek Formation may control direction of groundwater movement, the primary water-bearing zone at the study site is the Quaternary alluvial fan and valley-fill deposits overlying the Muddy Creek Formation. Near the Pittman Lateral site, the ground surface, water table and the top of the Muddy Creek Formation all dip gently to the north and northeast toward Las Vegas Wash (Figures 7, 9, and 11). Ground water generally flows to the north, but gradients may vary locally with changes in the surface of the clay aquitard, or with heterogeneities within the Quaternary deposits. Depth to ground water along the Lateral is approximately 3 m, although it may vary from 2 m to 4 m. Saturated thickness of the near-surface aquifer ranges from 8 m to approximately 14 m across the breadth of the Pittman Lateral Transect. The similarities between the gradients of the water table and the top of the Muddy Creek Formation suggest that the configuration of the surface of the Muddy Creek Formation is controlling the direction of ground-water flow at this site, just as Geraghty and Miller, Inc., (1980) concluded for the Stauffer site.

The Muddy Creek Formation, at the Pittman Lateral site and throughout much of the surrounding area, generally consists of thick units of clay and silt interbedded with a few thin layers of sand and gravel. The low

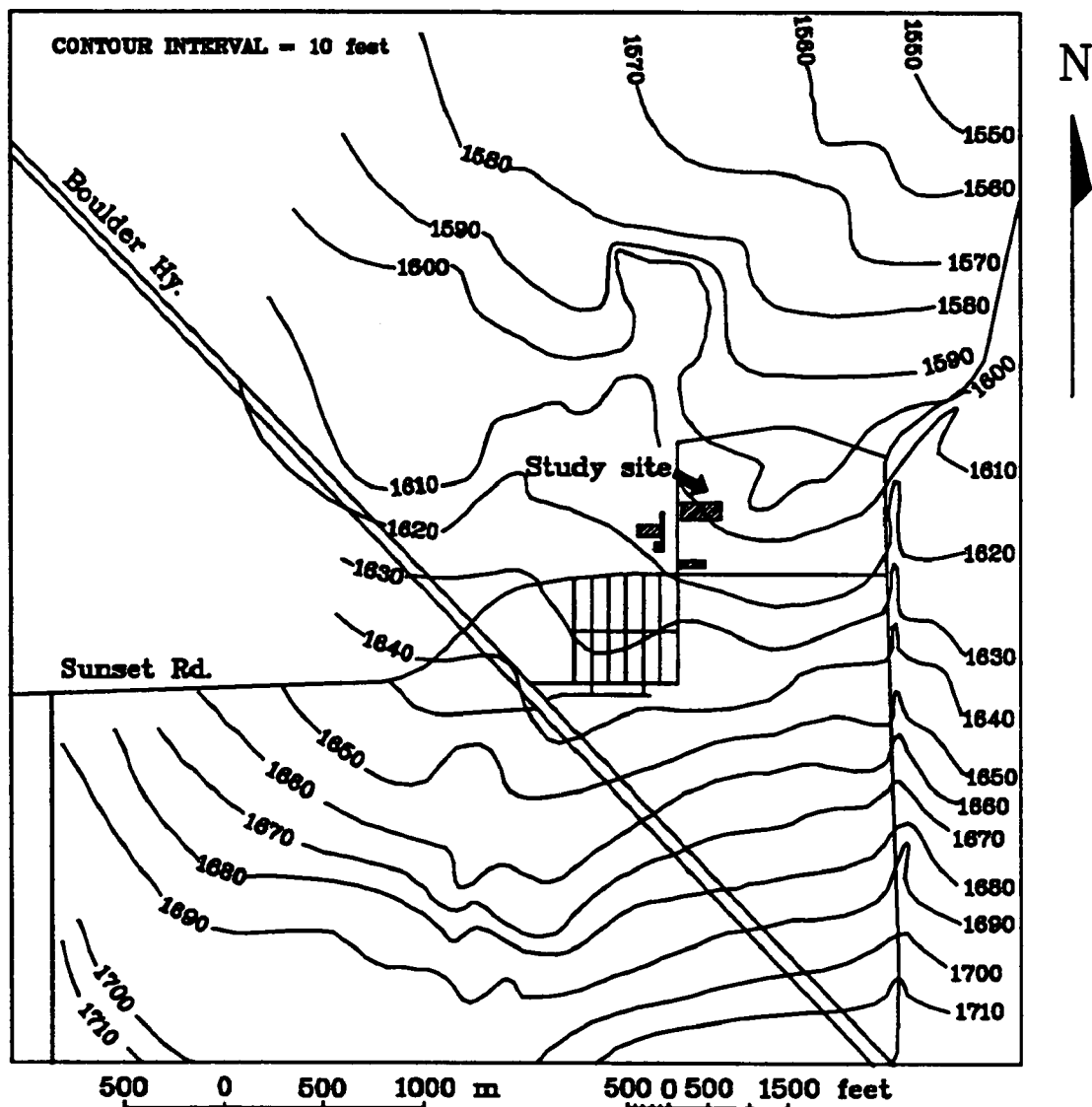


Figure 11. - Water table elevation map, Henderson, Nevada (elevations in feet above mean sea level) (adapted from U.S. Bureau of Reclamation, 1984).

permeability of these sediments creates an effective lower barrier to ground-water flow from the overlying aquifer. However, very little information regarding the hydraulic characteristics of the alluvial aquifer or the Muddy Creek Formation in the lower valley region is available. While some information has been published for sites within the BMI complex, little has been produced for the Pittman area. Geraghty and Miller, Inc., (1980) performed no formal aquifer tests on wells penetrating a saturated sand layer in the upper Muddy Creek Formation, but noted the extremely low yield indicated by the large drawdowns measured while pumping at low rates. However, vertical permeability tests were performed on undisturbed cores taken from the upper Muddy Creek Formation. Values ranged from 2.0×10^{-8} to 5.6×10^{-10} m/s, confirming the extremely low permeability of the upper Muddy Creek Formation. Hall (1986) reported a transmissivity of 1.3×10^{-5} m²/s obtained during an aquifer test on the Stauffer site.

Aquifer tests performed by Geraghty and Miller, Inc. (1980), on two wells located within the BMI complex and completed in the Quaternary alluvium resulted in estimated transmissivities ranging from 1.9×10^{-4} to 2.3×10^{-4} m²/s. These values were considered to be typical of the near-surface aquifer. A third well, completed in one of the deep channels in the surface of the Muddy Creek Formation, yielded a calculated transmissivity of 2.1×10^{-3} m²/s. Another well, located in a larger channel, yielded a transmissivity of 9.1×10^{-3} m²/s. Hall (1986) reported transmissivities ranging from 2.0×10^{-5} to 4.5×10^{-3} m²/s within the alluvial aquifer on the Stauffer site. The large range in values was attributed to the anisotropic conditions common in alluvial fan deposits. Calculated hydraulic conductivities were found to be greatest in the channel-fill deposits within the paleochannels of the Muddy Creek Formation surface. Fordham *et al.* (1984) note that on the TIMET, Inc., site (on BMI property), ground-water flow is generally down the slope of the Muddy Creek Formation toward the deep channels, which transmit the bulk of the flow to the north toward the Pittman Lateral site and Las Vegas Wash.

Estimates of ground-water flow rates vary from site to site. Geraghty and Miller, Inc., (1980) estimated a maximum ground-water velocity of 1.5 m/day to 6.1 m/day, based on the greatest calculated transmissivity at the Stauffer site. Similarly, Fordham *et al.* (1984) estimated a maximum flow rate of 10.7 m/day based on a similar transmissivity, but with a slightly higher gradient and a porosity of 0.3. Ecology and Environment, Inc., (1984) report a hydraulic gradient of 0.012 and a flow velocity in excess of 0.8 m/day in the Pittman area. Hall (1986) reported a velocity of 1.6 m/day with a maximum of 7.3 m/day at the Stauffer site.

The barrier to downward vertical ground-water flow presented by the low-permeability sediments of the Muddy Creek Formation is augmented by an upward vertical gradient from the deeper artesian aquifers. Geraghty and Miller, Inc., (1980) cite head data from wells tapping confined sand zones within the Muddy Creek Formation. Measured heads in these wells ranged up to 10.4 m higher than in adjacent wells completed in the near-surface aquifer. The U.S. Bureau of Reclamation (1982) noted upward gradients in the Pittman area and below the BMI ponds near Las Vegas Wash.

HYDROCHEMISTRY

Ground water in the near-surface aquifer in the lower Las Vegas Valley is generally of very poor quality. The chemical composition of the water is a reflection of the type of material through which the water moves, residence time, length of flow path, and the direct and indirect effects of urbanization and industrialization within the valley (Malmberg, 1965; Fordham *et al.*, 1984). The ground water in this region is characterized by high concentrations of total dissolved solids (TDS), sodium, chloride, and sulfate. Locally, significant levels of organic contaminants are found.

Large portions of the lower valley contain shallow ground water with greater than 5,000 mg/L TDS (Figure 12). The high dissolved solids content may be attributed to several factors. Where high water table conditions exist, evapotranspiration processes concentrate salts in the subsurface. Dissolution of evaporite minerals along flow paths may add considerable amounts of dissolved constituents to ground water. U.S. Bureau of Reclamation (1982) noted that many high-TDS areas correspond to large deposits of evaporite minerals. Sulfate, chloride, and sodium ion concentrations tend to increase from west to east across the valley, and these increases are generally attributed to dissolution of gypsum and halite, both of which are abundant in the valley fill materials, particularly in the Muddy Creek Formation (U.S. Bureau of Reclamation, 1982). Urbanization within the valley has contributed both directly and indirectly to the high dissolved solids content of ground water in the near-surface aquifer. Infiltrating water from lawn watering, agricultural development, or industrial waste-water disposal leaches salts from the soil profile and into the underlying aquifer. Where infiltration is excessive, a rising water table brings ground water into direct contact with readily dissolved salts stored in the vadose zone. Dissolution of these minerals increases the TDS content of the ground water (U.S. Bureau of Reclamation, 1984; Kaufman, 1978).

Ground water at the study site is contaminated by a variety of organic and inorganic compounds. Much of the organic contamination may be traced to the accidental storage tank leak in 1976 noted earlier. Since that

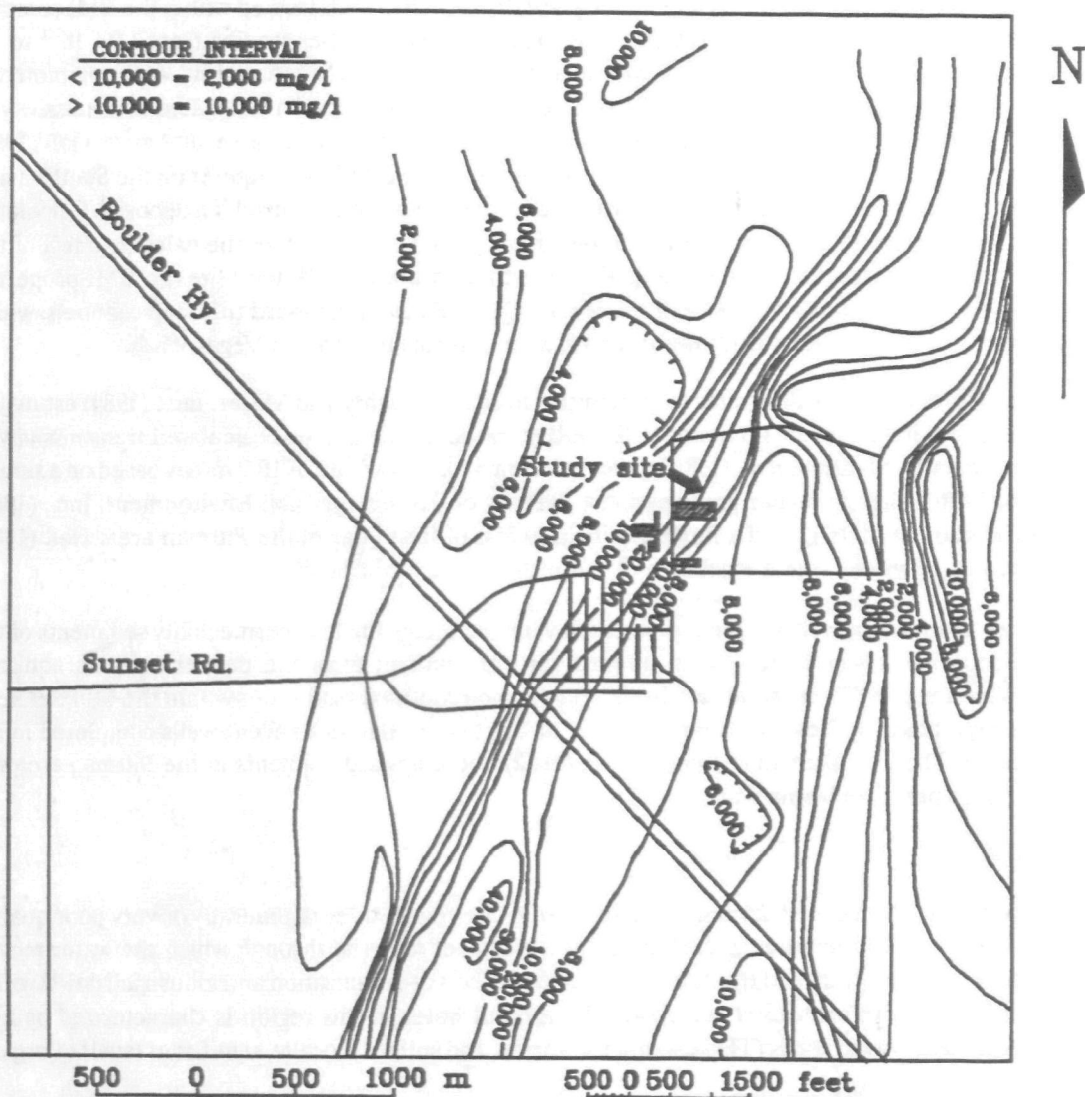


Figure 12. - Contour map of total dissolved solids concentrations (mg/L) in ground water, Henderson, Nevada (adapted from U.S. Bureau of Reclamation, 1984).

time, a benzene plume has migrated to the north and northeast toward Las Vegas Wash (Figure 13). Ecology and Environment, Inc., (1984) and Geraghty and Miller, Inc., (1980) cite benzene concentrations which range from in excess of 500,000 mg/L near the source of the leak down to approximately 10 mg/L near Pittman. Chlorobenzene and chloroform have also been detected in relatively high concentrations in the wells which make up the Pittman Lateral Transect.

Passage of the plume under older waste disposal areas as it moved downgradient has raised additional concerns. Geraghty and Miller, Inc., (1980) and Ecology and Environment, Inc., (1985) suggest the possibility that other organic compounds present in these disposal areas have been mobilized in the presence of the high benzene concentrations and have moved downgradient with the contaminant plume.

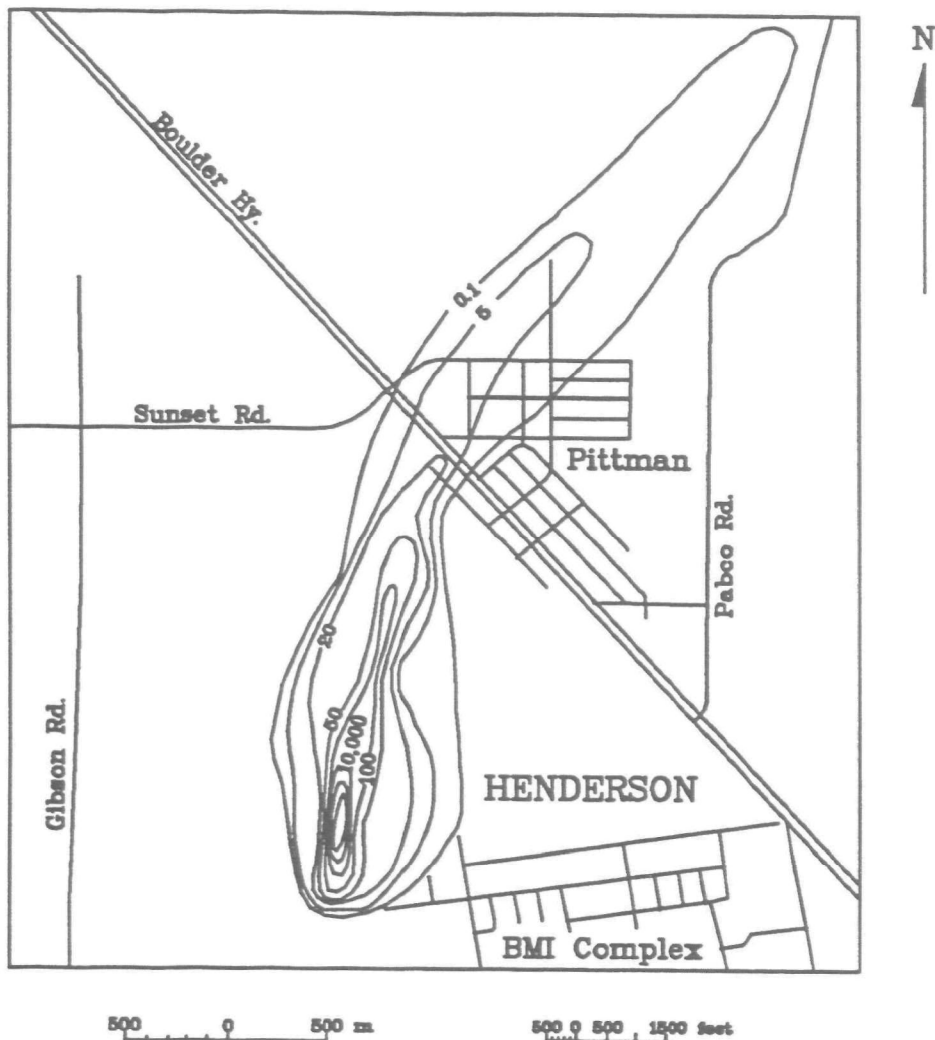


Figure 13. - Map of benzene concentrations (ppm) in ground water, Henderson, Nevada (adapted from Ecology and Environment, Inc., 1984).

MONITORING WELL INSTALLATION

Due to the design and operating procedures of the selected sampling devices, as well as the objectives of the study, it was necessary to install the wells close to each other. Six wells were installed in late July 1987 near the mid-point of the Pittman Lateral Transect. Although it was desirable for the wells to be close to each other, it was also necessary for the wells to be spaced far enough apart so that the effects of pumping at one well would not significantly impact the distribution of VOCs near adjacent wells. To determine the minimum well separation, drawdown, and capture-zone, calculations were made utilizing estimates of hydraulic properties of the aquifer. These calculations indicated that a well-spacing of 6 m would provide sufficient hydraulic isolation between wells. The 6-m spacing was also felt to be small enough to result in similar geologic and hydrochemical conditions over the site. The wells are arranged approximately 6 m apart in a rectangular grid with the long axis of the rectangle roughly paralleling the northward direction of ground-water flow (Figure 14).

A dual-tube percussion hammer drill rig was utilized to install the wells. Lithologic logs from each borehole typically showed approximately 6.4 m to 7.5 m of silty sands and gravels overlying a very hard layer of

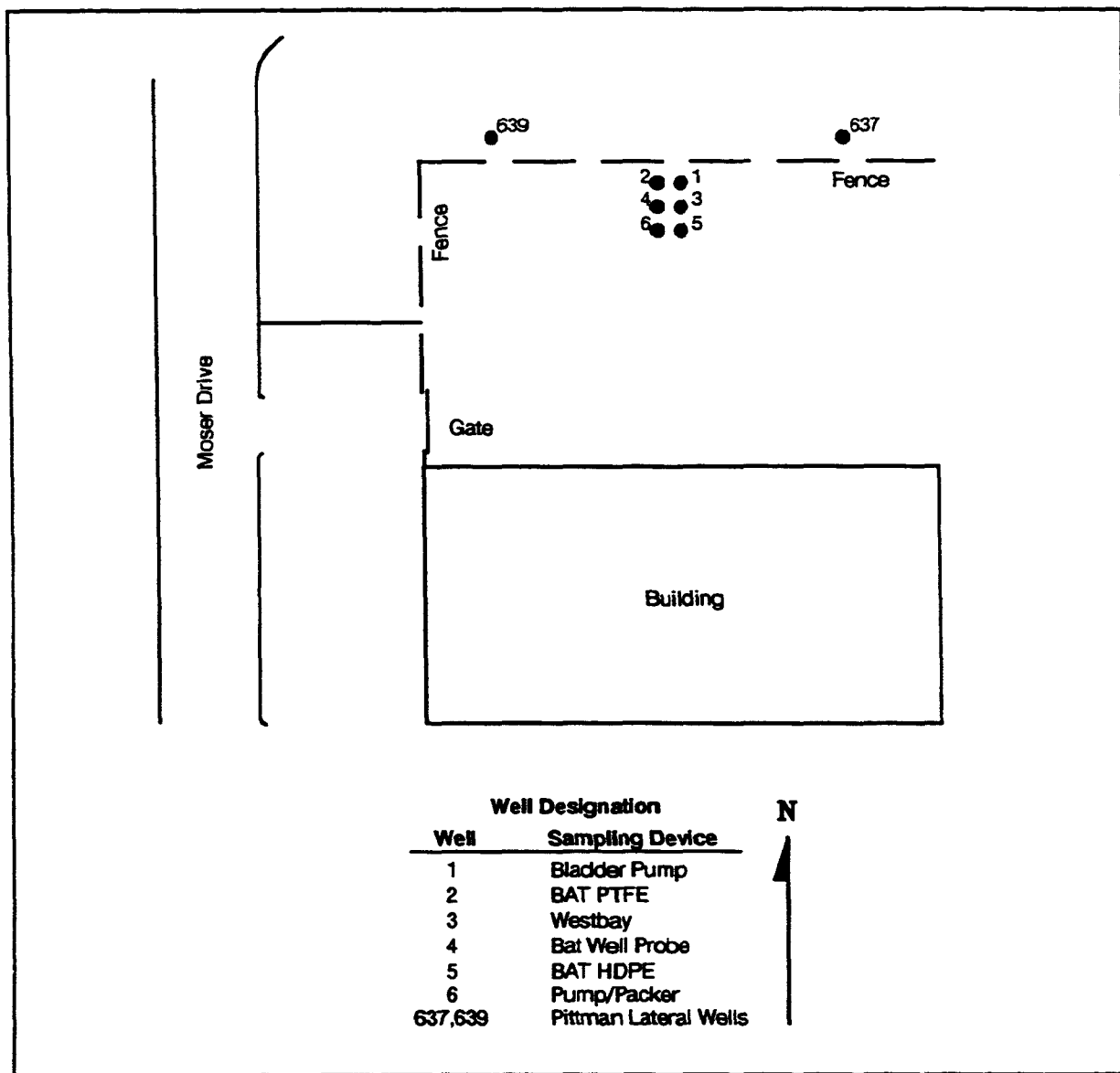


Figure 14. – Monitoring well layout, Pittman Lateral site (not to scale).

cemented sands and gravels (caliche), which was found at depths ranging from 6.4 m to 7.6 m below ground surface. This layer was penetrated in well 6 at 9.6 m, at which point the drill bit immediately entered a greenish-white clay interpreted to be the Muddy Creek Formation. Drilling for all other wells was terminated before or directly after contacting the top of the caliche layer, although some of the holes were driven further into the caliche to facilitate placement of the well intakes. Depth to ground water was found to be approximately 3 m.

To further establish the similarities between the six wells, as well as to select the proper depths for well intake placement, two boreholes at opposite corners of the rectangular grid (wells 1 and 6) were logged with magnetic induction and natural-gamma logging tools. Prior to logging, the holes were temporarily cased with 10.2-cm PVC pipe to prevent collapse of the borehole walls. Interpretation of the geophysical and lithologic logs suggested that each well intake should be placed within a zone extending from 6 to 7 m below ground surface.

The logs suggested a lower clay content and perhaps better flow characteristics in this zone than in the deposits above or below. Since the two logged boreholes were at opposite corners of a very small rectangular grid, it was assumed that the hydrogeologic conditions would be very similar in the other wells. After running the geophysical logs, the temporary casing was removed from the borehole.

Five of the six wells were cased with 5.1-cm-diameter Teflon casing with well intakes placed within the targeted zone described above. Three of the wells (1, 4, and 6) were screened over a 0.3 m-interval. Two more contained the HDPE and PTFE filter tips with 5.1-cm-diameter Teflon riser pipes (wells 2 and 5). The sixth monitoring well consisted of the stainless steel multi-port with measurement ports placed at 3 m, 4.5 m, and 6 m below ground surface (well 3). Only data from the lowermost port would be utilized in the comparison study. The other two ports were installed to investigate vertical variations within the contaminant plume. Each well was backfilled with a gravel pack extending approximately 0.6 m above and below the well intake point. A thin layer of fine silica sand was installed above the gravel pack followed by a surface seal consisting of a 5 percent cement-bentonite slurry. The multi-port well design was somewhat complicated by the multiple monitoring zones, but the installation was completed in the same general manner as for the other wells. Well completion diagrams and generalized lithologic logs are presented in Appendix A.

The three conventional monitoring wells were developed by pumping at a rate of approximately 2.8 L/min with one of the bladder pumps. Volumes of 278, 320, and 354 L were removed during development from wells 6, 1, and 4, respectively. The multi-port installation was developed by opening the pumping port and airlifting about 150 L from the casing at a rate of approximately 1.9 L/min. The two filter tip installations were developed by collecting five 500 mL sample vials from each. At all installations, development continued until sample temperature, pH, and electrical conductivity stabilized and a clear sample was obtained. All water was disposed of off-site. The lower volume needed for the development of the filter tips may have resulted from the smaller volume around the filter tip that was impacted by development and the much lower sampling rate (estimated to be about 60 mL/min under these conditions). After development of the multi-port installation was completed, the pumping port was closed and any water remaining inside the casing airlifted out.

SECTION 4

EXPERIMENT A

EXPERIMENTAL DESIGN

The experimental design of the initial portion of this study included the evaluation of differences between the six wells, selection of a suitable sampling frequency, and implementation of the sampling program. Because 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 the sample are much more likely than increases. Therefore, a relative approximation of accuracy can be made based on the concentrations of VOCs recovered during the sampling process (i.e., those devices which recover the highest levels of VOCs may be considered the most accurate). A detailed accounting of the experimental design, as well as sampling procedures and quality assurance objectives, may be found in Desert Research Institute (1987), an EPA-approved quality assurance plan.

Because sampling device variability was the source of variability of most interest to this study, all other sources of variability present in any field study were minimized as much as possible. As previously described, since the comparison of sampling devices could not be based on samples collected from a single monitoring well, six wells were installed in a manner that resulted in similar geologic conditions at each well. However, due to the natural variability in lithology and stratigraphy of alluvial materials, geologic conditions cannot be considered identical at each well. 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.

To compare between sampling devices installed in separate wells, the further assumption was made that hydrochemical conditions were the same at each of the six well sites. To test this assumption and to determine the magnitude of expected laboratory errors, a "survey" sampling round was conducted in which an initial set of samples was collected from wells 1, 4, and 6. These three 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. Due to their design, the other three wells (2, 3, and 5) could not be sampled with the bladder pump and, therefore, were not included in the survey sampling. Each of the sampled wells was purged at a rate of approximately 1 L/min until a minimum of five well volumes had been removed. A bulk sample was then collected from each well in a 19-L container and divided into five sample splits. Samples were analyzed for pH, electrical conductivity, gross chemistry, total dissolved solids, dissolved silica, iron, manganese, total organic carbon, benzene, and chlorobenzene. Laboratory analysis methods are briefly summarized in Appendix B. The analytical results for the sample splits and calculated means and standard deviations are presented in Appendix C.

Plots of the benzene, chlorobenzene, and total organic carbon (TOC) data and their mean values and standard deviations are shown in Figures 15 through 17. The means of the five splits from each well are all within

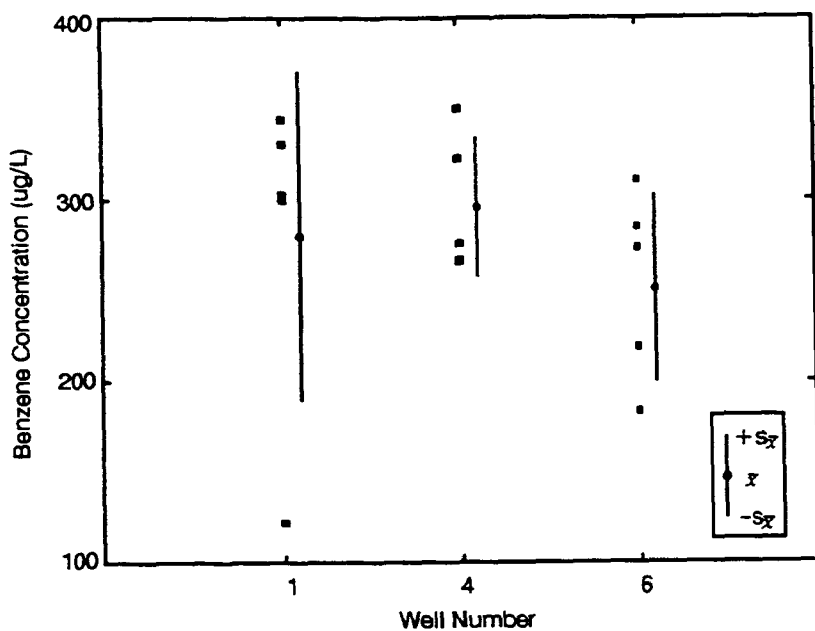


Figure 15. - Plot of benzene concentration ($\mu\text{g/L}$) for each of five sample splits from wells 1, 4, and 6.

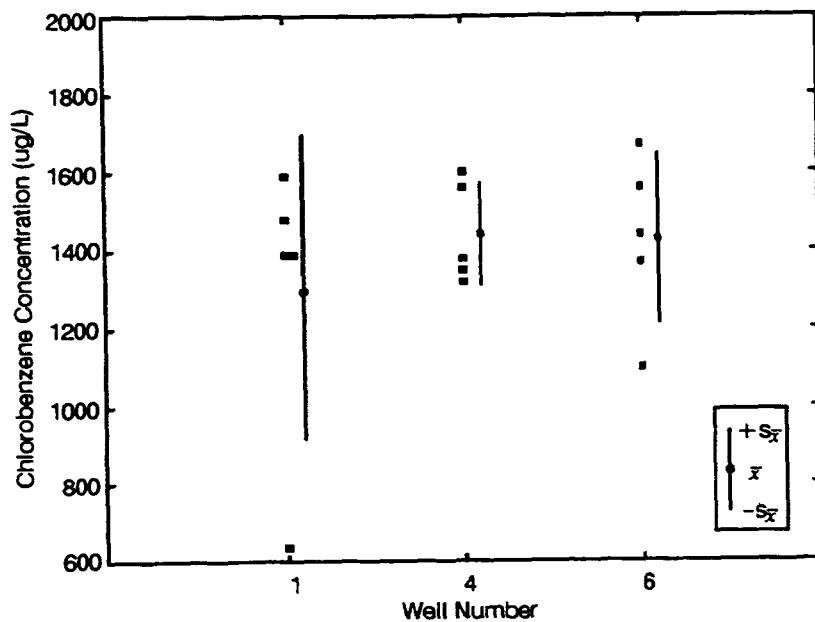


Figure 16. - Plot of chlorobenzene concentration ($\mu\text{g/L}$) for each of five sample splits from wells 1, 4, and 6.

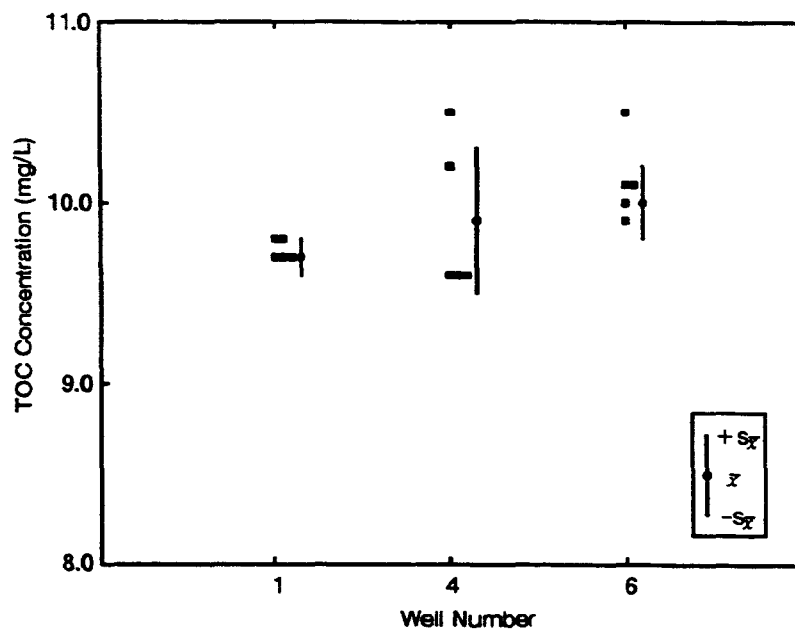


Figure 17. - Plot of TOC concentration (mg/L) for each of five sample splits from wells 1, 4, and 6.

approximately one standard deviation of each other, while the differences between wells for all the splits fall well within the stated analytical error of ± 20 percent for benzene and chlorobenzene and ± 5 percent for TOC. The ranges in concentration means between the three wells were approximately $50 \mu\text{g/L}$, $150 \mu\text{g/L}$, and 0.4 mg/L for benzene, chlorobenzene, and TOC respectively. Inspection of the inorganic data showed that, with the exception of manganese, the differences between the sample means of the three wells were also all within laboratory-stated analytical error.

The low, although present, hydrochemical variation indicated by the survey sampling, close proximity of the wells, and the similar lithologic and geophysical logs, all suggest that the geological and hydrochemical conditions at the site are fairly uniform. For the purposes of the sampler comparison, these conditions formed the basis for the assumption that geologic and hydrochemical conditions were essentially the same at each of the six well sites. However, the magnitude of the small hydrochemical variation observed during the survey sampling was kept in mind when analyzing the data for sources of concentration variation. Unfortunately, because of the nature of this field study, the devices used, and the time period over which the study took place, the hydrochemical variation could only be approximated during the survey sampling and could not be further investigated as the study proceeded. As a result, temporal and spatial hydrochemical variation remained a possible source of variation in sampler performance.

Because of the overall project emphasis on sampling device effect on VOC concentration, only the VOC and TOC data were utilized in the experiment A comparisons. While inorganic chemistry samples were collected, the resulting data were not statistically analyzed for this report. The inorganic data were used primarily for understanding geochemical conditions.

Sampling frequency was chosen based on the need to collect a large number of samples at closely spaced intervals and the desire to examine temporal variations associated with varying sampling intervals. Samples were collected weekly during the first month, biweekly during the second month, and during the 13th and 19th weeks. The first set of samples was collected during the week of February 8, 1988. Each sampling week, the wells were

sampled in a random order determined with the aid of a table of random digits. Table 1 lists the sampling devices that were utilized during Experiment A.

TABLE 1. SAMPLING DEVICES UTILIZED IN EXPERIMENT A

| Device Type | Well Number |
|---------------------|-------------|
| Bladder Pump | 1 |
| Bladder Pump/Packer | 6 |
| HDPE Filter Tip | 5 |
| Multi-Port | 3 |
| PTFE Filter Tip | 2 |
| Standard Bailer | 1 |
| Well Probe | 4 |

Wells 1 and 6 were purged prior to sampling by pumping (with the respective dedicated bladder pumps) at a rate of 1 L/min until solution parameters (temperature, pH, electrical conductivity) stabilized (± 10 percent over two successive well volumes) and at least five well volumes had been removed from the well. Pump discharge was then reduced to less than 500 mL/min for sampling. Sampling from well 1 was always accomplished by purging and sampling with the bladder pump prior to sampling with the bailer. The first two bailer volumes collected were discarded in order for the device to be thoroughly rinsed with formation water prior to collecting a sample. Bailer samples were first transferred to a clean glass beaker, then poured into appropriate sample bottles.

Samples were collected from well 6 with the bladder pump/packer. The well was purged and sampled only after inflation of the packer. Well volume calculations accounted only for that volume of water in the well below the packer.

Sampling procedures for the *in situ* devices and well probe were carried out as previously described. Because the wells were shallow and hydraulic heads low, a small vacuum was applied to the multi-port sample bottles to obtain a full bottle. This was accomplished through the use of a special adapter and a hand-held vacuum pump. This procedure was not expected to adversely affect sample integrity because the flow-through design of the sample probe meant that the sample collected was the last water to pass through the bottle, when pressure conditions were near static.

Sample temperature, pH, electrical conductivity, dissolved oxygen, and bicarbonate concentration were measured in the field. Measurements taken after the final purge volume had been removed from wells 1 and 6 were considered to be representative of *in situ* conditions. Measurements from bailed samples took place only after the two initial bailer volumes had been discarded. Measurements from the *in situ* installations and the well probe took place only after at least one sample volume had been removed and discarded.

Each full set of samples collected during the week also included two sets of equipment blanks (one set each for the bailer and bladder pump), one set of standards solutions, one set of trip blanks, and one set of duplicate samples collected from a randomly selected well.

RESULTS

The ground-water chemistry data resulting from the analysis of samples collected with each sampling device, as well as standard solutions and blank samples, are given in Appendix C. As noted earlier, project emphasis was placed on the effect of the devices on VOC and TOC concentrations. The comparison described below was based on the organic chemistry data alone.

Benzene and Chlorobenzene

The laboratory analysis results for benzene and chlorobenzene recovery revealed variation in the data between sampling devices as well as with time. Plots of recovered concentration versus time (sampling week) for both benzene and chlorobenzene graphically illustrate the differences that exist between sampling devices or sites with regard to VOC recovery (Figures 18 and 19). For benzene, the HDPE filter tip recovered the highest concentrations followed by the well probe and bladder pump, while, with the exception of sample round 6, the multi-port recovered the lowest concentrations. For chlorobenzene, the results are more variable but the general trends are that all devices recovered comparable concentrations although the multi-port and bailer recovered lower concentrations.

In a subsequent experiment, the cause of the low concentrations recovered by the multi-port was identified as being related to the manufacturer's recommended procedures for sample collection. Correction of this problem resulted in collection of much higher VOC concentrations, and will be further discussed later in this report. Owing to this change, the multi-port results from experiment A are not representative of the more effective sampling procedures incorporated in later experiments, but are included here because they were collected for this experiment using the originally-stated manufacturer's procedures.

Figures 18 and 19 also reveal a definite decrease in VOC concentration with time, particularly with regard to the benzene concentrations. Possible explanations include natural degradation of the organic contaminants as the plume moves downgradient, a gradual shift of the spatial configuration of the plume, or the movement of cleaner recharge water, possibly due to upgradient irrigation, ground-water remediation efforts, wastewater disposal practices, or precipitation patterns throughout the study area. Because the concentration decreases appear to have affected all six wells in the same general manner, and because pre-sampling *in situ* conditions were considered to have been essentially the same at each well, it may be suggested that VOC conditions are changing at each well location in the same manner.

A comparison of experiment A results with the results of the survey sampling indicates that, in general, apparent sampler variation exceeded estimated hydrochemical variation. The experiment A benzene data from wells 1, 4, and 6 (the only wells that could be sampled during the survey sampling) showed a range in concentrations between wells at least twice the range in benzene concentration means observed during the survey sampling. It is important to note, however, that a significant portion of sampler variation in benzene concentrations observed in some rounds of experiment A may be attributed to hydrochemical variation, although the magnitude of this variation was not known during the sampling rounds themselves. This suggests that the differences between sampling devices, at least for the bladder pumps, bailer, and well probe, which were used in wells 1, 4, and 6, may in some cases be small enough to be indistinguishable from hydrochemical variation. For chlorobenzene, the sampler variation was considerably greater than the range in concentration means observed in the survey sampling, so it appears that sampler variation may be an important source of variation in the experiment A chlorobenzene data.

The benzene and chlorobenzene data 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 variation to the data. For both compounds, the results of the analysis show that both factors were significant at the 5 percent level, suggesting that the devices differ in their ability to recover volatile organic compounds in ground-water samples. However, the analysis does not reveal where the significant differences occur. Although beyond the scope of this study, additional research will evaluate the temporal trends observed in the chemical data.

To quantify the importance of the observed concentration differences between devices, a Tukey multiple comparison test (Steel and Torrie, 1960) was conducted on the data set. The Tukey test, which tests for significance between individual pairs of sample means, can determine which means of individual devices differ at the desired significance level. The devices may then be grouped accordingly by bracketing those devices whose mean concentrations show no significant differences. To apply the Tukey test to Experiment A data, the means

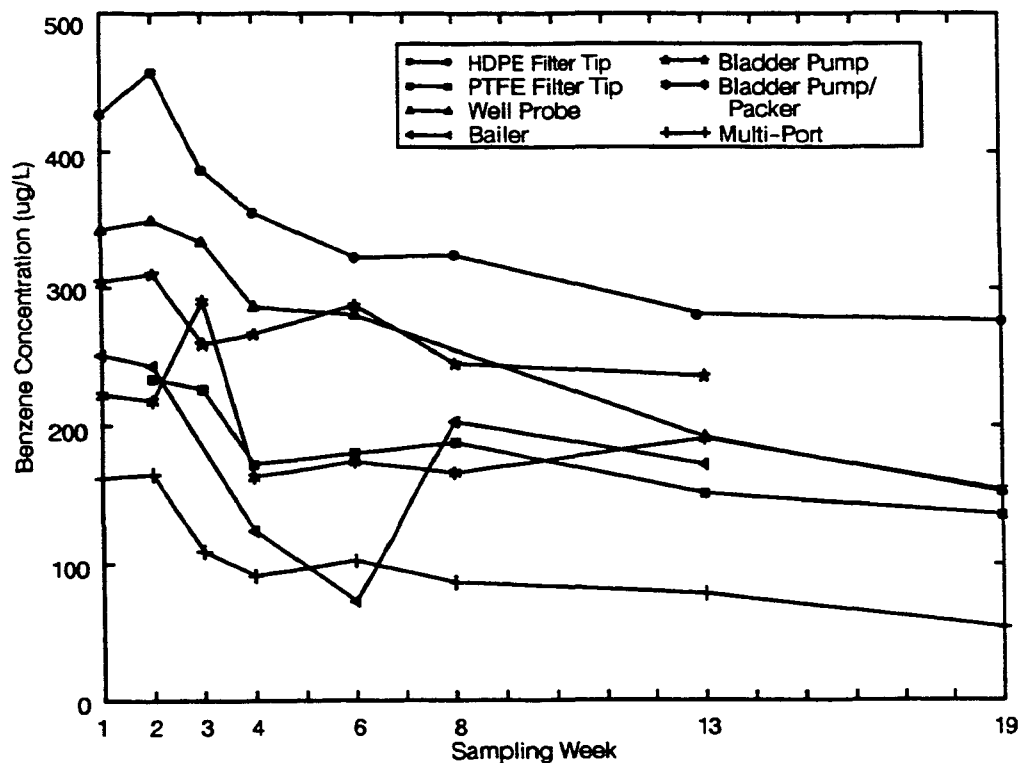


Figure 18. - Benzene concentration ($\mu\text{g/L}$) recovered by each sampling device as a function of time.

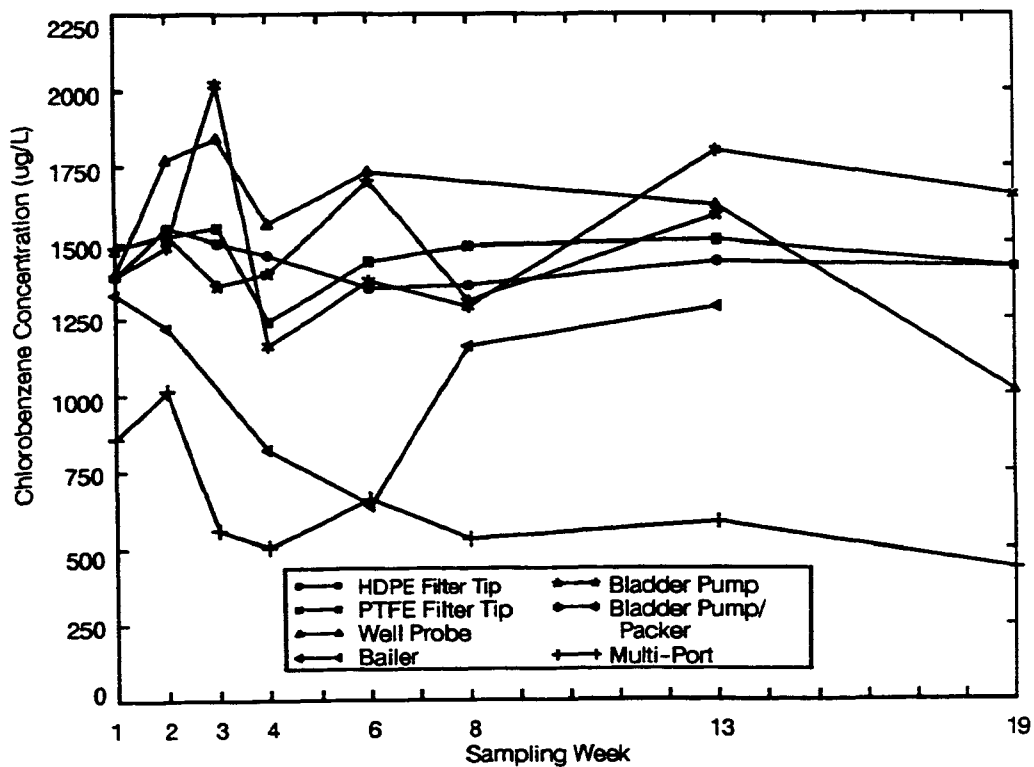


Figure 19. - Chlorobenzene concentration ($\mu\text{g/L}$) recovered by each sampling device as a function of time.

of the concentrations recovered by each device over the eight sample rounds were calculated and compared to each other. This results in an overall comparison based on all the samples collected over the 19-week experiment, but the application of the Tukey test in this way is only valid if the concentrations follow similar trends over time for each device. As shown on Figures 18 and 19, the benzene trends for each device are fairly similar while the chlorobenzene trends are variable. For this reason, the results of the Tukey test may be less valid for the chlorobenzene data than for the benzene data.

The results, shown in Table 2, indicate that at the 5 percent confidence level the HDPE filter tip recovered significantly higher benzene concentrations than the other devices. The well probe and bladder pump results, which were indistinguishable from each other, were lower than the HDPE filter tip and significantly higher than the other devices. The bladder pump/packer, PTFE filter tip, and bailer formed a third grouping lower than the devices mentioned above but significantly higher than the multi-port, which recovered the lowest benzene concentrations. Again, these low multi-port results were related to sample collection procedures that were later modified to incorporate more effective methods.

TABLE 2. TUKEY TEST RESULTS FOR EXPERIMENT A

| Rank* | Benzene | Chlorobenzene |
|-------|---------------------|---------------------|
| 1 | HDPE Filter Tip | Well Probe |
| 2 | Well Probe | Bladder Pump/Packer |
| 3 | Bladder Pump | Bladder Pump |
| 4 | Bladder Pump/Packer | PTFE Filter Tip |
| 5 | PTFE Filter Tip | HDPE Filter Tip |
| 6 | Standard Bailer | Standard Bailer |
| 7 | Multi-Port | Multi-Port |

*Ranked from highest to lowest concentrations

The lack of consistent chlorobenzene concentration trends between devices suggests that the Tukey test may not be strictly valid for this compound, however, some conclusions may be drawn if the results are used in conjunction with the trends evident on Figure 19. Although considerable variation is evident in the concentration trends, the HDPE filter tip, PTFE filter tip, well probe, bladder pump, and bladder pump/packer form a group that exhibits similar mean values over the eight sample rounds. In contrast, the bailer shows considerable variation and lower concentrations than this group and the multi-port consistently recovered the lowest concentrations. By combining this information with the chlorobenzene Tukey test results, it appears that all of the devices form a general grouping with the exception of the multi-port, which recovered significantly lower concentrations, and the bailer, which varied in concentration between the multi-port and the group of other devices.

Total Organic Carbon

A plot of the concentrations of total organic carbon (TOC) recovered by each sampling device versus sampling week (Figure 20) shows an overall decrease in concentration with time similar to that seen in the benzene and chlorobenzene data. However, these data are highly variable, and a clear distinction between sampling devices is not readily apparent. For most sample rounds, the variation between samplers in wells 1, 4, and 6 was less than the TOC concentration variation observed during the survey sampling. In addition, continual

problems with contamination of TOC samples added a component of variation that makes most of these results suspect. In general, however, the bladder pumps, well probe, and PTFE filter tip recovered the highest TOC concentrations while the HDPE filter tip recovered the lowest.

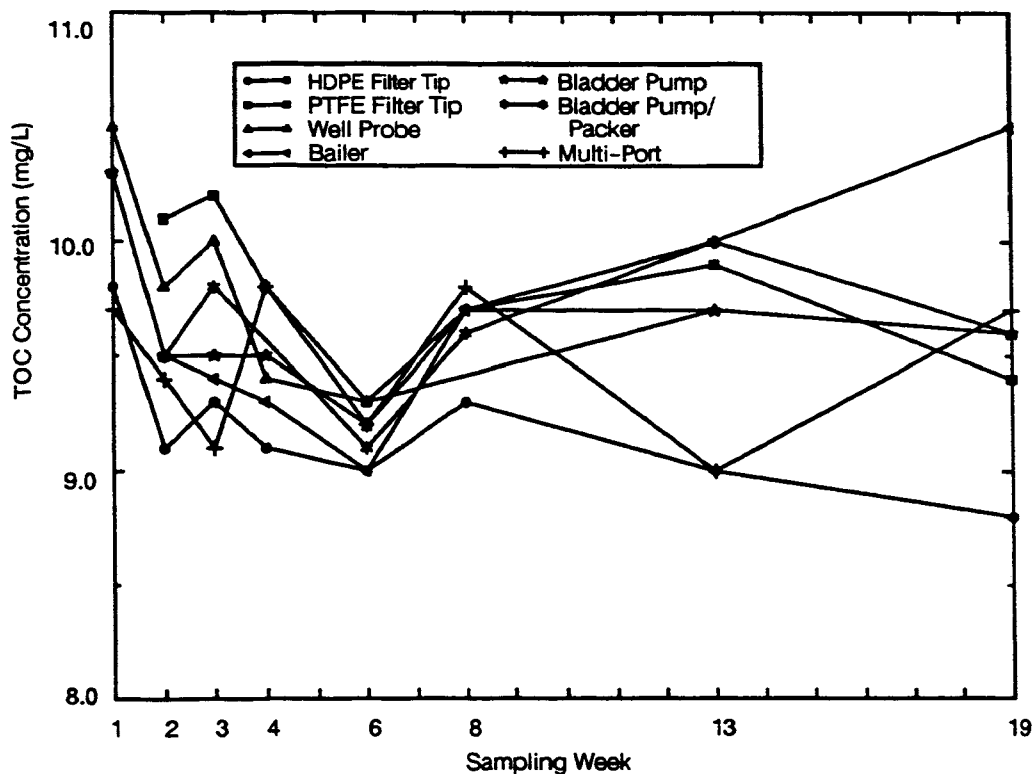


Figure 20. – TOC concentration (mg/L) recovered by each sampling device as a function of time.

The TOC data were subjected to a two-way analysis of variance similar to that performed on the benzene and chlorobenzene data. Again, both factors, sampling device and sampling time, were found to be significant at the 95 percent level of significance, but due to the high variability in the TOC data, the Tukey test could not be applied and no estimate of device accuracy could be made.

Week 19 Experiments

The relatively low VOC concentrations recovered by the multi-port prompted development of an additional set of experiments designed to isolate the cause of this apparent problem. These experiments consisted of collecting multiple sample replicates from the multi-port utilizing a variety of sampling methods and sample handling procedures. Detailed descriptions of these experiments are contained in Appendix C. The results indicate that VOC sample integrity was adversely affected by perforated septa that resulted from the manufacturer's recommended sample collection method. Multi-port samples that utilized unpunctured septa exhibited benzene and chlorobenzene concentrations that were approximately three times higher than those samples utilizing punctured septa. In addition, the samples with unpunctured septa showed benzene and chlorobenzene concentrations comparable to those collected with the filter tips and bladder pump/packer (the bladder pump and well probe samples were compromised prior to analysis). The sample collection procedures were subsequently modified by the manufacturer to include replacement of punctured septa with new, unpunctured ones.

The Week 19 data suggest that the low VOC concentrations observed in the multi-port samples during sample weeks 1 through 13 were the result of losses of VOCs from the sample vials themselves and were probably not related to the multi-port device, installation, or the presence of lower VOC concentrations near the multi-port installation.

Punctured septa on the 40 mL VOA vials may have contributed to VOC losses by several mechanisms. First, it is possible that partial evacuation of the VOA vials gave rise to large pressure differences between the aquifer and the vial during sample collection, possibly leading to volatilization of VOCs into air bubbles inside the vial that could pass out through the punctured septa. Second, passage of air into the VOA vials through the punctured septa during sample shipment and storage could also have led to formation of air bubbles into which VOCs could volatilize. Finally, direct volatilization of VOCs to the atmosphere may have occurred through the vial septa.

DISCUSSION

The primary objectives of this study were to compare the accuracy and precision of ground-water sampling devices and determine if either of the *in situ* sampling methods yields representative data. But, since this study was conducted in the field, a true assessment of representativeness was not possible because the actual *in situ* VOC concentrations were unknown. Under these conditions, as was previously discussed, it was assumed that those devices that recovered the highest VOC concentrations were the most accurate and produced samples that were the most representative of *in situ* conditions.

During experiment A, statistical assessments of accuracy and precision were difficult due to the trend of decreasing VOC concentrations with time and the lack of adequate numbers of sample replicates. The analysis of variance indicated that VOC concentrations for all devices changed significantly with time causing a high degree of temporal variability within the data set while the lack of sufficient replicates resulted in an incomplete understanding of the variability that each sampling method produced during a single sample round. In addition, variation observed during the survey sampling suggests that hydrochemical conditions at the site may vary spatially, and that this variation may be most important for the benzene and TOC data. These possible sources of error made it difficult to distinguish between variability due to the device and variability due to spatial and temporal concentration changes.

If the assumption is made that spatial variation between samplers is of lower magnitude than sampler variation, the results of experiment A suggest that, for benzene, the HDPE filter tip was the most accurate of the seven devices tested; it recovered significantly higher benzene concentrations than the other devices. For chlorobenzene no single device was consistently the most accurate, as the bladder pumps, well probe, and PTFE filter tip all recovered the highest concentrations for at least one sample round and as a group the means over time of these devices and the HDPE filter tip were similar, as suggested by the plot of concentrations and the Tukey test results. The least accurate devices for both compounds appeared to be the bailer and multi-port using the original sampling procedures. The findings of additional experiments showed that the multi-port was capable of performing as accurately as the bladder pumps and filter tips.

The relatively low benzene recovery of the PTFE filter tip, in comparison to the HDPE filter tip, was of interest because the devices recovered comparable chlorobenzene concentrations and because the operating procedures were identical for the two devices. The only difference between the two devices is the materials used in the filter tip. The PTFE filter tip material has a permeability an order of magnitude lower than the HDPE filter tip material (1.7×10^{-4} cm/s versus 1.7×10^{-3} cm/s). As a result of the PTFE filter's lower permeability, higher hydraulic gradients may form across this filter during sampling, resulting in more turbulence as water flows through the filter. These more turbulent flow conditions may have a greater effect on benzene concentrations than chlorobenzene concentrations because of benzene's higher volatility, possibly causing lower benzene recoveries with the PTFE filter tip than with the HDPE filter tip. A similar effect was observed in experiment C.

Although the well probe recovered VOC concentrations comparable to the bladder pump, difficulties were experienced in recovering full sample bottles during several sample rounds and no samples could be

recovered during week 8. This problem seemed to be related to improper connections between the sample housing guide sleeve and the well probe cap, which prevented penetration of the hypodermic needle into the cap septum. Inspection of the cap revealed no damage, and little sediment had built up above the cap, so the cause of this problem was not identified. Furthermore, water was observed in the well bore above the well probe during several sample rounds. The source of this water may have been leakage past the probe O-rings or through the filter tip cap, although the actual cause could not be identified. The manufacturer has subsequently made several design changes to this well probe; the tested version is no longer commercially available.

The TOC data contained a great deal of variability but, in general, the bladder pumps, well probe, and PTFE filter tip appeared to be the most accurate, much like the chlorobenzene results. The HDPE filter tip appeared to be the least accurate of the seven devices for TOC recovery. Excessive variability in the TOC data prevented determination of device precision.

The overall results suggest that the well probe and *in situ* filter tips, which require only minimal purging, may perform as well as a bladder pump. The unexpected performance of the multi-port was related to the loss of VOCs through punctured septa on the sample vials during transport and storage, as shown by the results of the week 19 sampling. Multi-port samples collected during weeks 1 through 13 were probably all affected by the perforated septa, resulting in low VOC recoveries. This problem was corrected during subsequent experiments by replacing the punctured septa on each sample vial with new septa prior to packaging and shipment to the laboratory.

The design of subsequent experiments in the comparison study was based upon the pattern of responses observed during this experiment, the increased familiarity with the devices, and the sampling procedure modifications that needed to be made to obtain the most representative samples from each device. This was particularly important for the multi-port sampling procedures because this study was designed in part to investigate *in situ* devices. More complete information about device accuracy and precision was obtained from the subsequent studies (experiments B and C) which are discussed in the following sections.

The analysis of duplicate samples, standard solutions, and blank samples (Appendix C) yielded results which fell well within the quality assurance objectives outlined in Desert Research Institute (1987). However, these quality assurance procedures did reveal a few problems, most notably the possible contamination of the TOC samples, which may have contributed to significant variability in the TOC results.

Also of some concern were the duplicate VOC samples and VOC standards. Duplicate samples collected during weeks 2 through 4 varied greatly in terms of benzene and chlorobenzene recovery. The lack of analytical reference standards during these weeks made it difficult to determine whether most of the variation lies within the laboratory analysis or in the sampling methodology. In either case, the high variation among these samples pointed out the need to collect multiple replicate samples from each device during each sampling period.

The laboratory analysis of the VOC standard solutions resulted in concentrations which were consistently lower than the theoretical value. While this deviation is most likely due to poor standard preparation, or analytical variability, it may also be indicative of a limited sample shelf life. Although all of the samples were analyzed within the maximum allowed holding time of 14 days (U.S. Environmental Protection Agency, 1986), most analyses were completed near the end of this time period. If it can be assumed that the solutions were prepared and handled properly, then sample degradation during storage should be considered as a possible source of sample bias.

SECTION 5

EXPERIMENT B

EXPERIMENTAL DESIGN

The results of Experiment A provided a great deal of information regarding site and sampling device characteristics and resulted in a preliminary comparison of the seven sampling devices. However, the original experimental design needed modification to obtain a more complete evaluation of each type of sampling device. Experiment B was conducted to resolve some of the problems encountered during Experiment A.

Many of the original assumptions and procedures outlined in the design of Experiment A were incorporated into the new experimental design. Most importantly, the assumption that there were no significant differences between wells, as well as most sampling procedures, remained unchanged. However, the high natural variability observed in the Experiment A data required that changes be made with regard to sampling frequency and the number and type of samples collected. To avoid the high temporal variation found within the VOC data, sampling was restricted to a single occasion. Only VOC samples were collected for this experiment. Multiple replicate samples were collected in an effort to make the ensuing statistical analysis less susceptible to outliers and high variability within the data (including analytical variability), and to reduce the effect of lost sample data. Six replicate VOC samples were collected with each sampling device and full VOC analysis results were requested (as opposed to only the benzene, chlorobenzene, and chloroform concentrations requested during Experiment A). Quality assurance samples (two standards, one trip blank, and two equipment blanks) were also prepared or collected.

Sampling procedures for the second experiment remained virtually identical to those used during the first phase of the study. However, after experiment A, known or suspected problems with the HDPE filter tip and well probe precluded their use during this phase of the comparison study. The HDPE filter tip installation was damaged by on-site construction activity, and problems experienced with the well probe in experiment A were discussed previously. Because well probe design was significantly modified by the manufacturer and the tested probe was no longer commercially available, it was decided to remove it from further comparisons. In addition, although the bladder pump/packer appeared to perform well in experiment A, this device was removed from subsequent study because the project focus was primarily on *in situ* devices. VOC sampling with the multi-port continued as in Experiment A, except that the septum in each sample vial was carefully replaced with an unperforated septum after sample recovery. Samples were also collected with the PTFE filter tip, bladder pump, and bailer, as shown in Table 3. Sample replicates were collected with six separate trips of the sampling devices in the PTFE filter tip and multi-port, in sequence from the bladder pump discharge, and with two volumes with the standard bailer. All sampling for Experiment B took place on November 8, 1988.

RESULTS

Ground-water chemistry data resulting from analyses of samples collected for Experiment B are presented in Table C.17 of Appendix C. Nine VOCs were detected in each ground-water sample. A 10th,

TABLE 3. SAMPLING DEVICES UTILIZED IN EXPERIMENT B

| Device Type | Well Number |
|-----------------|-------------|
| Standard Bailer | 1 |
| Bladder Pump | 1 |
| Multi-Port | 3 |
| PTFE Filter Tip | 2 |

acetone, was also detected in a few of the samples. Results for the quality assurance samples (standards, blanks) are presented in Table C.18 of Appendix C.

The VOC data are presented in Figures D.1 through D.9 in Appendix D and in Table 4. In general, the results of these analyses reveal little of the variation that was so notable during the first experiment. This is to be expected since this experiment was designed to minimize the potential for temporal variations produced by sampling over long time periods. A preliminary review of the data also suggests very little difference between the four sampling devices with regard to recoveries of VOCs. However, there are a few notable exceptions (benzene recoveries, bailer recovery of chlorobenzene).

The tabulated data shown in Table 4 allow for a generalized comparison of the devices based on recovered VOC concentrations. All four of the sampling devices recovered comparable levels of all the VOCs except benzene (and bailer recovery of chlorobenzene). The bladder pump recovered the highest mean concentrations of benzene, followed by the bailer, the multi-port and the PTFE filter tip. The PTFE filter tip recovered the highest concentrations of six compounds, while the multi-port recovered the highest concentrations of the remaining two. The raw data suggest little overall difference between the performances of these devices and that of the bladder pump (with the exception of benzene, the multi-port and PTFE filter tip sample means were generally greater than, or within one standard deviation of, the respective bladder pump mean recovered concentrations). In addition, overall variation between devices was slightly less (for benzene) and of roughly the same magnitude (for chlorobenzene) than the variation observed in the concentrations of these compounds during the survey sampling. Because benzene concentrations had declined significantly since the survey

TABLE 4. VOC CONCENTRATION MEANS ($\mu\text{g/L}$) AND STANDARD DEVIATIONS OF THE FOUR SAMPLING DEVICES UTILIZED IN EXPERIMENT B

| | PTFE Filter Tip | Standard Bailer | Bladder Pump | Multi- Port |
|---------------------|--------------------|--------------------|-----------------|-----------------|
| Benzene | 42 \pm 1.4 | 53 \pm 1.2 | 65 \pm 1.1 | 50 \pm 1.0 |
| Chlorobenzene | 1290 \pm 25.3 | 1060 \pm 25.1 | 1250 \pm 23.5 | 1240 \pm 20.4 |
| 1,2-Dichlorobenzene | 219 \pm 5.72 | 195 \pm 7.12 | 210 \pm 6.25 | 203 \pm 7.31 |
| 1,3-Dichlorobenzene | 20 \pm 0.98 | 18 \pm 1.7 | 19 \pm 0.82 | 18 \pm 0.52 |
| 1,4-Dichlorobenzene | 358 \pm 15.4 | 306 \pm 11.8 | 338 \pm 6.81 | 335 \pm 12.8 |
| 1,1-Dichloroethane | 33 \pm 0.75 | 31 \pm 0.82 | 33 \pm 1.7 | 34 \pm 1.0 |
| 1,2-Dichloroethane | 10 \pm 0.41 | 9 \pm 0.41 | 10 \pm 0.75 | 9 \pm 0.75 |
| Ethylbenzene | 29 \pm 1.1 | 22 \pm 0.52 | 25 \pm 0.52 | 28 \pm 1.2 |
| Trichloroethene | 10 \pm 0.41 | 11 \pm 0.84 | 11 \pm 0.85 | 11 \pm 0.00 |

sampling, is was difficult to relate the survey sampling results to the benzene concentration variation observed during experiment B.

With the exception of benzene and trichloroethene recoveries, the bailer exhibited the lowest mean concentrations (only the mean recovered concentrations of trichloroethene, 1,3-dichlorobenzene, and 1,1-dichloroethane were within one standard deviation of those recovered by the bladder pump). The standard deviations of the means differed little between individual sampling devices. This suggests that the precision of the PTFE filter tip and multi-port is similar to that of the bladder pump. It is also interesting to note that the bailer samples produced a standard deviation very similar to that of the other devices for each organic compound.

The VOC data were statistically analyzed by a multivariate analysis of variance, followed by one-way analyses of variance and multiple comparison tests. The multivariate analysis, run on software produced by BMDP Statistical Software, Inc. (1988), revealed significant differences between sampling devices when all nine detected VOCs were included.

The one-way analyses of variance were designed to determine if significant differences existed between the sampling devices based on recoveries of individual VOCs. With the exception of trichloroethene, this analysis of variance showed that the mean values of the replicate samples for each device were significantly different from each other. This suggests that, at the 5 percent significance level, the devices differed significantly in their ability to recover VOCs. For the recovery of trichloroethene, the devices did not differ significantly.

The Tukey multiple comparison test was utilized to test for significant differences between individual pairs of sample means. The results, shown in Table 5, confirm much of what may be interpreted from an inspection of the data shown in Table 4. In all cases (except benzene recovery), the *in situ* devices recovered VOCs at concentrations at least as great as, or not significantly different from, those of the bladder pump. The PTFE filter tip was part of the groups recovering the significantly highest concentrations for eight of the nine compounds, while the bladder pump was included in this group for six compounds. The multi-port was part of the highest group for three compounds, while the bailer was part of the highest group for one compound.

The bailer yielded the lowest mean concentrations for seven of the nine detectable VOCs, and for three of these compounds (chlorobenzene, ethylbenzene, and 1,4-dichlorobenzene), the means differed significantly from those of all other sampling devices. For six of the nine VOCs, the bailer produced mean concentrations which were significantly lower than those of the bladder pump.

DISCUSSION

The objectives of this phase of the study were to compare the accuracy and precision of each of the sampling devices. Again, because of the nature of a field study, the assessment of sampling device accuracy must be based on the relative concentrations of VOCs recovered (higher mean concentrations imply greater accuracy). Precision is estimated from a comparison of the standard deviations about the mean values.

Based on inspection of the data and the results of the statistical analyses, it may be stated that Experiment B has shown that the PTFE filter tip produces samples with an accuracy as great as or greater than those collected with the bladder pump, multi-port, or the bailer. The PTFE filter tip and bladder pump results were fairly comparable, while the multi-port and bailer appeared to be less accurate. The bailer appears to be the least accurate of the four devices tested. Considering the likely spatial variation in hydrochemistry at the site, these results also suggest that under field conditions the bladder pump, PTFE filter tip, and multi-port may produce comparable results. Because the bailer sampled the same well as the bladder pump, spatial variation should not have been a factor in the bailer's response, further indicating its lower accuracy. Based on a comparison of standard deviations, all four of the devices exhibited comparable precisions.

The PTFE filter tip proved to be capable of providing ground-water samples with an accuracy and precision rivaling that of the bladder pump. It is unfortunate that the HDPE filter tip installation was damaged

TABLE 5. TUKEY TEST RESULTS FOR EXPERIMENT B

| Rank* | Benzene | Chlorobenzene | 1,2-Dichlorobenzene |
|-------|-----------------|-----------------|---------------------|
| 1 | Bladder Pump | PTFE Filter Tip | PTFE Filter Tip |
| 2 | Standard Bailer | Bladder Pump | Bladder Pump |
| 3 | Multi-Port | Multi-Port | Multi-Port |
| 4 | PTFE Filter Tip | Standard Bailer | Standard Bailer |

| Rank* | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane |
|-------|---------------------|---------------------|--------------------|
| 1 | PTFE Filter Tip | PTFE Filter Tip | Multi-Port |
| 2 | Bladder Pump | Bladder Pump | PTFE Filter Tip |
| 3 | Multi-Port | Multi-Port | Bladder Pump |
| 4 | Standard Bailer | Standard Bailer | Standard Bailer |

| Rank* | 1,2-Dichloroethane | Ethylbenzene | Trichloroethane |
|-------|--------------------|-----------------|-----------------|
| 1 | PTFE Filter Tip | PTFE Filter Tip | Multi-Port |
| 2 | Bladder Pump | Multi-Port | Bladder Pump |
| 3 | Multi-Port | Bladder Pump | Standard Bailer |
| 4 | Standard Bailer | Standard Bailer | PTFE Filter Tip |

*Ranked from highest to lowest concentration

and could not be included in this phase of the study. A continued evaluation of the differences between the two materials may have provided valuable information that might explain some of the discrepancies between the two types of filter tips noted during Experiment A.

Experiment B also confirmed the need to replace the perforated sample vial septum on those samples collected with the multi-port device. The six replicate samples showed no sign of the apparent high losses of volatiles noted during the Experiment A sampling phase. Precision of the samples produced by the multi-port was comparable to those of the bladder pump and PTFE filter tip, although accuracy appeared to be somewhat less.

The bailer again produced relatively low concentrations of most of the VOCs and a precision comparable to the other devices. However, these results are somewhat misleading: samples collected with the bailer were transferred from the bailer to a glass beaker, from which they were then transferred to individual sample vials. As a result, the six samples collected with the bailer were not obtained from six successively collected bailer volumes. Instead, these samples are actually splits from two successive bailer volumes (the beaker was filled and the contents used to fill three sample vials), and, therefore, are not the kind of results that might have been obtained with individual bailer samplings. This would explain, in part, why the precision of the bailed samples appears

higher than might be expected based on the results of other studies. Overall accuracy and precision may have been different if the replicates had been collected from six successive bailer volumes. In light of the procedures used to collect the bailer samples, these results are of little use in evaluating the performance of the bailer.

As was found during Experiment A, the VOC standard solution concentrations were much lower than the stated true values (Table C.18). Again, the deviations can probably be attributed to volatilization during sample preparation rather than sample degradation. The two standards are duplicates produced from the same batch sample, and both analysis results are in close agreement.

The source of detectable levels of acetone in the standards, trip blank, bailer equipment blank, and two bladder pump field samples was not determined during this experiment. However, the bailer decontamination process can probably be eliminated as the source in the bailer equipment blank because acetone was not used for equipment decontamination during this experiment. It is also unlikely that the source of acetone was the ground water at the site because acetone has not been detected during any other sampling at this site and because acetone was only detected in two out of the 24 field samples collected during this sample round. The presence of acetone in several types of samples (field samples, trip blanks, equipment blanks, and standards) suggests that the contamination occurred at a time when many of the samples could be affected simultaneously; for example, during the VOA bottle-cleaning process. In an effort to eliminate the problem, the remaining bottles in that batch were discarded and new, pre-cleaned VOA bottles were utilized during subsequent experiments. In any case, the acetone contamination did not appear to affect the results of the experiment.

SECTION 6

EXPERIMENT C

EXPERIMENTAL DESIGN

While experiment B resulted in a valid comparison of the four devices for a single sampling event, that experiment did not include all the devices of interest, nor did it provide information about long-term VOC concentration trends and device performance. The final phase of the comparative study, experiment C, was designed to monitor long-term VOC recovery patterns of the included sampling devices. Collecting more samples over several sample rounds would allow comparisons to be made over a longer time period so that patterns between devices could be better defined. This information would be useful in the determinations of individual device accuracy and precision as well as understanding how the devices as a group responded to changing conditions. In addition, the ability of the devices to collect samples over long time periods without mechanical failure was of additional interest to the study. It was hoped that this information would provide an indication of device reliability.

The six devices utilized during experiment C included the four from experiment B plus the HDPE filter tip and the BED bailer (bailer with a bottom emptying device) as shown in Table 6. The HDPE filter tip installation, which had been damaged by construction activity prior to experiment B, was repaired and returned to use for this experiment. As the filter tip itself was not affected by the damage, results of subsequent sampling were not expected to be adversely impacted. The BED bailer, which was described in an earlier section of this report, had not been used in any of the previous experiments. It was tested here to determine if its design would reduce the variability observed with the standard bailer in experiments A and B.

TABLE 6. SAMPLING DEVICES UTILIZED IN EXPERIMENT C

| Device Type | Well Number |
|-----------------|-------------|
| BED Bailer | 1 |
| Bladder Pump | 1 |
| HDPE Filter Tip | 5 |
| Multi-Port | 3 |
| PTFE Filter Tip | 2 |
| Standard Bailer | 1 |

The experiment involved four sampling rounds conducted at intervals of approximately 12 weeks for the duration of one year. Three sample replicates were collected with each device, as opposed to the six replicates collected during experiment B. Samples were collected for complete VOC analysis (EPA Method 624), trace metals Fe and Mg, and gross chemistry. As in the previous experiments and with the exception of well 1, the order

in which each device was sampled during each round was randomized to prevent bias. The order in which well 1 was sampled was chosen randomly from the group of four wells but the device sampling order within well 1 was generally not random. During the previous experiments and during the early rounds of this experiment the bladder pump samples were collected first, directly after the purging procedures were complete. This meant that the pump did not have to be removed from the well, stored during sampling with the other devices, and then decontaminated prior to reinstallation in the well for sampling. As this procedure might have introduced bias into the experiment, the order with which the well 1 devices were used was randomized during sample rounds 3 and 4.

Quality assurance samples (trip blanks and equipment blanks) were collected during each round. Although standards were not prepared during this experiment because of the difficulties encountered in their preparation (as previously discussed), laboratory replicate analyses were performed on approximately 20 percent of the samples submitted.

This experiment utilized the same assumptions as the previous experiments, namely that VOC concentrations were uniformly distributed across the study site and that the highest VOC concentrations recovered provided the most accurate representation of aquifer VOC concentrations.

RESULTS

The VOC analytical data resulting from experiment C are tabulated in Tables C.19 through C.22 and graphically presented in Figures D.10 through D.18. The same nine VOCs that were detected in experiment B were also detected in each of the samples in this experiment. In contrast to that experiment, however, considerable variation is apparent in these data, both between devices and over time for each device. The compounds continued the generally declining VOC concentration trends observed in the earlier experiments. In fact, concentrations of several of the compounds fell well below 50 µg/L, making their usefulness for further analysis limited.

Appendix C presents the results of the analyses of the quality assurance blanks and laboratory analytical precision evaluations. Contamination was not detected in any of the quality assurance blanks, so the change in bottles had a positive impact on bottle cleanliness. Furthermore, the duplicate analyses of random field samples show that all of the VOC concentration determinations were within a ± 10 percent concentration range. In fact, many analyses fell within a ± 5 percent range. These results demonstrate that analytical precision was well within laboratory-stated bounds and that analytical variability may be of lower magnitude than other potential sources of variability in the study.

Although there was considerable variation in device ranking (based on VOC concentration recovered) during each sample round, the bladder pump and filter tips generally recovered the highest concentrations of the nine compounds. The only exception to this pattern was sample round 1 where the standard bailer also recovered the highest concentrations of some compounds. However, the bailers, particularly the BED bailer, recovered the lowest concentrations of most compounds during sample rounds 2 through 4, while the multi-port and standard bailer each recovered the lowest concentrations for several compounds during sample round 1. Most devices recovered the lowest concentrations of at least one compound at some time during the experiment, though the bailers usually recovered the lowest concentrations. The lack of clear device-dependent concentration trends suggests that site conditions may have been changing non-uniformly during the study and that a certain amount of variation might be expected from any sampling device under these conditions.

Because three sample replicates were collected with each device in experiment C, unlike the six collected in experiment B, the estimates of standard deviation made in this experiment are likely to be less representative of the true standard deviations. In addition, loss of one of the three replicates for two devices in round 2 resulted in only two replicates for those devices. As a result, for individual sample rounds in experiment C, the variation exhibited may be more strongly influenced by random fluctuations than device-dependent fluctuations.

TABLE 7. TEST OF EFFECTIVENESS OF BOTTOM-EMPTYING DEVICE, SAMPLE ROUND 4

| Compound | Mean Concentrations and Standard Deviations of Three Replicates | | | |
|---------------------|---|--------|--------------------------|-------|
| | Bottom-Emptying Device | | Decanted from Bailer Top | |
| Benzene | 11.0 | ± 1.9 | 9.0 | ± 0.0 |
| Chlorobenzene | 684 | ± 134 | 523 | ± 5.6 |
| 1,2-Dichlorobenzene | 125 | ± 17.6 | 98.4 | ± 2.3 |
| 1,3-Dichlorobenzene | 13.0 | ± 0.7 | 11.9 | ± 0.1 |
| 1,4-Dichlorobenzene | 172 | ± 47.0 | 112 | ± 2.5 |
| 1,1-Dichloroethane | 26.3 | ± 1.1 | 26.1 | ± 1.4 |
| 1,2-Dichloroethane | 7.4 | ± 0.4 | 7.6 | ± 1.1 |
| Ethylbenzene | 19.4 | ± 3.0 | 15.8 | ± 0.1 |
| Trichloroethene | 8.3 | ± 0.3 | 7.9 | ± 0.3 |

However, variations that exhibit consistent patterns over the four sample rounds are more likely to result from device-dependent fluctuations than chance fluctuations.

The standard deviations of the replicate sample means for each device generally showed less variation between sample rounds than the sample means themselves. Overall, the multi-port exhibited the lowest standard deviations for most compounds and sample rounds. As a group, the HDPE filter tip, bladder pump, and multi-port consistently had the lowest standard deviations. The standard deviations of the PTFE filter tip were variable over the four rounds, while the bailers generally had the highest standard deviations. The BED bailer produced the highest standard deviation for almost every compound and sample round.

Because the replicate samples collected with the bailers during this experiment were from separate bailer volumes (unlike experiment B), these high deviations suggest a true lack of repeatability or precision for sampling with bailers. In fact, the BED bailer standard deviations were unexpectedly high, especially during the sample rounds 3 and 4, considering the use of the bottom-empty device which was expected to provide more representative samples. In addition, these high standard deviations usually correlated with mean concentrations that were lower than the other devices. The effectiveness of the bottom emptying device was tested during sample round 4 by decanting three replicate samples from the top of the bailer (samples could not be obtained by the method used with the standard bailer because the bottom ball valve could not be accessed to release the sample). The results show (Table 7) that decanting the sample generally led to lower mean concentrations and lower standard deviations about those means than using the bottom emptying device. It appears that, in comparison to decanting from the top of the bailer, the bottom emptying device may lead to more variation in the concentrations of recovered samples although the overall resultant concentrations are higher.

The VOC data were analyzed using a multivariate analysis of variance (BMDP Statistical Software, 1988) to determine if there existed statistically significant differences between device sample means and sample rounds. The analysis was conducted for all nine detected VOCs with the six sampling devices and four sampling rounds as the classification variables. The hypothesis tested was that the observed VOC concentrations were independent of sampling device, with the effect of time removed. The multivariate analysis indicated that there were significant differences between device sample means and sample rounds at the 5 percent confidence level.

Univariate analyses of variance were then conducted to determine if significant differences existed between device sample means based on recovery of each individual compound. Nine one-way analyses were conducted for each sample round, one for each compound, thereby removing the effect of interactions between

devices over time that was observed in the VOC data plots. These analyses revealed that for most compounds significant differences existed between sample means at the 5 percent level, although there were a few exceptions. Trichloroethene and 1,2-dichloroethane sample means of the six devices did not differ during sample rounds 1, 2, and 3; 1,4-dichlorobenzene sample means did not differ during sample round 1; and 1,1-dichloroethane sample means did not differ during sample round 3. With the exception of 1,4-dichlorobenzene, the lack of significant differences between the devices for these compounds is due to their recovered concentrations near the detection levels for the analytical methods used (1 µg/L). Because distinctions could not be made below 1 µg/L, resolution at these low concentrations was reduced by the loss of a significant figure in the reported values and led to grouping of the concentrations at lower levels of resolution (higher concentration). This resulted in the appearance of more similar means than actually existed in the data set.

Tukey multiple comparison tests were then conducted to determine which individual pairs of sample means during each sample round were significantly different at the 5 percent level. The results of these analyses are shown in Tables D.1 through D.4. The devices are divided into groups of devices with sample means that are similar. Devices in each individual group have sample means that are significantly different from those in other, separate groups, although devices can be part of more than one group if their sample means are similar to the sample means in both groups. There is considerable overlap between groups but generally the devices with the highest sample means are significantly different from those with the lowest.

The results of all the Tukey tests are summarized in Tables 8 and 9, which show the number of times each device had the highest or lowest sample means of each compound or the sample mean for that device was not significantly different from the highest or lowest sample mean for that compound. Individual Tukey test results show that during sample round 1, the standard bailer and BED bailer most often recovered concentrations that were significantly higher than the other devices. The bladder pump and *in situ* devices recovered slightly lower concentrations than the bailers, with the multi-port in the lowest grouping most often. During sample round 2, the filter tips and bladder pump were most often in the top grouping while the bailers were most often in the lowest groupings. It is interesting to note, however, that although the filter tips were most often in the top grouping, they also occasionally appear in the lowest group. The bladder pump, which was also often in the top grouping, in round 2 never appeared in the lowest group. The bladder pump and all three *in situ* devices were all in the top grouping during sample round 3, with all six devices occasionally appearing in the lowest grouping, although the bladder pump and filter tips were in the lowest group least often. During sample round 4, the bladder pump and filter tips were again part of the highest grouping most often. As in sample round 2, the bladder pump was never in the lowest group of round 4, although the filter tips occasionally were. The BED bailer was in the lowest group for eight of the nine compounds and was never in the top group for round 4.

Overall, the bladder pump and PTFE filter tip were both most often in the top group (recovering the highest concentrations), followed closely by the HDPE filter tip. The multi-port, standard bailer, and BED bailer then followed in order of frequency of their appearance in the top group. The bladder pump was least often in the lowest group, followed by the PTFE filter tip, HDPE filter tip, standard bailer, multi-port, and BED bailer. The bailers were least often in the top group and, with the multi-port, most often in the lowest group.

DISCUSSION

The results of experiment C provide an estimation of device accuracy and precision based on the ranking of individual device sample means and standard deviations. Much like experiment B, the most effective devices were the bladder pump and *in situ* devices while the least effective were the bailers.

Based on the univariate analysis and Tukey tests, the bladder pump appears to be the most accurate of the six devices tested. It most often collected the highest VOC concentrations or concentrations that were not significantly different from the highest recovered concentrations. The bladder pump also recovered the lowest concentrations of the nine compounds considerably fewer times than the other devices which suggests that there

TABLE 8. RANKINGS OF DEVICES BASED ON TUKEY TEST RESULTS - HIGHEST VOC RECOVERY

| Device | Number of times in highest concentration group* | | | | Overall |
|-----------------|---|---|---|---|---------|
| | Sample Round | | | | |
| | 1 | 2 | 3 | 4 | |
| Bladder Pump | 5 | 7 | 8 | 6 | 26 |
| PTFE Filter Tip | 5 | 6 | 8 | 7 | 26 |
| HDPE Filter Tip | 5 | 7 | 7 | 6 | 25 |
| Multi-Port | 5 | 4 | 8 | 3 | 20 |
| Bailer | 7 | 2 | 4 | 3 | 16 |
| BED Bailer | 6 | 2 | 3 | 0 | 11 |

*Number of times the device recovered the highest mean concentration of a compound, or the concentration was not significantly different from the highest concentration recovered by any device.

TABLE 9. RANKINGS OF DEVICES BASED ON TUKEY TEST RESULTS - LOWEST VOC RECOVERY

| Device | Number of times in lowest concentration group* | | | | Overall |
|-----------------|--|---|---|---|---------|
| | Sample Round | | | | |
| | 1 | 2 | 3 | 4 | |
| BED Bailer | 2 | 5 | 5 | 8 | 20 |
| Multi-Port | 4 | 3 | 4 | 5 | 16 |
| Bailer | 1 | 4 | 4 | 5 | 14 |
| HDPE Filter Tip | 2 | 3 | 2 | 5 | 12 |
| PTFE Filter Tip | 3 | 2 | 2 | 1 | 8 |
| Bladder Pump | 3 | 0 | 2 | 0 | 5 |

*Number of times the device recovered the lowest mean concentration of a compound, or, the concentration was not significantly different from the lowest concentration recovered by any device. Results only include those compounds where there were significant differences between devices.

might be less variability inherent to the bladder pump sampling procedures between sample rounds when compared to the other devices. The precision of the bladder pump was on the same order as the HDPE filter tip and multi-port, which, as a group, produced the lowest standard deviations about their replicate sample means. It is not surprising that the bladder pump performed well during these experiments as it has been proven during several previous investigations to be an accurate and precise device for the collection of VOCs.

The PTFE filter tip collected significantly higher VOC concentrations than the other devices as often as the bladder pump, but, on the other hand, collected samples that had significantly lower concentrations than the other devices more often than the bladder pump. This difference was slight, however, making the PTFE filter tip just as accurate as the bladder pump under field conditions. The PTFE filter tip replicate sample standard

deviations were more variable and usually higher over the four rounds than those of the bladder pump, HDPE filter tip, and multi-port suggesting that the PTFE filter tip is less precise than these devices.

The HDPE filter tip was roughly as accurate as the bladder pump and PTFE filter tip, based on its overall high VOC sample means, and was as precise as the bladder pump and multi-port. It is interesting to note that although overall they recovered about the same mean concentrations, the HDPE filter tip was considerably more precise than the PTFE filter tip. This disparity is difficult to explain because their design is similar and their operating procedures are identical. As discussed in experiment A, the source of imprecision may lie within the characteristics of the individual filter tips which are composed of different materials and have different pore sizes and apparent permeabilities. The PTFE filter has an average pore size twice that of the HDPE (35 μm versus 15 μm) but the permeability is an order of magnitude lower (1.7×10^{-4} cm/s versus 1.7×10^{-3} cm/s). The lower permeability of the PTFE filter may result in slightly more turbulence and possible volatilization of VOCs as ground water passes through the filter material and could lead to more variation in the recovered concentrations. The production of the PTFE filter tip has been discontinued by the manufacturer, although for different reasons.

The multi-port recovered somewhat lower mean concentrations than the filter tips and bladder pump and so might be considered slightly less accurate. It did, however, generally result in lower standard deviations than most devices during most sample rounds. A possible explanation for this combination of lower apparent accuracy and high precision is that the device functions well but that ambient VOC concentrations may be somewhat lower at the multi-port installation than at the others. Another possible explanation might be loss of volatiles associated with the sampling device design, such as potential orifice effects around the measurement port and sampling probe valves, excessive vacuum applied to the sample vial holder, escape of volatiles through the vent needle and into the interior of the VOA bottle holder, or well installation and development procedures. The replacement of punctured sample vial septa with unpunctured septa did apparently lead to consistently higher concentrations than had been observed during experiment A.

The standard bailer and BED bailer results confirmed some of the conclusions reached during other investigations regarding the relative inconsistencies associated with sampling VOCs with bailers. Of the six devices tested in this study, the bailers exhibited the lowest overall accuracy and precision, with the BED bailer's performance the lower of the two. The inaccuracy of a standard bailer is generally attributed to problems associated with how sampling personnel handle the bailer and the resultant sample. In this study, there is little doubt that the practice of discharging the sample from the standard bailer through the check valve and into a beaker contributed to the loss of VOCs from the sample. Pouring the sample from the bailer vent hole without causing agitation was also found to be difficult and was not an effective way of transferring the sample from the bailer to a sample bottle. It was thought that this problem would be reduced by using the BED bailer because it was designed to gently release the sample through the bottom check valve by means of the bottom emptying device. In practice, however, the bottom emptying device seemed to increase the accuracy of the device slightly but reduced the precision when compared to decanting the sample from the top of the bailer (again, not a very effective way of retrieving the sample, but the only alternative available considering the design of the BED bailer). The problem may be related to the formation of air bubbles at the bottom of the bailer when the bottom emptying device is installed into the bottom check valve assembly. These bubbles, which appeared to be introduced into the bailer body from the bottom emptying device, traveled up through the bailer body (and sample) to the top of the device. It is possible that as these bubbles traveled through the sample VOCs in solution, they volatilized into the available head space and were carried out of the sample as the bubbles rose to the surface.

As in experiment B, a portion of the variation observed between devices in experiment C may be attributed to spatial variation in hydrochemical conditions. If the assumption of identical conditions between devices is made, the above described relationships apply. However, if spatial variation in these parameters exists at the site, it may be an important part of the total variation observed. In this case, as in experiment B, the overall variation observed in the bladder pump and *in situ* device results did not greatly exceed the spatial variation to be expected under these field conditions.

With the exception of the well probe, few mechanical problems were experienced with the sampling devices during the more than two year extent of this experiment. The bailers caused no problems at all, due to the simplicity of their construction and operation. Handling, decontamination, and storage were easily accomplished under all conditions. The bladder pump experienced only one minor problem: the nitrogen supply tube fitting on the pump loosened during purging in sample round 4, allowing nitrogen to enter the well casing and causing considerable agitation of the well water. This problem was easily repaired in the field and, after additional purging, did not appear to affect sampling results for that round. Otherwise, the bladder pump performed smoothly.

Although none of the problems were major, the *in situ* devices tended to have more difficulties associated with them due to their specialized and more complicated design. Both filter tips occasionally had problems delivering samples when foreign materials inadvertently entered their well bores and covered the filter tip septa. This problem was rectified by rinsing the interior of the filter tip casing with distilled water and pumping out the materials with a peristaltic pump. This treatment was required only once during the experiment. In addition, although not a mechanical problem, decontamination of the specially designed sample bottles in the laboratory was a time-consuming procedure whose consistency and effectiveness were difficult to evaluate.

The multi-port sampling device performed well throughout the experiment with only two problems. An air leak in the pneumatic control box required an interruption in sampling and repair in the shop. Although not generally recommended by the manufacturer, the multi-port sampling probe, and all stainless-steel sample bottles, were disassembled after each sample round and thoroughly cleaned. This procedure was time-consuming and considerable care was required when reassembling all the components. A second problem involved the inability to collect a sample from the measurement port at the 4.5-m depth. Although samples from this port were not designed to be included in the comparison study, several attempts were made to make the port operational. All methods attempted were unsuccessful, and the problem was attributed to a small leak in the sampling probe-measurement port connection.

SECTION 7

SUMMARY AND CONCLUSIONS

The collection of representative ground-water samples is commonly a very difficult and often hazardous undertaking. Many of the problems relate to the process of purging a well of stagnant water prior to sample collection, a necessary procedure when using most commercially available sampling devices in conventional monitoring wells. During this investigation, field experiments were designed to evaluate the effectiveness of four relatively new sampling systems (two filter tips, a well probe, and a multi-port system) which require little or no pre-sample purging. The evaluation involved a comparison of these newer devices with two relatively common sampling devices, a bladder pump and a bailer.

The devices were field-tested at a site where a shallow alluvial aquifer was contaminated by a VOC plume. Six wells were installed on 6-m centers in a rectangular grid pattern, with the sampling zones of each device placed at a depth of approximately 6 m. Heterogeneous geologic and hydrochemical conditions represented possible sources of variability in the results, although they were assumed to be uniform over the site in order to make comparisons between the samplers. The comparisons were based on the ability of each device to accurately and precisely recover samples of ground water contaminated with VOCs. Those devices that recovered the highest concentrations were considered the most accurate.

The results of Experiment A suggest 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. The design of this system is also flexible enough to allow for other methods of sample collection which do not involve a punctured septum, but still have the potential to recover accurate samples. This system and the various methods of sample collection could be evaluated further.

Experiment B, based on many of the results and problems noted during the first experiment, confirmed many of the original findings. Multiple replicate samples were collected with four of the original sampling devices during a single sampling interval. 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, which included four sample rounds, six devices, and multiple replicate samples from each device, followed several of the trends established during the previous two experiments, but provided more 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.

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, these experiments indicate 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.

The results show that, under the field conditions of this study, the tested *in situ* devices 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 these *in situ* devices significantly reduce the volume of stagnant water normally associated with conventional monitoring wells. As a result, the *in situ* devices can provide consistently representative VOC samples in sand and gravel aquifers, while virtually eliminating the need for well purging prior to sample collection.

In addition to collection of representative samples and minimizing purging volumes, the *in situ* devices also 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. 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 this report.

To obtain a more accurate evaluation of these sampling devices, it is suggested that additional studies be developed and implemented, such as application of these systems in various hydrogeochemical conditions, including low-permeability environments, or areas with different types of contaminants. In addition, the effects of these devices on the concentrations of naturally-occurring ground-water chemical constituents should be studied. 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.

REFERENCES

- Barcelona, M.J., J.A. Helfrich, E.E. Garske, and J.P. Gibb, 1984. A laboratory evaluation of ground water sampling mechanisms: Ground Water Monitoring Review. Vol. 4. No. 2. pp. 32-41.
- BAT Envitech, Inc., 1987, BAT groundwater monitoring system, special equipment notice for Desert Research Institute (DRI). 10 p.
- Black, W.H., H.R. Smith, and F.D. Patton, 1986. Multiple-level ground water monitoring with the MP system. In: *Proceedings of the Surface and Borehole Geophysical Methods and Ground Water Instrumentation Conference and Exposition*. Denver, Colorado. National Water Well Association. Water Well Journal Publishing Company, Dublin, Ohio. pp. 41-61.
- Blegen, R.P., K.F. Pohlmann, and J.W. Hess, 1987. Bibliography of ground-water sampling methods. U.S. Environmental Protection Agency. EPA-600/X-87/325. 43 p.
- BMDP Statistical Software, Inc., 1988. BMDP Statistical Software Manual. Volume 2, Method PV4. ed. by W.J. Dixon, *et al.*. University of California Press.
- Desert Research Institute, 1987. Quality assurance plan for subsurface geophysical methods for hazardous waste site investigations and monitoring. Prepared for U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, Nevada. Cooperative Agreement CR812713-01 (unpublished).
- Ecology and Environment, Inc., 1984. Technical summary of soil and *in situ* gas sampling study. Basic Management, Inc., Henderson, Nevada. Report Number C(84)C345. 28 p.
- Ecology and Environment, Inc., 1985. Phase IIB sampling plan. Stauffer Chemical Company, BMI Complex, Henderson, Nevada. 52 p.
- Fordham, J.W., H. Kolterman, and J.W. Hess, 1984. Groundwater monitoring plan, part 1 - review of site hydrogeology and existing monitoring network. Prepared for TIMET, Inc., Henderson, Nevada. Water Resources Center, Desert Research Institute. 37 p.
- Geraghty and Miller, Inc., 1980. Ground-water investigation. Stauffer Chemical Company, Henderson, Nevada. 42 p.
- Gillham, R.W., M.J.L. Robin, J.F. Barker, and J.A. Cherry, 1983. Groundwater monitoring and sample bias. American Petroleum Institute, Environmental Affairs Department. API Publication No. 4367. 206 p.
- Gillham, R.W., M.J.L. Robin, J.F. Barker, and J.A. Cherry, 1985. Field evaluation of well flushing procedures. American Petroleum Institute, Health and Environmental Sciences Department. API Publication No. 4405. 110 p.

- Hall, L.E., 1986. Control of ground water contamination in an alluvial fan aquifer by a dual hydraulic barrier. In: *Proceedings of the First National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods*. Las Vegas, Nevada. National Water Well Association, Dublin, Ohio. Water Well Journal Publishing Company, Worthington, Ohio. pp. 125-142.
- Houghton, R.L. and M.E. Berger, 1984. Effects of well-casing composition and sampling method on apparent quality of ground water. In: *Proceedings of the Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring*. Columbus, Ohio, National Water Well Association. Water Well Journal Publishing Company, Worthington, Ohio. pp. 203-213.
- Imbrigiotta, T.E., J. Gibs, T.V. Fusillo, G.R. Kish, and J.J. Hochreiter, 1986. Field evaluation of seven sampling devices for purgeable organic compounds in ground water. Prepared for ASTM Symposium on Field Methods for Ground Water Contamination Studies and Their Standardization. February 2-7, 1986. Cocoa Beach, Florida. 23 p.
- JRB Associates, Inc., 1981. Henderson Industrial Complex hazardous waste investigation. U.S. Environmental Protection Agency Contract No. 68-01-5052. Directive of work #23.
- Kaufman, R.F., 1978. Land and water use effects on ground-water quality in Las Vegas Valley. U.S. Environmental Protection Agency. EPA-600/2-78-179. 216 p.
- Longwell, C.R., E.H. Pampeyan, B. Bowyer, and R.J. Roberts, 1965. Geology and mineral resources of Clark County, Nevada. Nevada Bureau of Mines and Geology. Bulletin 62. 218 p.
- Malmberg, G.T., 1965. Available water supply of the Las Vegas ground-water basin, Nevada. U.S. Geological Survey Water-Supply Paper 1780. 116 p.
- Maxey, G.B. and C.H. Jameson 1948. Geology and water resources of Las Vegas, Pahrump, and Indian Springs Valleys: Clark and Nye Counties, Nevada. State of Nevada, Office of the State Engineer. Water Resources Bulletin 5. 121 p.
- Muska, C.F., W.P. Colven, V.D. Jones, J.T. Scogin, B.B. Looney, and V. Price, 1986. Field evaluation of ground water sampling devices for volatile organic compounds. In: *Proceedings of the Sixth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring*. Columbus, Ohio, National Water Well Association. Water Well Journal Publishing Company, Worthington, Ohio. pp. 235-246.
- Nielsen, D.M. and G.L. Yeates, 1985. A comparison of sampling methods available for small-diameter ground water monitoring wells. *Ground Water Monitoring Review*. Vol. 5. No. 2. pp. 83-98.
- Pearsall, K.A. and D.A.V. Eckhardt, 1987. Effects of selected sampling equipment and procedures on the concentrations of trichloroethylene and related compounds in ground water samples. *Ground Water Monitoring Review*. Vol. 7. No. 2. pp. 64-73.
- Plumb, Jr., R.H. and A.M. Pitchford, 1985. Volatile organic scans: Implications for ground-water monitoring. In: *Proceedings of the Petroleum Hydrocarbons and Organic Chemicals in Ground Water - Prevention, Detection, and Restoration - A Conference and Exposition*. Houston, Texas. National Water Well Association and American Petroleum Institute. Water Well Journal Publishing Company, Dublin, Ohio. pp. 207-221.

- Pohlmann, K.F., W.L. Halligan, and J.W. Hess, 1990. Laboratory evaluation of purging techniques for low-yield wells. U.S. Environmental Protection Agency Internal Report. In preparation.
- Pohlmann, K.F. and J.W. Hess, 1988. Generalized ground-water sampling device matrix. *Ground Water Monitoring Review*. Vol. 8. No. 4. pp. 82-84.
- Scalf, M.R., J.F. McNabb, W.J. Dunlap, and R.L. Crosby, 1981. Manual of ground water quality sampling procedures. U.S. Environmental Protection Agency. Robert S. Kerr Environmental Research Laboratory. Ada, Oklahoma. 105 p.
- Skougstad, M.W., J.J. Fishman, L.C. Friedman, D.E. Erdmann, and S.S. Duncan, eds. 1979. Methods for the determination of inorganic substances in water and fluvial sediments. U.S. Geological Survey Techniques of Water Resources Investigations. Book 5. Chapter A1. 626 p.
- Steel, R.G.D. and J.H. Torrie, 1960. Principles and Procedures of Statistics. McGraw-Hill. New York. 481 p.
- Stolzenburg, T.R. and D.G. Nichols, 1985. Preliminary results on chemical changes in groundwater samples due to sampling devices. Electric Power Research Institute, Inc.. EPRI EA-4118. Madison, Wisconsin, 84 p.
- Torstensson, B., 1984. A new system for ground water monitoring. *Ground Water Monitoring Review*. Vol. 4. No. 4. pp. 131-138.
- Torstensson, B., and A.M. Peterson, 1986. A hermetically isolated sampling method for ground water investigation. Prepared for ASTM Symposium on Field Methods for Ground Water Contamination Studies and Their Standardization. February 2-7, 1986. Cocoa Beach, Florida. 23 p.
- U.S. Bureau of Reclamation, 1982. Hydrogeologic analysis of lower Las Vegas Valley. Colorado River Basin Salinity Control Project, Title II - Las Vegas Wash Unit. 106 p.
- U.S. Bureau of Reclamation, 1984. Verification plan report. Pittman verification program. 43 p.
- U.S. Environmental Protection Agency, 1979. Methods for chemical analysis of water and wastes. EPA-600/4-79-020.
- U.S. Environmental Protection Agency, 1986. RCRA ground-water monitoring technical enforcement guidance document. U.S. Environmental Protection Agency Office of Solid Waste and Emergency Response. OSWER-9950.1. 208 p.
- Unwin, J.P., 1984. Sampling ground water for volatile organic compounds: the effect of sampling method, compound volatility and concentration. In: *Proceedings of the Fourth National Symposium and Exposition on Aquifer Restoration and Ground Water Monitoring*. Columbus, Ohio, National Water Well Association. Water Well Journal Publishing Company, Worthington, Ohio. pp. 257-262.
- Whitbeck, M.R. and R. Williams, 1990. A simulated well environment for testing ground-water samplers. U.S. Environmental Protection Agency Internal Report. Submitted to U.S. EPA for review.
- Yeskis, D., K. Chiu, S. Meyers, J. Weiss, and T. Bloom, 1988. A field study of various sampling devices and their effects on volatile organic contaminants. In: *Proceedings of the Second National Outdoor Action Conference on Aquifer Restoration, Ground Water Monitoring and Geophysical Methods*. Las Vegas, Nevada, National Water Well Association. Water Well Journal Publishing Company, Dublin, Ohio. pp. 471-479.

APPENDIX A

WELL CONSTRUCTION DIAGRAMS

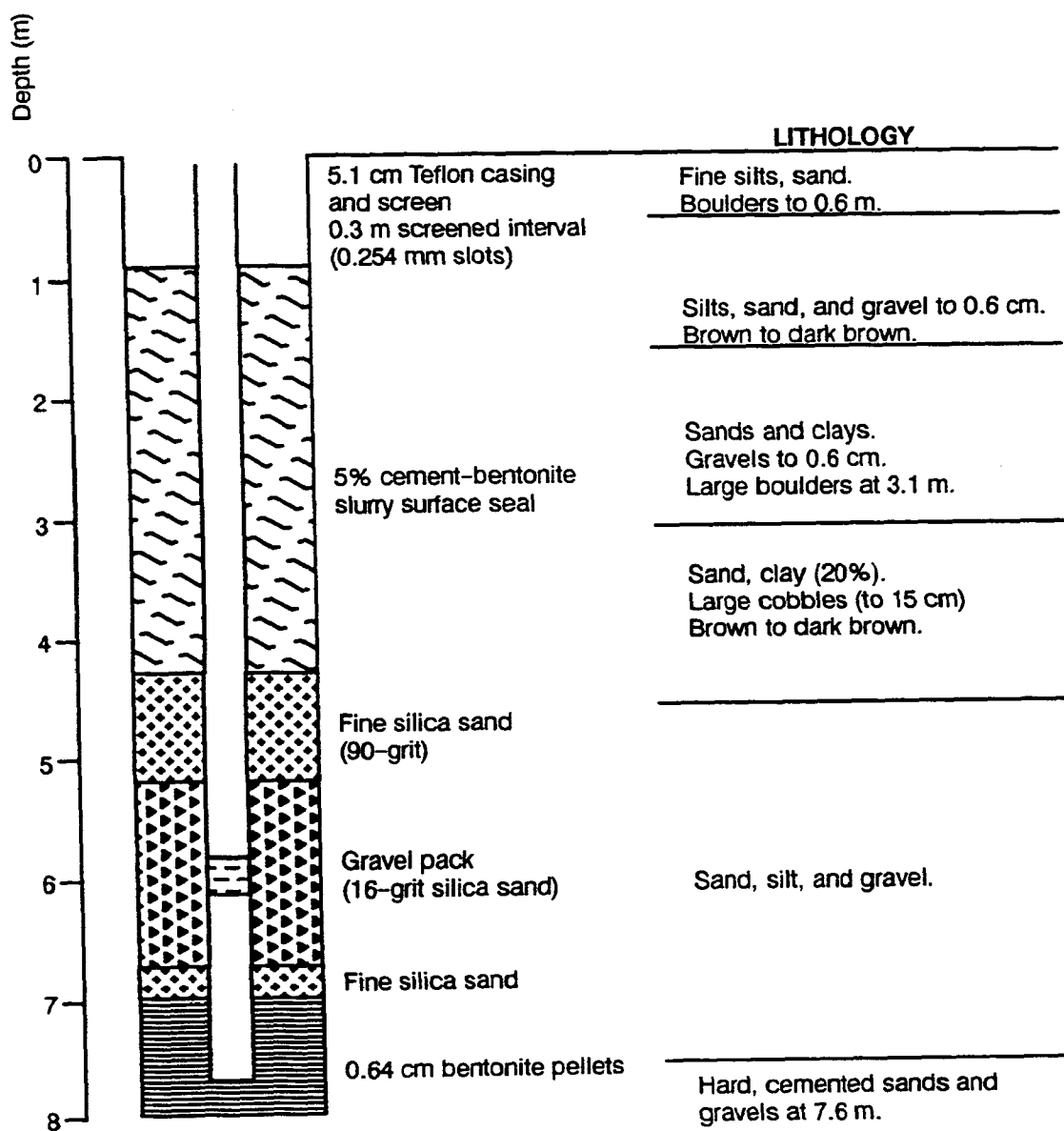


Figure A.1 – Well 1 construction diagram and lithologic log. Sampling devices: Bladder Pump, Bailer, BED Bailer.

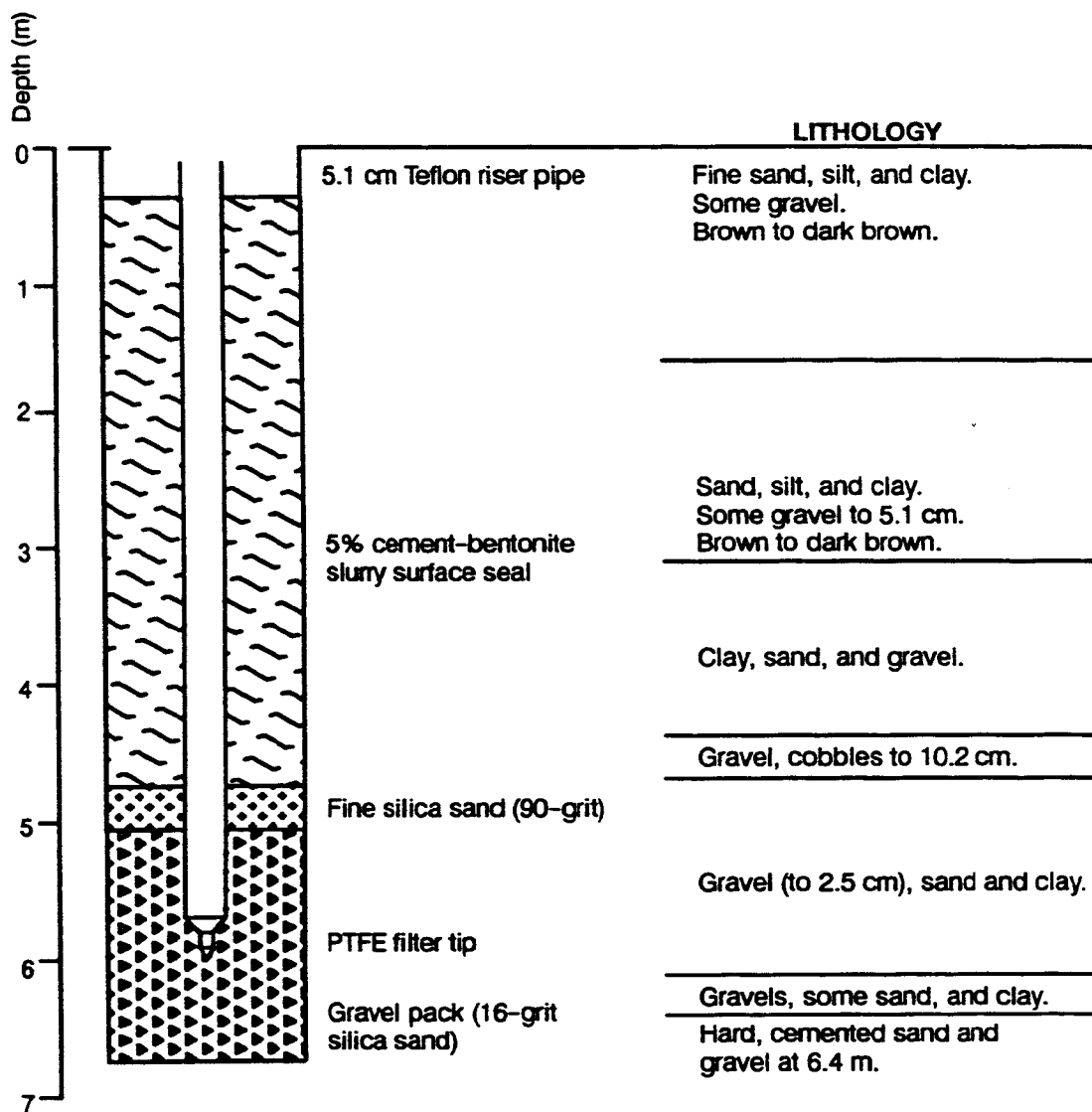


Figure A.2 - Well 2 construction diagram and lithologic log. Sampling device: PTFE Filter Tip.

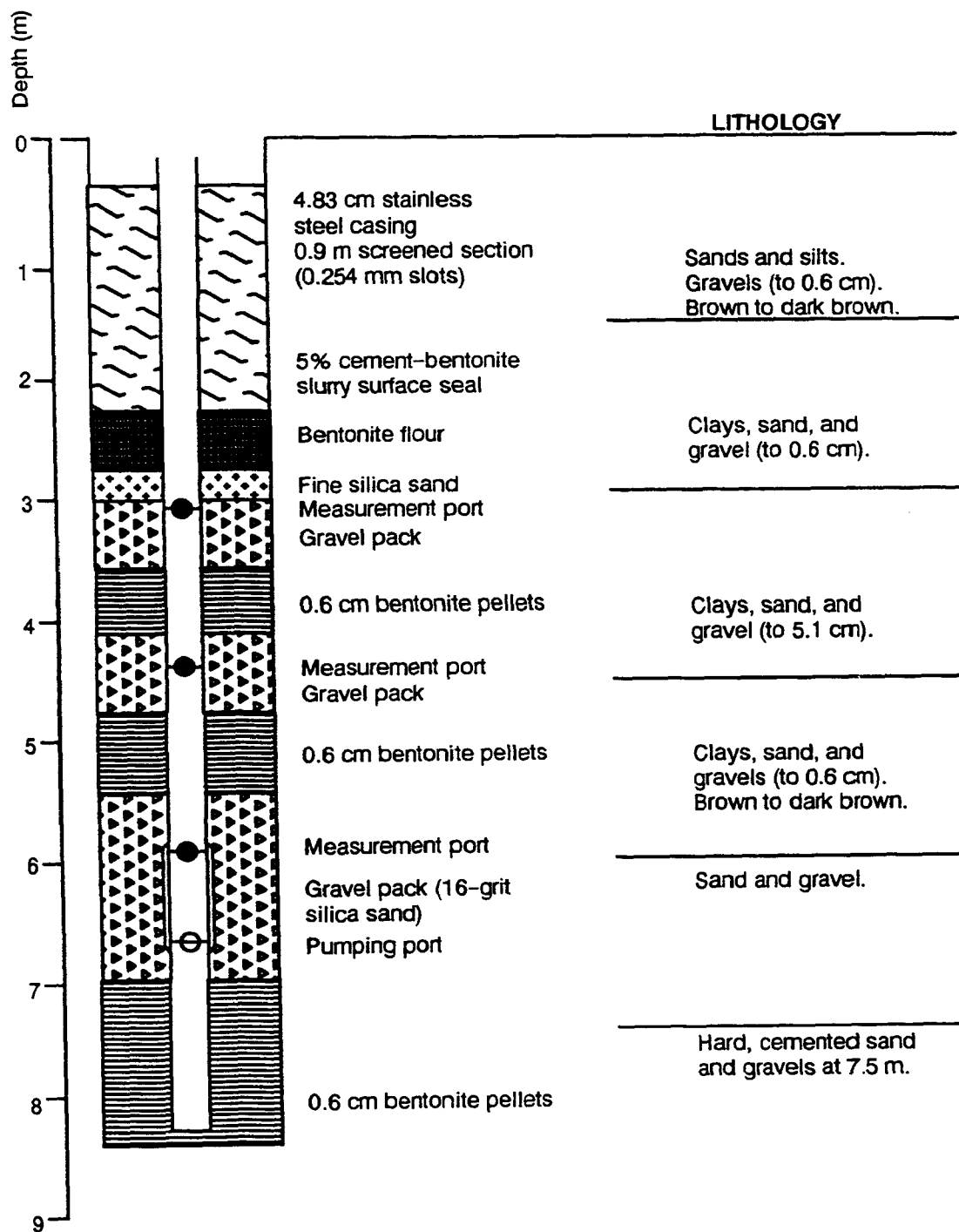


Figure A.3 – Well 3 construction diagram and lithologic log. Sampling device: MP System.

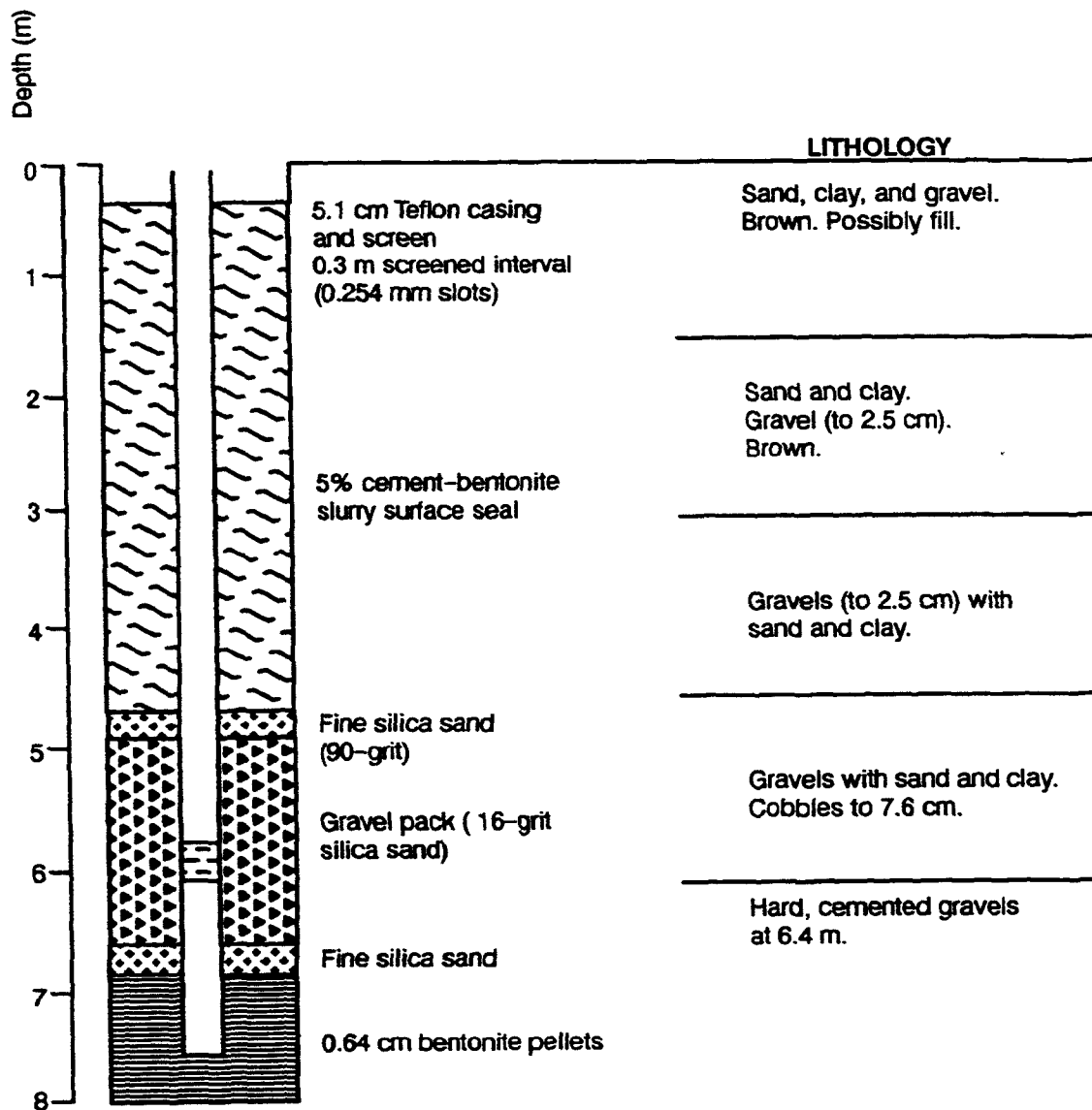


Figure A.4 - Well 4 construction diagram and lithologic log. Sampling device: Well Probe.

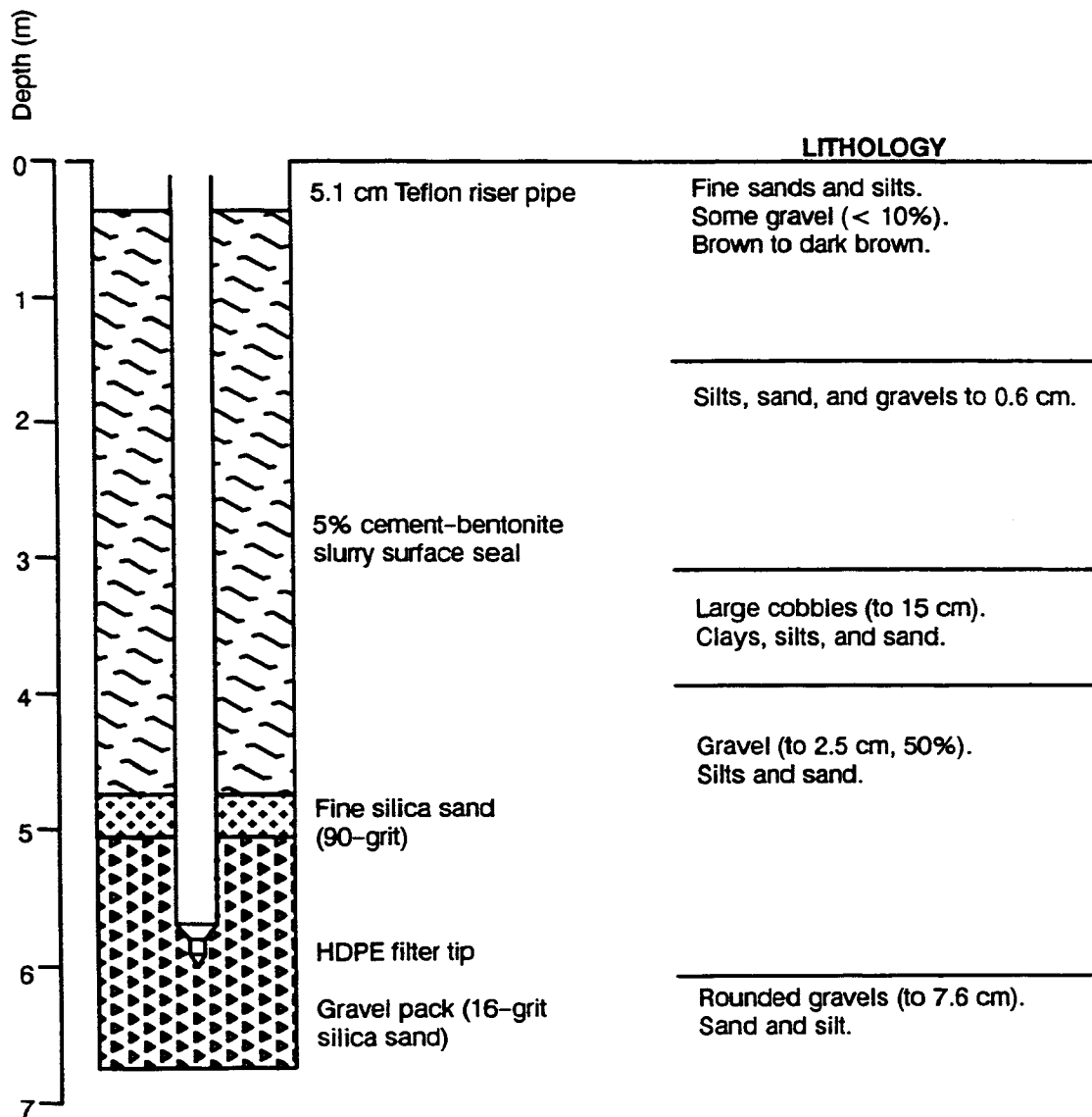


Figure A.5 – Well 5 construction diagram and lithologic log. Sampling device: HDPE Filter Tip.

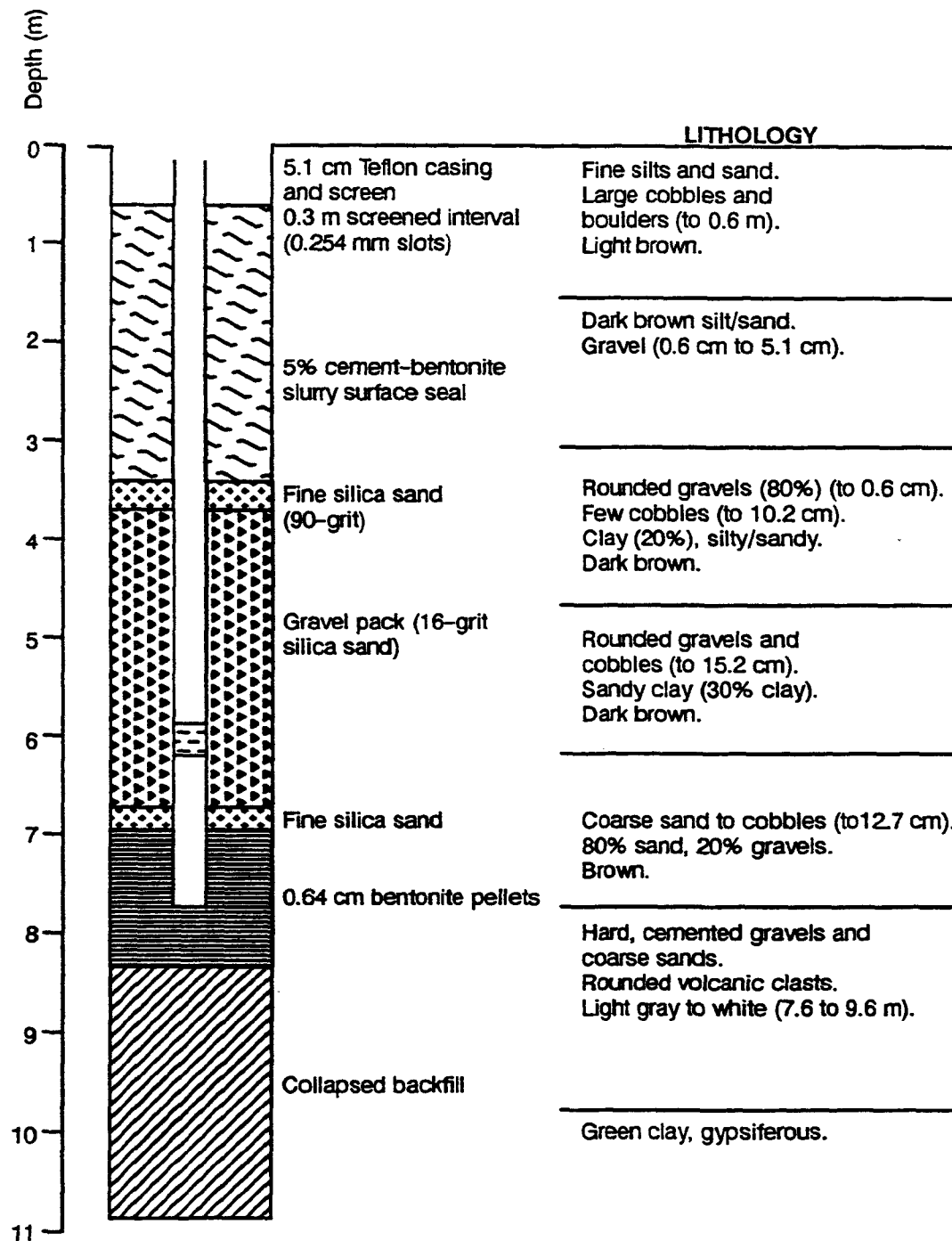


Figure A.6 - Well 6 construction diagram and lithologic log. Sampling device: Bladder Pump/Packer.

APPENDIX B

LABORATORY ANALYSIS METHODOLOGY

Samples for inorganic constituents and total organic carbon were analyzed by the Desert Research Institute Water Chemistry Laboratory in Reno, Nevada. Samples were analyzed for pH, electrical conductivity (EC), bicarbonate (HCO_3^-), chloride (Cl^-), sulfate (SO_4^{2-}), nitrate (NO_3^-), sodium (Na^+), potassium (K^+), magnesium (Mg^{2+}), calcium (Ca^{2+}), manganese (Mn^{2+}), iron (Fe^{2+}), dissolved silica (SiO_2), total dissolved solids (TDS), and total organic carbon (TOC).

Analyses for volatile organic compounds were conducted by Alpha Analytical, Inc., in Sparks, Nevada. Analysis requests for Experiment A samples were for benzene, chlorobenzene, and chloroform only. For Experiments B and C, a full EPA Method 624 analysis was conducted for all samples.

Table B.1 lists each chemical analysis, the appropriate laboratory method reference, and laboratory equipment used in the analysis.

REFERENCES

- Skougstad, M.W., M.J. Fishman, L.C. Friedman, D.E. Erdmann, and S.S. Duncan, eds., 1979. Methods for determination of inorganic substances in water and fluvial sediments. U.S. Geological Survey Techniques of Water Resources Investigations. Book 5. Chapter A1. 626 p.
- U.S. Environmental Protection Agency, 1979. Methods for chemical analysis of water and wastes. EPA-600/4-79-020.

**TABLE B.1 – CHEMICAL SPECIES, REFERENCED METHOD ANALYSIS,
AND LABORATORY ANALYSIS EQUIPMENT USED**

| Measurement Parameter | Reference Method | Equipment |
|-------------------------------|--|--|
| pH | EPA-600/4-79-020 (1979) Method 150.1 | Beckman 4500 Automated Titrator |
| Electrical Conductivity | EPA-600/4-79-020 (1979) Method 120.1 | Beckman Model RC-19 Conductivity Bridge |
| Bicarbonate (Alkalinity) | EPA-600/4-79-020 (1979) Method 305.1 | Brinkman Metrohm Automated Titrator Model E 636/series 02 |
| Chloride | EPA-600/4-79-020 (1979) Method 325.1 | Coulter Industrial Kemolab |
| Sulfate | EPA-600/4-79-020 (1979) Method 375.4 | Hack Model 2100 Turbidimeter |
| Nitrate | EPA-600/4-79-020 (1979) Method 353.2 | Two Channel Technicon Autoanalyzer |
| Sodium | EPA-600/4-79-020 (1979) Method 273.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Potassium | EPA-600/4-79-020 (1979) Method 258.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Magnesium | EPA-600/4-79-020 (1979) Method 242.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Calcium | EPA-600/4-79-020 (1979) Method 215.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Manganese | EPA-600/4-79-020 (1979) Method 243.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Iron | EPA-600/4-79-020 (1979) Method 236.1 | Instrumentation Laboratory AA/AE Spectrophotometer 952 |
| Silica | Skougstad <i>et al.</i> , (1979) | Coulter Automated Analyzer |
| TDS | EPA-600/4-79-020 (1979) Method 160.1 | Barnstead T-100A Water Bath/Mettler Analytical Balance |
| TOC | EPA-600/4-79-020 (1979) Method 415.1 | Astro Model 2001 |
| Volatile Organic Compounds | EPA-600/4-82-057 (1982) Method 624 | Hewlett-Packard 5970 Mass Selective Detector Hewlett-Packard 5890 Gas Chromatograph |

APPENDIX C

ANALYTICAL RESULTS OF SAMPLING METHODS EXPERIMENTS

RESULTS OF SURVEY SAMPLING

Wells 1,4, and 6 were sampled as a part of a survey sampling plan to determine expected laboratory errors and random errors between wells. Each well was sampled with the same all-Teflon bladder pump, which was decontaminated prior to use in each well. A 19 L bulk sample was then collected from each well and split into five sets of duplicate samples. The resulting data and calculated means and standard deviations are presented in Table C.1, C.2 and C.3.

TABLE C.1 – SURVEY SAMPLING RESULTS, WELL 1

Well No. 1
Sampling Date: December 18, 1987
Sampling Device: Bladder Pump

| Replicate | 1 | 2 | 3 | 4 | 5 | \bar{x} | s |
|-------------------------|--------|--------|--------|--------|--------|-----------|------|
| Temp. (°C) | 22.4 | | | | | | |
| Field EC | 27460 | | | | | | |
| Field pH | nm | | | | | | |
| Field HCO ₃ | nm | | | | | | |
| Field DO | 0.60 | | | | | | |
| Lab pH | 7.42 | 7.33 | 7.37 | 7.41 | 7.47 | 7.40 | 0.05 |
| Lab EC | 22000 | 22000 | 22000 | 22000 | 22100 | 22040 | 55 |
| TDS (mg/L) | 16700 | 16700 | 16700 | 16700 | 16700 | 16700 | - |
| SiO ₂ (mg/L) | 97 | 97 | 97 | 97 | 97 | 97 | - |
| HCO ₃ (mg/L) | 414 | 415 | 414 | 414 | 414 | 414 | 1 |
| Cl (mg/L) | 7350 | 7390 | 7230 | 7380 | 7410 | 7352 | 72 |
| SO ₄ (mg/L) | 2830 | 2830 | 2830 | 2830 | 2820 | 2828 | 5 |
| NO ₃ (mg/L) | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | - | - |
| Na (mg/L) | 4740 | 4690 | 4780 | 4720 | 4740 | 4734 | 33 |
| K (mg/L) | 68.7 | 64.4 | 64.9 | 64.0 | 63.5 | 65.1 | 2.1 |
| Ca (mg/L) | 546 | 556 | 551 | 556 | 551 | 552 | 4 |
| Mg (mg/L) | 251 | 249 | 250 | 250 | 249 | 250 | 1 |
| Fe (mg/L) | 0.04 | 0.04 | 0.03 | 0.04 | 0.04 | 0.04 | 0.01 |
| Mn (mg/L) | 1.55 | 1.48 | 1.50 | 1.48 | 1.51 | 1.50 | 0.03 |
| TOC (mg/L) | 9.7 | 9.7 | 9.8 | 9.8 | 9.7 | 9.7 | 0.1 |
| Benzene (µg/L) | 303 | 331 | 300 | 122 | 344 | 280 | 90 |
| Chlorobenzene (µg/L) | 1390 | 1480 | 1390 | 636 | 1590 | 1297 | 379 |

nm = no measurement

TABLE C.2 – SURVEY SAMPLING RESULTS, WELL 4

Well No. 4

Sampling Date: December 17, 1987

Sampling Device: Bladder Pump

| Replicate | 1 | 2 | 3 | 4 | 5 | \bar{x} | s |
|-------------------------|--------|--------|--------|--------|--------|-----------|------|
| Temp. (°C) | 21.6 | | | | | | |
| Field EC | 28920 | | | | | | |
| Field pH | 7.23 | | | | | | |
| Field HCO ₃ | nm | | | | | | |
| Field DO | 0.40 | | | | | | |
| Lab pH | 7.23 | 7.30 | 7.21 | 7.28 | 7.36 | 7.28 | 0.06 |
| Lab EC | 22500 | 22500 | 22500 | 22500 | 22500 | 22500 | – |
| TDS (mg/L) | 16800 | 16900 | 16900 | 16900 | 16900 | 16880 | 45 |
| SiO ₂ (mg/L) | 97 | 98 | 97 | 97 | 97 | 97 | 1 |
| HCO ₃ (mg/L) | 415 | 415 | 415 | 415 | 415 | 415 | – |
| Cl (mg/L) | 7480 | 7460 | 7550 | 7430 | 7470 | 7478 | 44 |
| SO ₄ (mg/L) | 2830 | 2830 | 2820 | 2820 | 2820 | 2824 | 6 |
| NO ₃ (mg/L) | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | – |
| Na (mg/L) | 4800 | 4800 | 4690 | 4730 | 4800 | 4764 | 51 |
| K (mg/L) | 66.3 | 66.3 | 65.4 | 65.4 | 66.3 | 65.9 | 0.5 |
| Ca (mg/L) | 567 | 562 | 562 | 562 | 556 | 562 | 4 |
| Mg (mg/L) | 262 | 260 | 258 | 257 | 259 | 259 | 2 |
| Fe (mg/L) | 0.10 | 0.09 | 0.09 | 0.09 | 0.10 | 0.09 | 0.01 |
| Mn (mg/L) | 1.29 | 1.30 | 1.30 | 1.33 | 1.32 | 1.31 | 0.02 |
| TOC (mg/L) | 9.6 | 9.6 | 9.6 | 10.2 | 10.5 | 9.9 | 0.4 |
| Benzene (µg/L) | 350 | 267 | 266 | 323 | 276 | 296 | 38 |
| Chlorobenzene (µg/L) | 1600 | 1350 | 1320 | 1560 | 1380 | 1442 | 129 |

nm = no measurement

TABLE C.3 - SURVEY SAMPLING RESULTS, WELL 6

Well No. 6

Sampling Date: December 16, 1987

Sampling Device: Bladder Pump

| Replicate | 1 | 2 | 3 | 4 | 5 | \bar{x} | s |
|-------------------------|--------|--------|--------|--------|--------|-----------|------|
| Temp. (°C) | 22.0 | | | | | | |
| Field EC | 22000 | | | | | | |
| Field pH | 6.15 | | | | | | |
| Field HCO ₃ | nm | | | | | | |
| Field DO | 0.38 | | | | | | |
| Lab pH | 7.14 | 7.08 | 7.18 | 7.19 | 7.36 | 7.16 | 0.05 |
| Lab EC | 22400 | 22400 | 22400 | 22400 | 22500 | 22400 | - |
| TDS (mg/L) | 16700 | 16700 | 16700 | 16700 | 16900 | 16700 | - |
| SiO ₂ (mg/L) | 99 | 99 | 99 | 100 | 97 | 100 | 1 |
| HCO ₃ (mg/L) | 410 | 410 | 410 | 409 | 415 | 410 | 1 |
| Cl (mg/L) | 7500 | 7550 | 7520 | 7550 | 7470 | 7538 | 28 |
| SO ₄ (mg/L) | 2800 | 2800 | 2800 | 2800 | 2820 | 2800 | - |
| NO ₃ (mg/L) | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | < 0.04 | - |
| Na (mg/L) | 4770 | 4810 | 4930 | 4870 | 4800 | 4838 | 63 |
| K (mg/L) | 64.4 | 63.5 | 64.9 | 64.4 | 66.3 | 64.2 | 0.5 |
| Ca (mg/L) | 556 | 546 | 546 | 551 | 556 | 549 | 5 |
| Mg (mg/L) | 253 | 248 | 247 | 250 | 259 | 250 | 2 |
| Fe (mg/L) | < 0.01 | < 0.01 | < 0.01 | < 0.01 | 0.10 | < 0.01 | - |
| Mn (mg/L) | 1.56 | 1.54 | 1.58 | 1.57 | 1.32 | 1.56 | 0.02 |
| TOC (mg/L) | 10.0 | 9.9 | 10.1 | 10.1 | 10.5 | 10.0 | 0.2 |
| Benzene (µg/L) | 219 | 183 | 285 | 311 | 276 | 251 | 51 |
| Chlorobenzene (µg/L) | 1370 | 1100 | 1560 | 1670 | 1380 | 1428 | 216 |

nm = no measurement

TABLE C.4 - EXPERIMENT A - BLADDER PUMP SAMPLING RESULTS

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 13 | 19 |
|-------------------------------|---------|---------|---------|--------|---------|---------|--------|---------|
| Sampling Date | 11Feb88 | 17Feb88 | 24Feb88 | 2Mar88 | 16Mar88 | 29Mar88 | 4May88 | 14Jun88 |
| Temp. (°C) | 23.7 | 23.9 | 22.3 | 22.7 | 22.8 | 22.5 | 22.6 | 25.4 |
| Field EC (µmhos/cm) | 24681 | 28511 | 29787 | 29326 | 31158 | 29362 | 28731 | 25800 |
| Field pH | 6.94 | 6.87 | 6.91 | 6.90 | 6.87 | 6.85 | 6.88 | 6.87 |
| Field HCO ₃ (mg/l) | 415 | 415 | 416 | 410 | 420 | 422 | 409 | nm |
| Field DO (mg/l) | 1.05 | 0.60 | 0.90 | 0.70 | nm | 0.90 | 1.00 | 2.80 |
| Lab pH | 7.33 | 7.42 | 7.53 | 7.59 | 7.52 | 7.16 | 7.56 | 7.66 |
| Lab EC (µmhos/cm) | 22300 | 22200 | 22200 | 22200 | 22300 | 22100 | 23300 | 21700 |
| TDS (mg/l) | 16600 | 16600 | 16600 | 16600 | 16600 | 16600 | 16500 | 16400 |
| SiO ₂ (mg/l) | 98 | 98 | 98 | 97 | 97 | 97 | 95 | 95 |
| HCO ₃ (mg/l) | 416 | 419 | 421 | 423 | 426 | 426 | 422 | 414 |
| Cl (mg/l) | 7480 | 7350 | 7280 | 7330 | 7310 | 7250 | 7180 | 7160 |
| SO ₄ (mg/l) | 2790 | 2880 | 2880 | 2830 | 2830 | 2840 | 2830 | 2740 |
| NO ₃ (mg/l) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| NO ₃ (mg/l as N) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Na (mg/l) | 4680 | 4750 | 4800 | 4780 | 4860 | 4670 | 4910 | 4890 |
| K (mg/l) | 67.3 | 67.7 | 68.0 | 67.8 | 64.7 | 64.2 | 64.7 | 69.2 |
| Ca (mg/l) | 562 | 575 | 552 | 557 | 540 | 550 | 560 | 526 |
| Mg (mg/l) | 249 | 248 | 249 | 247 | 246 | 248 | 247 | 242 |
| EPM Bal. (AN/CAT) | 1.087 | 1.065 | 1.053 | 1.057 | 1.045 | 1.055 | 1.018 | 1.020 |
| Fe (mg/l) | 0.02 | 0.02 | <0.01 | 0.01 | 0.02 | <0.01 | 0.01 | 0.01 |
| Mn (mg/l) | 1.41 | 1.50 | 1.50 | 1.40 | 1.40 | 1.40 | 1.50 | 1.40 |
| TOC (mg/l) | 10.3 | 9.5 | 9.5 | 9.5 | 9.2 | 9.7 | 9.7 | 9.6 |
| Benzene (µg/l) | 304 | 310 | 259 | 266 | 287 | 245 | 236 | 34* |
| Chlorobenzene (µg/l) | 1480 | 1530 | 1360 | 1400 | 1700 | 1310 | 1590 | <2* |
| Chloroform (µg/l) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |

* = samples may have been compromised prior to analysis

nm = no measurement

TABLE C.5 - EXPERIMENT A - BAILER SAMPLING RESULTS

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 13 | 19 |
|-------------------------------|---------|---------|---------|--------|---------|---------|--------|---------|
| Sampling Date | 11Feb88 | 17Feb88 | 24Feb88 | 2Mar88 | 16Mar88 | 29Mar88 | 4May88 | 14Jun88 |
| Temp. (°C) | 24.2 | 23.2 | 22.3 | 22.6 | 22.4 | 22.3 | 23.8 | 24.9 |
| Field EC (µmhos/cm) | 25617 | 29128 | 29149 | 29579 | 26020 | 30298 | 27880 | 26702 |
| Field pH | 6.93 | 6.86 | 6.92 | 6.92 | 6.89 | 6.86 | 6.89 | 6.87 |
| Field HCO ₃ (mg/l) | 384 | 394 | 414 | 417 | 415 | 417 | 409 | nm |
| Field DO (mg/l) | 0.90 | 0.80 | 1.60 | 1.00 | 1.30 | 1.00 | 0.80 | nm |
| Lab pH | 7.44 | 7.46 | 7.47 | 7.47 | 7.49 | 7.38 | 7.63 | 7.66 |
| Lab EC (µmhos/cm) | 22200 | 22200 | 22200 | 22200 | 22300 | 22100 | 23300 | 21700 |
| TDS (mg/l) | 16500 | 16600 | 16600 | 16600 | 16600 | 16600 | 16500 | 16400 |
| SiO ₂ (mg/l) | 98 | 98 | 98 | 98 | 97 | 97 | 96 | 96 |
| HCO ₃ (mg/l) | 410 | 419 | 420 | 422 | 426 | 424 | 419 | 413 |
| Cl (mg/l) | 7370 | 7410 | 7310 | 7370 | 7310 | 7300 | 7210 | 7190 |
| SO ₄ (mg/l) | 2800 | 2860 | 2890 | 2810 | 2890 | 2860 | 2870 | 2670 |
| NO ₃ (mg/l) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | 0.04 | <0.04 | <0.04 |
| NO ₃ (mg/l as N) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 | <0.01 |
| Na (mg/l) | 4740 | 4680 | 4930 | 4760 | 4810 | 4739 | 4880 | 4810 |
| K (mg/l) | 67.7 | 67.7 | 68.3 | 67.5 | 64.7 | 64.2 | 63.6 | 69.2 |
| Ca (mg/l) | 566 | 566 | 547 | 552 | 555 | 541 | 560 | 522 |
| Mg (mg/l) | 247 | 251 | 251 | 248 | 247 | 246 | 245 | 243 |
| EPM Bal. (AN/CAT) | 1.064 | 1.083 | 1.034 | 1.064 | 1.056 | 1.068 | 1.030 | 1.031 |
| Fe (mg/l) | 0.01 | <0.01 | 0.01 | <0.01 | 0.01 | <0.01 | <0.01 | 0.01 |
| Mn (mg/l) | 0.95 | 1.50 | 1.50 | 1.40 | 1.40 | 1.40 | 1.50 | 1.30 |
| TOC (mg/l) | 10.3 | 9.5 | 9.4 | 9.3 | 9.0 | 9.7 | 10.0 | 10.5 |
| Benzene (µg/l) | 251 | 243 | <2* | 124 | 72 | 203 | 172 | 8† |
| Chlorobenzene (µg/l) | 1330 | 1220 | 3* | 822 | 639 | 1160 | 1290 | <2† |
| Chloroform (µg/l) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |

* = anomalous results apparently the result of mislabeled sample bottle

† = samples may have been compromised prior to analysis

nm = no measurement

TABLE C.6 - EXPERIMENT A - PTFE FILTER TIP SAMPLING RESULTS

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 8 | 13 | 19 |
|-------------------------------|---------|---------|---------|---------|---------|---------|-------|--------|---------|
| Sampling Date | 9Feb88 | 16Feb88 | 23Feb88 | 29Feb88 | 14Mar88 | 30Mar88 | Dups. | 3May88 | 13Jun88 |
| Temp. (°C) | nm | 21.9 | 23.6 | 24.3 | 23.8 | 23.9 | | 24.6 | 24.6 |
| Field EC (µmhos/cm) | nm | 30319 | 30298 | 29116 | 29104 | 28737 | | 27312 | 29674 |
| Field pH | nm | 6.84 | 6.97 | 6.89 | 6.89 | 6.91 | | 6.88 | 6.90 |
| Field HCO ₃ (mg/L) | nm | 408 | 399 | 405 | 412 | 405 | | 400 | 411 |
| Field DO (mg/L) | nm | 3.0 | 1.5 | 1.7 | 2.3 | 1.3 | | 1.9 | 2.6 |
| Lab pH | No Data | 7.32 | 7.52 | 7.40 | 7.64 | 7.51 | 7.46 | 7.77 | 7.72 |
| Lab EC (µmhos/cm) | | 22600 | 22500 | 22500 | 22600 | 22500 | 22400 | 24200 | 22000 |
| TDS (mg/L) | | 16800 | 16800 | 16800 | 16800 | 16800 | 16800 | 16600 | 16600 |
| SiO ₂ (mg/L) | | 98 | 98 | 98 | 99 | 98 | 98 | 96 | 95 |
| HCO ₃ (mg/L) | | 412 | 413 | 413 | 413 | 412 | 411 | 410 | 408 |
| Cl (mg/L) | | 7480 | 7460 | 7520 | 7480 | 7460 | 7470 | 7390 | 7330 |
| SO ₄ (mg/L) | | 2750 | 2870 | 2820 | 2880 | 2770 | 2810 | 2890 | 2690 |
| NO ₃ (mg/L) | | 0.09 | <0.04 | 0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| NO ₃ (mg/L as N) | | 0.02 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Na (mg/L) | | 4740 | 4830 | 4950 | 4910 | 4790 | 4990 | 4880 | 4770 |
| K (mg/L) | | 68.6 | 69.4 | 69.0 | 65.7 | 65.2 | 65.4 | 65.0 | 69.6 |
| Ca (mg/L) | | 571 | 547 | 547 | 555 | 541 | 550 | 551 | 554 |
| Mg (mg/L) | | 251 | 250 | 251 | 250 | 250 | 250 | 249 | 248 |
| EPM Bal. (AN/CAT) | | 1.069 | 1.066 | 1.047 | 1.054 | 1.067 | 1.034 | 1.051 | 1.047 |
| Fe (mg/L) | No Data | 0.02 | <0.01 | 0.02 | 0.01 | 0.02 | 0.02 | 0.02 | <0.01 |
| Mn (mg/L) | | 1.40 | 1.30 | 1.30 | 1.40 | 1.30 | 1.40 | 1.40 | 1.40 |
| TOC (mg/L) | No Data | 10.1 | 10.2 | 9.8 | 9.3 | 9.6 | 9.8 | 9.9 | 9.4 |
| Benzene (µg/L) | No Data | 234 | 226 | 172 | 180 | 185 | 190 | 151 | 136 |
| Chlorobenzene (µg/L) | | 1520 | 1550 | 1240 | 1440 | 1490 | 1490 | 1510 | 1420 |
| Chloroform (µg/L) | | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |

Dups = duplicate samples nm = no measurement

No Data = unable to collect sample, or sample lost

TABLE C.7 - EXPERIMENT A - MULTI-PORT SAMPLING RESULTS

| Week | 1 | 2 | 2 | 3 | 4 | 6 | 8 | 13 | 19 |
|-------------------------------|--------|---------|-------|---------|---------|---------|---------|--------|---------|
| Sampling Date | 9Feb88 | 16Feb88 | Dups. | 23Feb88 | 29Feb88 | 14Mar88 | 30Mar88 | 2May88 | 13Jun88 |
| Temp. (°C) | 25.5 | 23.5 | | 26.3 | 22.5 | 20.5 | 23.0 | 22.6 | 27.1 |
| Field EC (µmhos/cm) | 31438 | 29936 | | 27979 | 28989 | 30265 | 28702 | 28889 | 25440 |
| Field pH | 6.91 | 6.98 | | 6.90 | 6.92 | 6.88 | 6.94 | 6.92 | 6.92 |
| Field HCO ₃ (mg/L) | 405 | 409 | | 405 | 395 | 406 | 409 | 399 | nm |
| Field DO (mg/L) | 1.30 | 0.90 | | 0.90 | 0.70 | 1.40 | 1.10 | 0.90 | 2.50 |
| Lab pH | 7.55 | 7.48 | 7.48 | 7.58 | 7.72 | 7.62 | 7.35 | 7.68 | 7.78 |
| Lab EC (µmhos/cm) | 22200 | 22200 | 22200 | 22100 | 22100 | 22200 | 22100 | 23800 | 21800 |
| TDS (mg/L) | 16500 | 16500 | 16500 | 16500 | 16500 | 16500 | 16500 | 16400 | 16300 |
| SiO ₂ (mg/L) | 99 | 99 | 99 | 99 | 99 | 99 | 99 | 96 | 98 |
| HCO ₃ (mg/L) | 407 | 408 | 408 | 409 | 409 | 410 | 407 | 408 | 405 |
| Cl (mg/L) | 7320 | 7300 | 7310 | 7210 | 7260 | 7270 | 7260 | 7200 | 7160 |
| SO ₄ (mg/L) | 2800 | 2790 | 2790 | 2850 | 2810 | 2830 | 2810 | 2890 | 2680 |
| NO ₃ (mg/L) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| NO ₃ (mg/L as N) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Na (mg/L) | 4720 | 4660 | 4660 | 4720 | 4770 | 4800 | 4860 | 4850 | 4750 |
| K (mg/L) | 65.4 | 64.5 | 65.4 | 66.0 | 66.0 | 62.4 | 62.2 | 62.3 | 66.9 |
| Ca (mg/L) | 539 | 566 | 557 | 532 | 527 | 531 | 536 | 542 | 544 |
| Mg (mg/L) | 248 | 245 | 246 | 245 | 244 | 244 | 240 | 238 | 242 |
| EPM Bal. (AN/CAT) | 1.067 | 1.071 | 1.073 | 1.062 | 1.056 | 1.053 | 1.040 | 1.041 | 1.035 |
| Fe (mg/L) | 0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Mn (mg/L) | 1.38 | 1.40 | 1.40 | 1.40 | 1.40 | 1.40 | 1.40 | 1.40 | 1.30 |
| TOC (mg/L) | 9.7 | 9.2 | 9.6 | 9.1 | 9.8 | 9.2 | 9.8 | 9.0 | 9.7 |
| Benzene (µg/L) | 162 | 131 | 198 | 109 | 91 | 102 | 86 | 78 | 53 |
| Chlorobenzene (µg/L) | 858 | 790 | 1240 | 560 | 504 | 661 | 531 | 585 | 435 |
| Chloroform (µg/L) | <2 | <2 | <2 | <2 | 2 | <2 | <2 | <2 | <2 |

Dups = duplicate samples nm = no measurement

TABLE C.8 - EXPERIMENT A - WELL PROBE SAMPLING RESULTS

| Week | 1 | 2 | 3 | 3 | 4 | 6 | 8 | 13 | 19 |
|-------------------------------|--------|---------|---------|-------|--------|---------|---------|--------|---------|
| Sampling Date | 9Feb88 | 18Feb88 | 22Feb88 | Dups. | 1Mar88 | 17Mar88 | 28Mar88 | 3May88 | 13Jun88 |
| Temp. (°C) | 23.5 | 20.8 | 23.1 | | 24.3 | 23.0 | nm | 23.5 | 23.8 |
| Field EC (µmhos/cm) | 31257 | 29354 | 29271 | | 28884 | 30191 | nm | 27957 | 28630 |
| Field pH | 6.95 | 6.86 | 6.91 | | 7.08 | 6.88 | nm | 6.86 | 6.88 |
| Field HCO ₃ (mg/l) | 356 | 411 | 419 | | nm | 410 | nm | 397 | nm |
| Field DO (mg/l) | 0.5 | 3.2 | 2.0 | | 2.7 | 1.8 | nm | 2.4 | 0.92 |
| Lab pH | 7.22 | 7.18 | 7.48 | 7.67 | 7.62 | No Data | No Data | 7.72 | 7.78 |
| Lab EC (µmhos/cm) | 22600 | 22500 | 22500 | 22500 | 22500 | | | 24200 | 22100 |
| TDS (mg/l) | 16900 | 16900 | 16900 | 16900 | 16900 | | | 16700 | 16700 |
| SiO ₂ (mg/l) | 94 | 93 | 94 | 94 | 94 | | | 92 | 90 |
| HCO ₃ (mg/l) | 417 | 420 | 420 | 419 | 420 | | | 413 | 411 |
| Cl (mg/l) | 7470 | 7510 | 7530 | 7490 | 7490 | | | 7320 | 7310 |
| SO ₄ (mg/l) | 2880 | 2920 | 2910 | 2850 | 2860 | | | 2970 | 2780 |
| NO ₃ (mg/l) | 0.04 | <0.04 | <0.04 | <0.04 | 0.09 | | | <0.04 | 0.09 |
| NO ₃ (mg/l as N) | 0.01 | <0.01 | <0.01 | <0.01 | 0.02 | | | <0.01 | 0.02 |
| Na (mg/l) | 4660 | 4720 | 4850 | 4800 | 4850 | | | 4910 | 4770 |
| K (mg/l) | 71.0 | 71.4 | 72.0 | 71.5 | 70.9 | | | 66.7 | 71.3 |
| Ca (mg/l) | 593 | 606 | 627 | 582 | 582 | | | 591 | 589 |
| Mg (mg/l) | 273 | 274 | 274 | 274 | 274 | | | 268 | 271 |
| EPM Bal. (AN/CAT) | 1.081 | 1.075 | 1.049 | 1.058 | 1.050 | | | 1.031 | 1.037 |
| Fe (mg/l) | 0.16 | 0.14 | 0.13 | 0.13 | 0.12 | No Data | No Data | 0.11 | 0.25 |
| Mn (mg/l) | 1.38 | 1.50 | 1.30 | 1.40 | 1.30 | | | 1.40 | 1.40 |
| TOC (mg/l) | 10.5 | 9.8 | 9.2 | 10.8 | 9.4 | 9.3 | No Data | 9.7 | 9.6 |
| Benzene (µg/l) | 342 | 349 | 386 | 280 | 286 | 280 | No Data | 192 | 152 |
| Chlorobenzene (µg/l) | 1400 | 1770 | 2060 | 1610 | 1560 | 1730 | | 1620 | 1010 |
| Chloroform (µg/l) | <2 | <2 | <2 | <2 | <2 | <2 | | <2 | <2 |

Dups = duplicate samples nm = no measurement

No Data = unable to collect sample, or sample lost

TABLE C.9 - EXPERIMENT A - HDPE FILTER TIP SAMPLING RESULTS

| Week | 1 | 2 | 3 | 4 | 4 | 6 | 8 | 13 | 13 | 19 |
|-------------------------------|---------|---------|---------|--------|-------|---------|---------|--------|-------|---------|
| Sampling Date | 10Feb88 | 18Feb88 | 22Feb88 | 1Mar88 | Dups. | 14Mar88 | 29Mar88 | 3May88 | Dups. | 13Jun88 |
| Temp. (°C) | 25.4 | 22.6 | 24.7 | 23.9 | | 24.1 | 24.3 | 22.9 | | 24.0 |
| Field EC (µmhos/cm) | 29230 | 28375 | 28625 | 29053 | | 29833 | 28681 | 28258 | | 28043 |
| Field pH | 6.90 | 6.95 | 6.89 | 6.95 | | 6.91 | 6.91 | 6.88 | | 6.90 |
| Field HCO ₃ (mg/l) | 398 | 400 | 400 | 406 | | 420 | 409 | 403 | | 412 |
| Field DO (mg/l) | 2.20 | 2.70 | 2.30 | 1.30 | | 2.10 | 1.70 | 1.30 | | 3.00 |
| Lab pH | 7.28 | 7.23 | 7.64 | 7.66 | 7.61 | 7.54 | 7.53 | 7.39 | 7.67 | 7.66 |
| Lab EC (µmhos/cm) | 22000 | 21900 | 21800 | 21900 | 21900 | 22000 | 21900 | 23500 | 23500 | 21500 |
| TDS (mg/l) | 16300 | 16500 | 16500 | 16500 | 16500 | 16300 | 16400 | 16300 | 16300 | 16300 |
| SiO ₂ (mg/l) | 98 | 98 | 98 | 98 | 98 | 97 | 97 | 95 | 96 | 94 |
| HCO ₃ (mg/l) | 404 | 408 | 410 | 409 | 409 | 409 | 407 | 407 | 406 | 402 |
| Cl (mg/l) | 7200 | 7200 | 7190 | 7190 | 7190 | 7230 | 7150 | 7050 | 7100 | 7030 |
| SO ₄ (mg/l) | 2900 | 2890 | 2930 | 2860 | 2870 | 2880 | 2900 | 2890 | 2950 | 2730 |
| NO ₃ (mg/l) | 2.92 | 0.04 | <0.04 | <0.04 | <0.04 | <0.04 | 0.04 | <0.04 | <0.04 | <0.04 |
| NO ₃ (mg/l as N) | 0.66 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 | <0.01 | <0.01 |
| Na (mg/l) | 4640 | 4700 | 4610 | 4690 | 4720 | 4590 | 4690 | 4740 | 4770 | 4600 |
| K (mg/l) | 66.8 | 66.3 | 66.5 | 66.5 | 66.5 | 63.4 | 62.9 | 63.1 | 62.3 | 67.6 |
| Ca (mg/l) | 566 | 584 | 562 | 562 | 552 | 564 | 564 | 578 | 582 | 574 |
| Mg (mg/l) | 267 | 264 | 262 | 259 | 259 | 262 | 262 | 261 | 260 | 267 |
| EPM Bal. (AN/CAT) | 1.064 | 1.050 | 1.074 | 1.055 | 1.052 | 1.078 | 1.052 | 1.029 | 1.034 | 1.037 |
| Fe (mg/l) | 0.02 | <0.01 | <0.01 | 0.01 | 0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 |
| Mn (mg/l) | 1.38 | 1.50 | 1.40 | 1.50 | 1.40 | 1.50 | 1.40 | 1.50 | 1.50 | 1.50 |
| TOC (mg/l) | 9.8 | 9.1 | 9.3 | 8.8 | 9.3 | 9.0 | 9.3 | 9.1 | 8.9 | 8.8 |
| Benzene (µg/l) | 427 | 458 | 386 | 293 | 417 | 322 | 324 | 263 | 298 | 276 |
| Chlorobenzene (µg/l) | 1390 | 1550 | 1500 | 1150 | 1770 | 1350 | 1360 | 1330 | 1550 | 1420 |
| Chloroform (µg/l) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |

Dups = duplicate samples

TABLE C.10 - EXPERIMENT A - BLADDER PUMP/PACKER SAMPLING RESULTS

| Week | 1 | 1 | 2 | 3 | 4 | 6 | 6 | 8 | 13 | 19 | 19 |
|-------------------------------|---------|-------|---------|---------|---------|---------|-------|---------|--------|---------|-------|
| Sampling Date | 11Feb88 | Dups. | 17Feb88 | 22Feb88 | 1Mar88 | 17Mar88 | Dups. | 28Mar88 | 2May88 | 16Jun88 | Dups. |
| Temp. (°C) | 22.5 | | 22.2 | 23.2 | 22.2 | 23.0 | | 21.9 | 22.3 | 23.7 | |
| Field EC (µmhos/cm) | 26511 | | 29681 | 27708 | 30000 | 29840 | | 28632 | 29333 | 28280 | |
| Field pH | 7.00 | | 6.95 | 6.89 | 6.87 | 6.87 | | 6.83 | 6.90 | 6.89 | |
| Field HCO ₃ (mg/l) | 415 | | 394 | 392 | 397 | 409 | | 407 | 394 | nm | |
| Field DO (mg/l) | 0.60 | | 0.70 | 0.75 | 0.80 | 1.00 | | 0.80 | 1.10 | nm | |
| Lab pH | 7.58 | 7.33 | 7.41 | 7.70 | 7.56 | 7.42 | 7.44 | 7.38 | 7.66 | 7.70 | 7.71 |
| Lab EC (µmhos/cm) | 22300 | 22300 | 22200 | 22200 | 22200 | 22300 | 22300 | 22200 | 23900 | 21700 | 21700 |
| TDS (mg/l) | 16600 | 16600 | 16600 | 16600 | 16600 | 16600 | 16600 | 16600 | 16400 | 16400 | 16400 |
| SiO ₂ (mg/l) | 99 | 99 | 99 | 99 | 99 | 98 | 99 | 98 | 96 | 98 | 98 |
| HCO ₃ (mg/l) | 408 | 408 | 409 | 409 | 410 | 409 | 409 | 408 | 408 | 405 | 405 |
| Cl (mg/l) | 7490 | 7480 | 7370 | 7370 | 7370 | 7340 | 7340 | 7290 | 7220 | 7140 | 7160 |
| SO ₄ (mg/l) | 2820 | 2810 | 2810 | 2790 | 2820 | 2820 | 2790 | 2780 | 2850 | 2750 | 2790 |
| NO ₃ (mg/l) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 |
| NO ₃ (mg/l as N) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Na (mg/l) | 4700 | 4700 | 4700 | 4770 | 4880 | 4860 | 4840 | 4890 | 4880 | 4750 | 4770 |
| K (mg/l) | 67.4 | 67.3 | 67.3 | 67.5 | 67.5 | 63.9 | 63.9 | 63.9 | 64.5 | 68.2 | 67.6 |
| Ca (mg/l) | 557 | 566 | 566 | 532 | 547 | 545 | 531 | 545 | 564 | 544 | 549 |
| Mg (mg/l) | 250 | 250 | 246 | 247 | 247 | 248 | 244 | 245 | 247 | 242 | 241 |
| EPM Bal. (AN/CAT) | 1.087 | 1.083 | 1.072 | 1.065 | 1.045 | 1.045 | 1.050 | 1.032 | 1.028 | 1.038 | 1.040 |
| Fe (mg/l) | <0.01 | <0.01 | <0.01 | <0.01 | No Data | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Mn (mg/l) | 1.45 | 1.46 | 1.50 | 1.50 | No Data | 1.40 | 1.40 | 1.40 | 1.40 | 1.30 | 1.40 |
| TOC (mg/l) | 10.5 | 10.0 | 9.5 | 9.8 | No Data | 9.1 | 9.0 | 9.6 | 10.0 | 9.5 | 9.7 |
| Benzene (µg/l) | 221 | 223 | 218 | 290 | 163 | 170 | 177 | 166 | 191 | 148 | 159 |
| Chlorobenzene (µg/l) | 1360 | 1420 | 1490 | 2020 | 1160 | 1360 | 1390 | 1290 | 1800 | 1600 | 1710 |
| Chloroform (µg/l) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |

Dups = duplicate samples nm = no measurement

No Data = unable to collect sample, or sample lost

TABLE C.11 - EXPERIMENT A - LVVWD STANDARD SOLUTIONS

| Week | 1 | 2 | 3 | 4 | 13 |
|-----------------------------|---------|---------|---------|---------|--------|
| Sampling Date | 11Feb88 | 17Feb88 | 23Feb88 | 29Feb88 | 2May88 |
| Lab pH | | 8.03 | 8.10 | 8.10 | 8.16 |
| Lab EC (μ mhos/cm) | | 823 | 825 | 828 | 859 |
| TDS (mg/l) | | 532 | 533 | 534 | 545 |
| SiO ₂ (mg/l) | | 9 | 9 | 10 | 9 |
| HCO ₃ (mg/l) | | 155 | 153 | 154 | 159 |
| Cl (mg/l) | | 60.4 | 60.0 | 59.5 | 60.1 |
| SO ₄ (mg/l) | | 218 | 215 | 219 | 212 |
| NO ₃ (mg/l) | | 1.42 | 1.37 | 1.46 | 1.68 |
| NO ₃ (mg/l as N) | | 0.32 | 0.31 | 0.33 | 0.38 |
| Na (mg/l) | | 71.9 | 75.5 | 73.1 | 77.0 |
| K (mg/l) | | 4.20 | 3.97 | 4.27 | 4.16 |
| Ca (mg/l) | | 68.8 | 63.7 | 66.2 | 69.5 |
| Mg (mg/l) | | 25.6 | 25.7 | 25.6 | 26.2 |
| Fe (mg/l) | <0.01 | 0.01 | 0.02 | <0.01 | |
| Mn (mg/l) | <0.01 | 1.50 | <0.01 | <0.01 | |
| TOC (mg/l) | 3.2 | 3.2 | 3.8 | 3.3 | |
| Benzene (μ g/l) | <2 | <2 | <2 | <2 | |
| Chlorobenzene (μ g/l) | <2 | <2 | <2 | <2 | |
| Chloroform (μ g/l) | 48 | 39 | 43 | 35 | |

TABLE C.12 - EXPERIMENT A - EPA STANDARD SOLUTIONS

| Week | True Value | 95% C.I. | 6 | 8 | 13 | 19 |
|-----------------------------|------------|-----------------|---------|---------|--------|---------|
| Sampling Date | | | 14Mar88 | 28Mar88 | 2May88 | 13Jun88 |
| Lab pH | 6.0 | 5.91 - 6.11 | 7.58 | | | |
| Lab EC (µmhos/cm) | 267 | 247 - 288 | 272 | | | |
| TDS (mg/l) | 145 | 114 - 177 | 130 | | | |
| SiO ₂ (mg/l) | | | <1 | | | |
| HCO ₃ (mg/l) | | | 33 | | | |
| Cl (mg/l) | 52.1 | 48.2 - 55.4 | 50.3 | | | |
| SO ₄ (mg/l) | 20.0 | 16.3 - 23.1 | 19.6 | | | |
| NO ₃ (mg/l) | | | <0.04 | | | |
| NO ₃ (mg/l as N) | | | <0.01 | | | |
| Na (mg/l) | 20.0 | 17.8 - 22.3 | 19.9 | | | |
| K (mg/l) | 5.0 | 4.17 - 5.71 | 5.22 | | | |
| Ca (mg/l) | 20.0 | 17.5 - 22.2 | 20.1 | | | |
| Mg (mg/l) | 5.0 | 4.18 - 5.62 | 5.1 | | | |
| Fe (mg/l) | 0.050 | 0.0475 - 0.0545 | 0.04 | 0.10 | 0.04 | |
| Mn (mg/l) | 0.050 | 0.0423 - 0.0560 | 0.05 | 0.11 | 0.05 | |
| TOC (mg/l) | 61.4 | 51.7 - 69.3 | 68.7 | 66.9 | 69.5 | |
| Benzene (µg/l) | 19.6 | na | 15 | 15 | 14 | |
| Chlorobenzene (µg/l) | 19.8 | na | | | | 16 |

Standards are subject to error during preparation (inaccurate dilution)

na = not available

TABLE C.13 - EXPERIMENT A - EQUIPMENT BLANKS - BLADDER PUMP

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 13 | 19 |
|-----------------------------|---------|---------|---------|--------|---------|---------|---------|---------|
| Sampling Date | 11Feb88 | 17Feb88 | 24Feb88 | 2Mar88 | 16Mar88 | 29Mar88 | 4May88 | 14Jun88 |
| Lab pH | 4.68 | 5.95 | 5.42 | 5.16 | 5.47 | 5.32 | No Data | 5.51 |
| Lab EC (μ mhos/cm) | 1.76 | 2.75 | 1.34 | 1.44 | 1.62 | 1.49 | | 2.37 |
| TDS (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | | <5 |
| SiO ₂ (mg/L) | 2 | 2 | <1 | <1 | <1 | <1 | | <1 |
| HCO ₃ (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | | <5 |
| Cl (mg/L) | <0.2 | <0.2 | 0.2 | <0.2 | <0.2 | <0.2 | | <0.2 |
| SO ₄ (mg/L) | 1.0 | <1 | 1.4 | 1.4 | <1 | <1 | | <1 |
| NO ₃ (mg/L) | <0.04 | <0.04 | 0.04 | <0.04 | <0.04 | 0.04 | | <0.04 |
| NO ₃ (mg/L as N) | <0.01 | <0.01 | 0.01 | <0.01 | <0.01 | 0.01 | | <0.01 |
| Na (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | | 0.1 |
| K (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | | <0.1 |
| Ca (mg/L) | <0.1 | 0.25 | <0.1 | <0.1 | <0.1 | <0.1 | | <0.1 |
| Mg (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | | <0.1 |
| Fe (mg/L) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | | <0.01 |
| Mn (mg/L) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | | <0.01 |
| TOC (mg/L) | 0.74 | 1.62 | 5.8 | <0.1 | 0.2 | <0.1 | | Lost |
| Benzene (μ g/L) | <2 | <2 | <2 | <2 | <2 | <2 | | <2 |
| Chlorobenzene (μ g/L) | <2 | 2 | <2 | <2 | <2 | 3 | | <2 |
| Chloroform (μ g/L) | <2 | <2 | <2 | <2 | <2 | <2 | | <2 |

No Data = no blanks collected

Lost = blank sample lost

TABLE C.14 - EXPERIMENT A - EQUIPMENT BLANKS - BAILER

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 13 | 19 |
|-----------------------------|---------|---------|---------|--------|---------|---------|--------|---------|
| Sampling Date | 11Feb88 | 17Feb88 | 24Feb88 | 2Mar88 | 16Mar88 | 29Mar88 | 4May88 | 13Jun88 |
| Lab pH | 4.90 | 5.26 | 5.36 | 5.01 | 5.28 | 5.47 | 4.84 | 5.37 |
| Lab EC (μ mhos/cm) | 2.83 | 1.42 | 2.39 | 1.83 | 1.72 | 1.93 | 3.00 | 2.17 |
| TDS (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| SiO ₂ (mg/L) | 2 | <1 | <1 | <1 | <1 | <1 | <1 | <1 |
| HCO ₃ (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 |
| Cl (mg/L) | 0.2 | <0.2 | 0.4 | <0.2 | <0.02 | <0.2 | <0.2 | <0.2 |
| SO ₄ (mg/L) | <1 | <1 | 1.8 | 1.3 | <1 | <1 | 1.0 | <1 |
| NO ₃ (mg/L) | <0.04 | 0.04 | 0.09 | <0.04 | <0.04 | 0.13 | <0.04 | <0.04 |
| NO ₃ (mg/L as N) | <0.01 | 0.01 | 0.02 | <0.01 | <0.01 | 0.03 | <0.01 | <0.01 |
| Na (mg/L) | <0.1 | <0.1 | <0.1 | 0.1 | <0.1 | <0.1 | 0.1 | <0.1 |
| K (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Ca (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Mg (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Fe (mg/L) | No Data | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| Mn (mg/L) | No Data | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 |
| TOC (mg/L) | 2.5 | 2.1 | 2.4 | 1.3 | 0.5 | 0.3 | 1.0 | 1.4 |
| Benzene (μ g/L) | <2 | <2 | <2 | <2 | <2 | Lost | <2 | <2 |
| Chlorobenzene (μ g/L) | <2 | <2 | <2 | <2 | <2 | Lost | <2 | <2 |
| Chloroform (μ g/L) | <2 | <2 | <2 | <2 | <2 | Lost | <2 | <2 |

No Data = no blanks collected

Lost = blank sample lost

TABLE C.15 - EXPERIMENT A - TRIP BLANKS

| Week | 1 | 2 | 3 | 4 | 6 | 8 | 13 | 19 | 19* |
|-----------------------------|---------|---------|---------|--------|---------|---------|--------|---------|---------|
| Sampling Date | 11Feb88 | 16Feb88 | 22Feb88 | 1Mar88 | 14Mar88 | 28Mar88 | 2May88 | 13Jun88 | 13Jun88 |
| Lab pH | 5.33 | 5.29 | 5.21 | 5.10 | 5.35 | 5.43 | 5.52 | 5.28 | 8.74 |
| Lab EC (μ mhos/cm) | 1.63 | 1.18 | 1.83 | 1.59 | 1.44 | 1.50 | 2.00 | 1.35 | 10.20 |
| TDS (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 | 10 |
| SiO ₂ (mg/L) | 2 | <1 | <1 | <1 | <1 | <1 | <1 | <1 | 7 |
| HCO ₃ (mg/L) | <5 | <5 | <5 | <5 | <5 | <5 | <5 | <5 | 4.7 |
| Cl (mg/L) | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 | <0.2 |
| SO ₄ (mg/L) | 1.4 | <1 | 1.0 | 1.1 | <1 | <1 | <1 | <1 | <1 |
| NO ₃ (mg/L) | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | <0.04 | 0.04 | <0.04 |
| NO ₃ (mg/L as N) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | 0.01 | <0.01 |
| Na (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.2 | <0.1 | 1.31 |
| K (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Ca (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | 0.86 |
| Mg (mg/L) | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 | <0.1 |
| Fe (mg/L) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | No Data |
| Mn (mg/L) | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | <0.01 | No Data |
| TOC (mg/L) | 1.2 | 1.6 | 1.4 | 1.1 | 0.8 | 1.2 | 0.7 | 0.6 | 0.7 |
| Benzene (μ g/L) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |
| Chlorobenzene (μ g/L) | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 | <2 |
| Chloroform (μ g/L) | <2 | <2 | <2 | <2 | <2 | <2 | 2 | <2 | <2 |

* - "Organic-free" distilled water used for blanks

No Data = no samples collected

ADDITIONAL PART I EXPERIMENTAL WORK

WEEK 19

The relatively low VOC concentrations recovered by the multi-port prompted the development of an additional set of field experiments designed to isolate the source of this apparent anomaly. The basic experimental design consisted of collecting multiple samples from the multi-port, utilizing a variety of sampling methods and sample handling procedures. Most of the samples were collected to investigate the effect of a perforated septum in a standard VOA bottle on sample integrity and the claim that inverting the VOA bottles during storage would have eliminated the loss of volatiles from the sample bottles.

EXPERIMENTAL DESIGN

During the week of June 13, 1988, full sets of samples from each well were collected to duplicate previous sampling conditions. In addition to sampling with the bladder pump and the bailer, well 1 was also sampled with the multi-port sampling probe and a small-diameter (1.91 cm) bailer. These samples were to be used to compare conditions between well 1 and well 3 (the multi-port) to determine if the low benzene and chlorobenzene concentrations were the result of different chemical conditions surrounding well 3.

A total of 14 VOA samples were collected from the multi-port. Of these, two samples (PL-531 and 536) were stored in an upright position, while the remaining samples were stored in an inverted position. Three bottles (PL-538, 540 and 562) were sealed with Parafilm® over the cap in an attempt to "seal" the needle punctures in the septum. Sample PL-539 was sealed with aluminum foil for the same reason. The septum on sample bottle PL-542 was replaced with a new, unperforated septum. Sample PL-543 was collected using a newer model of the MP VOA sample bottle holder which is designed to give the operator better needle control and allows a greater volume of water to pass through the VOA bottle before sample collection. Samples PL-544 and 545 were collected in a vented stainless steel container, carefully poured into a VOA bottle, and capped (no septum perforations). Sample PL-547 was collected in a stainless steel "high pressure vial." This vial is sealed by closing a valve and, therefore, does not rely upon a flexible, perforated septum.

When all of the standard sampling procedures had been completed, the pumping port on the multi-port was opened. After purging the well with a peristaltic pump, a sample (PL-561) was collected from inside the well casing with the small-diameter bailer. As noted earlier, this sample was to be compared to a sample collected from well 1 with the same bailer. Sample PL-562 was collected from the lowermost measurement port to check for variations in VOC concentration after the installation had been purged.

RESULTS

A summary of the sampling results is presented in Table C.16. Based on the results of the experiment, it appears that all of the multi-port samples which were collected and stored with a perforated septum experienced high losses of both benzene and chlorobenzene relative to those samples stored in bottles with an unperforated septum. Inverting the bottles apparently had little or no effect on VOC losses. Sealing the bottle with Parafilm or foil apparently diminished the losses somewhat, but did not eliminate them.

Unfortunately, samples PL-514, 519, 520, and 521 were all apparently compromised in some unknown fashion. Benzene and chlorobenzene concentrations in all of these samples were anomalously low or below detection limits despite normal results from the analyses of the internal and surrogate standards. Therefore, these data are not shown in Figures 18 through 20. Samples collected from well 1 during later experiments contained VOC concentrations which were comparable to those from other wells. As a result, comparison between wells 1 and 3 based on the small-diameter bailer samples was not possible. However, the benzene and chlorobenzene concentrations found in sample PL-561 suggest that the conditions near well 3 are, at the very least, similar to conditions surrounding the other wells. Therefore, it is unlikely that the low VOC concentrations

associated with the multi-port throughout the seven previous sampling weeks could be attributed to anomalously low concentrations of benzene and chlorobenzene surrounding well 3.

The effect of a perforated septum on sample integrity can also be seen in the standard samples submitted to the laboratory (PL-548, 549, and 550). The septa in two of the bottles were punctured with the same type of needles used for multi-port sampling, while a third bottle was simply inverted. The chlorobenzene concentrations in these standards should have been 19.8 ppb. The low concentrations found in samples PL-549 and 550 suggest a greater than 50 percent loss of chlorobenzene due to the perforations in the sample bottle septum. The 16 ppb chlorobenzene concentration found in sample PL-548 may indicate possible losses through even an unperforated septum. However, these losses are probably due to volatilization during sample preparation.

The mechanism for the loss of VOCs from the sample is not clear, but two possibilities appear likely:

- Passage of air through the septum and into the sample bottle, forming bubbles into which the VOCs may volatilize; and
- Direct volatilization to the atmosphere through the perforated septum.

Air bubbles have been known to form in the samples during storage. However, the losses may be due to a combination of the possibilities noted above.

Based on the results of the additional field experiments, it is apparent that a perforated septum in a standard VOA bottle can have a considerable effect on sample integrity and should be replaced. The questions raised concerning perforated septa should also be applied to the filter tip system in light of the fact that this sampling device also utilizes flexible septum in sample vials. While it appears that the filter tip sample vials have not experienced the high VOC losses characteristic of the multi-port, the potential for such losses, particularly after the septum has been perforated several times, should be investigated.

TABLE C.16 - EXPERIMENT A - WEEK 19 SAMPLING RESULTS

| Sample Number | Benzene (µg/L) | Chlorobenzene (µg/L) | Well | Device | Treatment |
|---------------|----------------|----------------------|------|-----------------------|--|
| PL-486 | 276 | 1420 | 5 | HDPE Filter Tip | |
| PL-491 | 136 | 1510 | 2 | PTFE Filter Tip | |
| PL-496 | < 2 | < 2 | | | Equip. Blank - Bailer |
| PL-501 | 152 | 1010 | 4 | Well Probe | |
| PL-506 | < 2 | < 2 | | | Trip Blank |
| PL-507 | < 2 | < 2 | | | Trip Blank - Organic-free H ₂ O |
| PL-514 | 34 | < 2 | 1 | Bladder Pump | |
| PL-519 | < 2 | < 2 | 1 | multi-port | Invert |
| PL-520 | < 2 | < 2 | 1 | Small-Diameter Bailer | Invert |
| PL-521 | 8 | < 2 | 1 | Bailer | |
| PL-526 | < 2 | < 2 | | | Equip. Blank - Bladder Pump |
| PL-531 | 53 | 435 | 3 | multi-port | Upright |
| PL-536 | 44 | 312 | 3 | multi-port | Duplicate PL-531 |
| PL-537 | 48 | 399 | 3 | multi-port | Invert |
| PL-538 | 81 | 609 | 3 | multi-port | Invert, paraseal |
| PL-539 | 67 | 542 | 3 | multi-port | Invert, foil seal |
| PL-540 | 80 | 741 | 3 | multi-port | Duplicate PL-538 |
| PL-541 | 63 | 616 | 3 | multi-port | Duplicate PL-537 |
| PL-542 | 144 | 1500 | 3 | multi-port | Invert, new septum |
| PL-543 | 70 | 650 | 3 | multi-port | New holder, invert |
| PL-544 | 129 | 1380 | 3 | multi-port | Vented bottle ^a , invert |
| PL-545 | 130 | 1370 | 3 | multi-port | Vented bottle ^b , invert |
| PL-546 | < 2 | < 2 | | | Trip Blank - Organic-Free H ₂ O |
| PL-547 | 134 | 1310 | 3 | multi-port | High pressure vial |
| PL-548 | < 2 | 16 | | Standard ^c | No puncture, invert |
| PL-549 | < 2 | 6 | | Standard ^c | 2 punctures, invert |
| PL-550 | < 2 | 8 | | Standard ^c | 2 punctures, upright |
| PL-551 | 148 | 1600 | 6 | Pump/packer | |
| PL-556 | 159 | 1710 | 6 | Pump/packer | Duplicate PL-551 |
| PL-561 | 160 | 1450 | 3 | Small-Diameter Bailer | (Open Pumping Port) Invert |
| PL-562 | 99 | 954 | 3 | multi-port | Invert, paraseal |

Upright = VOA bottle stored in upright position

Invert = VOA bottle stored in inverted position

^a = Vented bottle, short delivery tube

^b = Vented bottle, long delivery tube

^c = Chlorobenzene standard; Concentration should be 19.8 µg/L

**TABLE C.17 - EXPERIMENT B - VOC ANALYTICAL RESULTS FOR SIX
REPLICATE SAMPLES COLLECTED WITH EACH SAMPLING DEVICE -
NOVEMBER 8, 1988**

| VOC (µg/L) | PTFE Filter Tip | Bailer | Bladder Pump | Multi-Port |
|---------------------|-----------------|--------|--------------|------------|
| Benzene | 44 | 54 | 65 | 49 |
| | 42 | 52 | 66 | 51 |
| | 40 | 53 | 63 | 51 |
| | 42 | 52 | 65 | 49 |
| | 41 | 55 | 66 | 49 |
| | 41 | 54 | 65 | 50 |
| Chlorobenzene | 1290 | 1070 | 1280 | 1230 |
| | 1270 | 1050 | 1220 | 1230 |
| | 1310 | 1070 | 1250 | 1250 |
| | 1310 | 1010 | 1220 | 1210 |
| | 1310 | 1050 | 1260 | 1270 |
| | 1250 | 1080 | 1240 | 1240 |
| 1,2-Dichlorobenzene | 217 | 197 | 214 | 196 |
| | 213 | 196 | 214 | 196 |
| | 225 | 189 | 216 | 207 |
| | 222 | 185 | 202 | 202 |
| | 223 | 202 | 210 | 200 |
| | 211 | 203 | 202 | 215 |
| 1,3-Dichlorobenzene | 21 | 17 | 18 | 18 |
| | 19 | 16 | 20 | 18 |
| | 21 | 16 | 19 | 19 |
| | 20 | 19 | 18 | 18 |
| | 21 | 20 | 18 | 19 |
| | 19 | 19 | 19 | 18 |
| 1,4-Dichlorobenzene | 369 | 314 | 345 | 324 |
| | 355 | 300 | 332 | 315 |
| | 381 | 315 | 337 | 340 |
| | 352 | 285 | 330 | 345 |
| | 360 | 308 | 337 | 348 |
| | 336 | 314 | 347 | 336 |
| 1,1-Dichloroethane | 33 | 32 | 36 | 34 |
| | 32 | 31 | 31 | 34 |
| | 34 | 32 | 32 | 34 |
| | 33 | 30 | 33 | 33 |
| | 34 | 31 | 32 | 35 |
| | 33 | 32 | 33 | 32 |
| 1,2-Dichloroethane | 11 | 9 | 11 | 10 |
| | 10 | 9 | 9 | 8 |
| | 10 | 9 | 10 | 10 |
| | 10 | 9 | 9 | 9 |
| | 10 | 9 | 10 | 9 |
| | 10 | 8 | 10 | 9 |
| Ethylbenzene | 28 | 22 | 25 | 27 |
| | 28 | 22 | 25 | 29 |
| | 30 | 22 | 26 | 29 |
| | 29 | 22 | 25 | 27 |
| | 29 | 23 | 25 | 30 |
| | 27 | 23 | 26 | 28 |
| Trichloroethene | 11 | 11 | 11 | 11 |
| | 10 | 10 | 11 | 11 |
| | 10 | 10 | 11 | 11 |
| | 10 | 10 | 11 | 11 |
| | 10 | 12 | 10 | 11 |
| | 10 | 10 | 9 | 11 |
| Acetone | ND | ND | ND | ND |
| | ND | ND | 44 | ND |
| | ND | ND | ND | ND |
| | ND | ND | 58 | ND |
| | ND | ND | ND | ND |
| | ND | ND | ND | ND |

ND = Not Detected

TABLE C.18 – EXPERIMENT B – QUALITY ASSURANCE SAMPLES

| VOC (µg/L) | Standard 1* | Standard 2* | Trip Blank | Equipment Blank Bailer | Equipment Blank Bladder Pump |
|---------------------|-------------|-------------|------------|---------------------------|---------------------------------|
| Benzene | ND | ND | ND | ND | ND |
| Chlorobenzene | ND | ND | ND | ND | ND |
| 1,2-Dichlorobenzene | ND | ND | ND | ND | ND |
| 1,3-Dichlorobenzene | 15 | 14 | ND | ND | ND |
| 1,4-Dichlorobenzene | ND | ND | ND | ND | ND |
| 1,1-Dichloroethane | ND | ND | ND | ND | ND |
| 1,2-Dichloroethane | ND | ND | ND | ND | ND |
| Ethylbenzene | ND | ND | ND | ND | ND |
| Trichloroethene | 13 | 14 | ND | ND | ND |
| Acetone | 92 | 104 | 97 | 79 | ND |
| Chloroform | 12 | 14 | ND | ND | ND |

ND = Not detected

* = Standard True Values: Chloroform 20.2 µg/L
m-Dichlorobenzene 20.0 µg/L

TABLE C.19 - EXPERIMENT C - VOC ANALYTICAL RESULTS FOR SAMPLE ROUND 1

| VOC (µg/L) | HDPE Filter Tip | PTFE Filter Tip | Standard Bailer | BED Bailer | Bladder Pump | Multi- Port |
|---------------------|--------------------|--------------------|--------------------|---------------|-----------------|----------------|
| Benzene | 44 | 15 | 28 | 31 | 34 | 20 |
| | 40 | 14 | 30 | 30 | 35 | 20 |
| | 39 | 16 | 30 | 30 | 33 | 20 |
| Chlorobenzene | 1120 | 1260 | 1030 | 1100 | 1250 | 1210 |
| | 1130 | 1190 | 1060 | 1050 | 1260 | 1250 |
| | 1130 | 1240 | 1060 | 1070 | 1230 | 1260 |
| 1,2-Dichlorobenzene | 213 | 166 | 234 | 280 | 218 | 206 |
| | 222 | 189 | 237 | 266 | 211 | 214 |
| | 227 | 204 | 246 | 250 | 203 | 210 |
| 1,3-Dichlorobenzene | 18 | 13 | 22 | 25 | 18 | 17 |
| | 18 | 17 | 23 | 25 | 19 | 18 |
| | 19 | 18 | 23 | 23 | 18 | 18 |
| 1,4-Dichlorobenzene | 354 | 386 | 329 | 369 | 365 | 339 |
| | 374 | 348 | 338 | 366 | 361 | 348 |
| | 379 | 377 | 350 | 340 | 355 | 354 |
| 1,1-Dichloroethane | 30 | 27 | 32 | 27 | 26 | 25 |
| | 30 | 26 | 30 | 27 | 27 | 26 |
| | 28 | 25 | 30 | 26 | 26 | 25 |
| 1,2-Dichloroethane | 8 | 7 | 8 | 7 | 7 | 7 |
| | 8 | 7 | 7 | 7 | 7 | 7 |
| | 7 | 7 | 8 | 7 | 7 | 7 |
| Ethylbenzene | 15 | 30 | 25 | 25 | 28 | 29 |
| | 17 | 27 | 35 | 23 | 27 | 32 |
| | 15 | 30 | 24 | 24 | 27 | 31 |
| Trichloroethene | 9 | 8 | 9 | 9 | 9 | 8 |
| | 9 | 7 | 0 | 9 | 9 | 8 |
| | 8 | 8 | 8 | 7 | 9 | 8 |

TABLE C.20 – EXPERIMENT C – VOC ANALYTICAL RESULTS FOR SAMPLE ROUND 2

| VOC (µg/L) | HDPE Filter Tip | PTFE Filter Tip | Standard Bailer | BED Bailer | Bladder Pump | Multi- Port |
|---------------------|--------------------|--------------------|--------------------|---------------|-----------------|----------------|
| Benzene | 44 | 14 | 23 | 20 | ND | 15 |
| | 45 | 13 | 23 | 21 | 25 | 14 |
| | 48 | ND | 22 | 23 | 24 | 14 |
| Chlorobenzene | 869 | 1040 | 894 | 818 | ND | 985 |
| | 843 | 1010 | 885 | 827 | 1020 | 971 |
| | 884 | ND | 867 | 839 | 1010 | 968 |
| 1,2-Dichlorobenzene | 188 | 179 | 165 | 158 | ND | 173 |
| | 181 | 175 | 163 | 155 | 184 | 174 |
| | 194 | ND | 163 | 157 | 183 | 172 |
| 1,3-Dichlorobenzene | 16 | 17 | 15 | 15 | ND | 15 |
| | 16 | 17 | 15 | 16 | 16 | 16 |
| | 17 | ND | 15 | 15 | 17 | 16 |
| 1,4-Dichlorobenzene | 283 | 285 | 261 | 239 | ND | 263 |
| | 269 | 273 | 253 | 234 | 284 | 261 |
| | 293 | ND | 248 | 243 | 279 | 260 |
| 1,1-Dichloroethane | 34 | 33 | 32 | 32 | ND | 30 |
| | 34 | 31 | 32 | 32 | 37 | 30 |
| | 34 | ND | 31 | 33 | 34 | 31 |
| 1,2-Dichloroethane | 9 | 8 | 8 | 8 | ND | 8 |
| | 9 | 9 | 8 | 7 | 10 | 8 |
| | 9 | ND | 8 | 9 | 9 | 8 |
| Ethylbenzene | 14 | 31 | 25 | 24 | ND | 30 |
| | 13 | 30 | 25 | 24 | 27 | 29 |
| | 15 | ND | 24 | 24 | 27 | 29 |
| Trichloroethene | 9 | 9 | 10 | 8 | ND | 10 |
| | 8 | 8 | 9 | 9 | 10 | 8 |
| | 9 | ND | 9 | 8 | 10 | 9 |

ND = No Data

TABLE C.21 - EXPERIMENT C - VOC ANALYTICAL RESULTS FOR SAMPLE ROUND 3

| VOC (µg/L) | HDPE Filter Tip | PTFE Filter Tip | Standard Bailer | BED Bailer | Bladder Pump | Multi- Port |
|---------------------|--------------------|--------------------|--------------------|---------------|-----------------|----------------|
| Benzene | 28 | 12 | 12 | 14 | 18 | 12 |
| | 27 | 13 | 17 | 10 | 19 | 12 |
| | 27 | 13 | 16 | 8 | 20 | 12 |
| Chlorobenzene | 787 | 977 | 673 | 740 | 917 | 910 |
| | 769 | 1050 | 901 | 557 | 959 | 947 |
| | 759 | 1080 | 840 | 474 | 969 | 940 |
| 1,2-Dichlorobenzene | 174 | 167 | 133 | 150 | 153 | 146 |
| | 171 | 163 | 171 | 132 | 159 | 154 |
| | 175 | 181 | 140 | 124 | 158 | 146 |
| 1,3-Dichlorobenzene | 18 | 16 | 14 | 15 | 15 | 16 |
| | 17 | 18 | 17 | 15 | 16 | 16 |
| | 18 | 18 | 14 | 14 | 16 | 15 |
| 1,4-Dichlorobenzene | 286 | 258 | 202 | 223 | 243 | 234 |
| | 274 | 267 | 255 | 190 | 253 | 241 |
| | 285 | 286 | 226 | 179 | 250 | 241 |
| 1,1-Dichloroethane | 31 | 30 | 27 | 32 | 29 | 30 |
| | 31 | 31 | 30 | 30 | 30 | 30 |
| | 32 | 33 | 29 | 27 | 31 | 32 |
| 1,2-Dichloroethane | 9 | 8 | 7 | 8 | 8 | 8 |
| | 8 | 9 | 8 | 8 | 8 | 8 |
| | 8 | 10 | 8 | 7 | 8 | 9 |
| Ethylbenzene | 7 | 32 | 21 | 22 | 28 | 30 |
| | 6 | 33 | 28 | 18 | 29 | 30 |
| | 6 | 35 | 24 | 16 | 29 | 31 |
| Trichloroethene | 8 | 9 | 9 | 9 | 8 | 9 |
| | 8 | 9 | 9 | 9 | 9 | 8 |
| | 8 | 9 | 8 | 8 | 10 | 9 |

TABLE C.22 – EXPERIMENT C – VOC ANALYTICAL RESULTS FOR SAMPLE ROUND 4

| VOC (µg/L) | HDPE Filter Tip | PTFE Filter Tip | Standard Bailer | BED Bailer | BED Bailer* | Bladder Pump | Multi- Port |
|---------------------|--------------------|--------------------|--------------------|---------------|----------------|-----------------|----------------|
| Benzene | 20.1 | 12.8 | 13.3 | 8.8 | 9.0 | 15.6 | 10.1 |
| | 18.2 | 12.7 | 13.0 | 12.3 | 9.0 | 15.0 | 10.7 |
| | 17.6 | 12.7 | 14.4 | 12.0 | 9.0 | 15.1 | 10.5 |
| Chlorobenzene | 666 | 1100 | 845 | 529 | 517 | 940 | 929 |
| | 645 | 1090 | 813 | 772 | 524 | 933 | 958 |
| | 625 | 1090 | 860 | 751 | 528 | 938 | 940 |
| 1,2-Dichlorobenzene | 175 | 176 | 144 | 105 | 95.8 | 156 | 154 |
| | 169 | 172 | 142 | 135 | 99.5 | 159 | 149 |
| | 172 | 166 | 140 | 136 | 100 | 158 | 148 |
| 1,3-Dichlorobenzene | 17.0 | 16.0 | 13.0 | 12.3 | 11.8 | 13.8 | 13.8 |
| | 16.9 | 15.9 | 13.8 | 13.2 | 12.0 | 14.6 | 13.5 |
| | 16.9 | 15.5 | 13.1 | 13.5 | 11.8 | 14.5 | 13.6 |
| 1,4-Dichlorobenzene | 294 | 289 | 225 | 118 | 112 | 245 | 250 |
| | 293 | 291 | 225 | 197 | 115 | 264 | 240 |
| | 292 | 275 | 223 | 202 | 110 | 256 | 242 |
| 1,1-Dichloroethane | 27.8 | 30.4 | 28.4 | 25.0 | 24.9 | 28.9 | 26.3 |
| | 27.4 | 29.8 | 29.1 | 27.0 | 25.8 | 28.2 | 27.4 |
| | 28.6 | 30.1 | 29.1 | 26.9 | 27.6 | 32.3 | 26.9 |
| 1,2-Dichloroethane | 7.7 | 9.1 | 8.8 | 7.1 | 6.8 | 8.7 | 7.3 |
| | 7.5 | 9.2 | 8.6 | 7.9 | 7.2 | 8.0 | 7.5 |
| | 8.4 | 9.3 | 8.6 | 7.3 | 8.8 | 9.9 | 7.1 |
| Ethylbenzene | 2.4 | 33.2 | 22.4 | 15.9 | 15.8 | 24.8 | 26.9 |
| | 1.7 | 33.3 | 21.6 | 21.3 | 15.7 | 25.8 | 27.6 |
| | 1.9 | 32.8 | 22.6 | 20.9 | 15.9 | 25.0 | 26.6 |
| Trichloroethene | 8.3 | 9.5 | 8.6 | 8.0 | 8.0 | 9.4 | 8.3 |
| | 8.3 | 9.1 | 8.6 | 8.6 | 7.5 | 8.8 | 9.4 |
| | 7.6 | 9.6 | 9.0 | 8.4 | 8.1 | 9.3 | 8.7 |

*Samples collected by decanting from top of bailer, as described in text.

TABLE C.23 - EXPERIMENT C - QUALITY ASSURANCE BLANKS

| Date | Blank Type | Device | Method 624 Compounds Detected and Concentrations |
|----------------|------------|--------------|--|
| Round 1 | | | |
| 17 Feb 89 | Rinsate | Bailer | ND |
| 21 Feb 89 | Trip | — | ND |
| 23 Feb 89 | Rinsate | Bladder Pump | chlorobenzene, 2 µg/L, 1,4-dichlorobenzene, 4µg/L |
| 23 Feb 89 | Trip | — | ND |
| Round 2 | | | |
| 3 Jun 89 | Rinsate | Bailer | ND |
| 3 Jun 89 | Rinsate | BED Bailer | ND |
| 3 Jun 89 | Rinsate | VOA Bottle | ND |
| 5 Jun 89 | Rinsate | Bladder Pump | ND |
| 5 Jun 89 | Trip | — | ND |
| 6 Jun 89 | Trip | — | ND |
| 7 Jun 89 | Rinsate | BAT Bottle | ND |
| 7 Jun 89 | Trip | — | ND |
| Round 3 | | | |
| 19 Aug 89 | Rinsate | Bailer | ND |
| 19 Aug 89 | Rinsate | BED Bailer | ND |
| 21 Aug 89 | Rinsate | VOA Bottle | ND |
| 21 Aug 89 | Trip | — | ND |
| 21 Aug 89 | Rinsate | Bladder Pump | ND |
| 22 Aug 89 | Trip | — | ND |
| 22 Aug 89 | Rinsate | BAT Bottle | ND |
| Round 4 | | | |
| 5 Dec 89 | Rinsate | BED Bailer | ND |
| 5 Dec 89 | Rinsate | Bailer | ND |
| 6 Dec 89 | Trip | — | ND |
| 6 Dec 89 | Trip | — | ND |
| 6 Dec 89 | Rinsate | BAT Bottle | ND |
| 6 Dec 89 | Rinsate | VOA Bottle | ND |
| 7 Dec 89 | Trip | — | ND |

ND = Not Detected

TABLE C.24 - DUPLICATE ANALYSES OF RANDOM SAMPLES

| Date Collected | Order of Analysis | Concentration (µg/L) | | | | | | | | |
|----------------|-------------------|----------------------|---------------|---------------------|---------------------|---------------------|--------------------|--------------------|--------------|-----------------|
| | | Benzene | Chlorobenzene | 1,2-Dichlorobenzene | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane | 1,2-Dichloroethane | Ethylbenzene | Trichloroethene |
| 23 Feb 89 | a | 30 | 1047 | 266 | 25 | 366 | 27 | 7 | 23 | 9 |
| | b | 30 | 1095 | 258 | 25 | 360 | 26 | 7 | 25 | 9 |
| 23 Feb 89 | a | ND | 2 | ND | ND | 4 | ND | ND | ND | ND |
| | b | ND | 2 | ND | ND | 3 | ND | ND | ND | ND |
| 5 Jun 89 | a | 20 | 818 | 158 | 15 | 239 | 32 | 8 | 24 | 8 |
| | b | 21 | 818 | 155 | 15 | 237 | 31 | 8 | 24 | 9 |
| 5 Jun 89 | a | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | b | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 6 Jun 89 | a | 14 | 1037 | 179 | 17 | 285 | 33 | 8 | 31 | 9 |
| | b | 13 | 1028 | 182 | 17 | 282 | 31 | 9 | 31 | 9 |
| 21 Aug 89 | a | 12 | 673 | 133 | 14 | 202 | 27 | 7 | 21 | 9 |
| | b | 12 | 685 | 134 | 14 | 210 | 28 | 8 | 22 | 8 |
| 21 Aug 89 | a | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| | b | ND | ND | ND | ND | ND | ND | ND | ND | ND |
| 22 Aug 89 | a | 13 | 1080 | 181 | 18 | 286 | 33 | 10 | 35 | 9 |
| | b | 13 | 1060 | 180 | 18 | 279 | 31 | 9 | 35 | 9 |
| 7 Dec 89 | a | 13 | 1090 | 166 | 16 | 275 | 30 | 9 | 33 | 10 |
| | b | 13 | 1070 | 171 | 16 | 288 | 30 | 9 | 33 | 10 |
| 7 Dec 89 | a | 15 | 938 | 158 | 15 | 256 | 32 | 10 | 25 | 9 |
| | b | 15 | 939 | 157 | 14 | 256 | 30 | 9 | 25 | 9 |
| 7 Dec 89 | a | 9 | 529 | 105 | 12 | 118 | 25 | 7 | 16 | 8 |
| | b | 9 | 515 | 98 | 12 | 112 | 24 | 7 | 15 | 7 |
| 7 Dec 89 | a | 13 | 845 | 144 | 13 | 225 | 28 | 9 | 22 | 9 |
| | b | 13 | 821 | 139 | 13 | 217 | 28 | 9 | 22 | 8 |

ND = Not Detected

APPENDIX D

DATA PLOTS AND STATISTICAL ANALYSES RESULTS

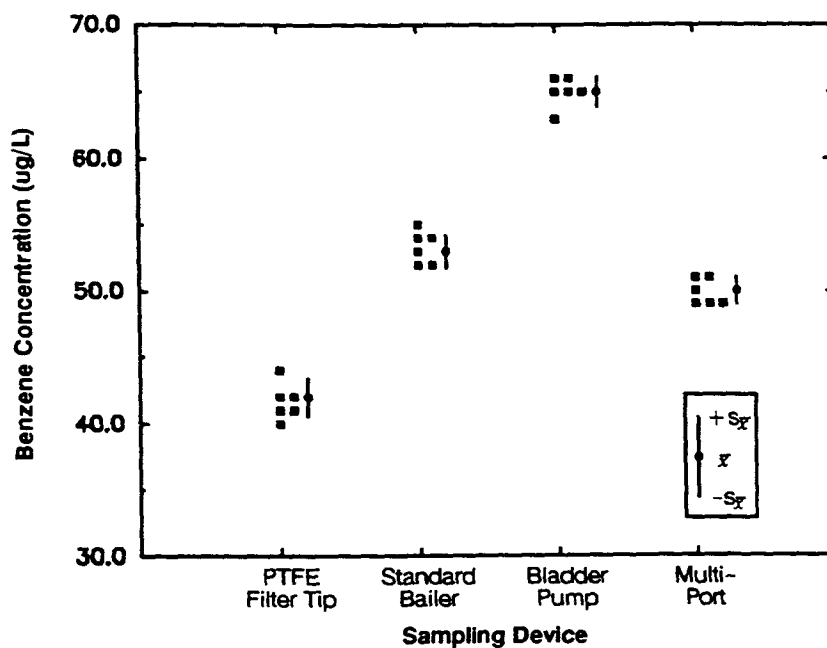


FIGURE D.1 - EXPERIMENT B - BENZENE DATA

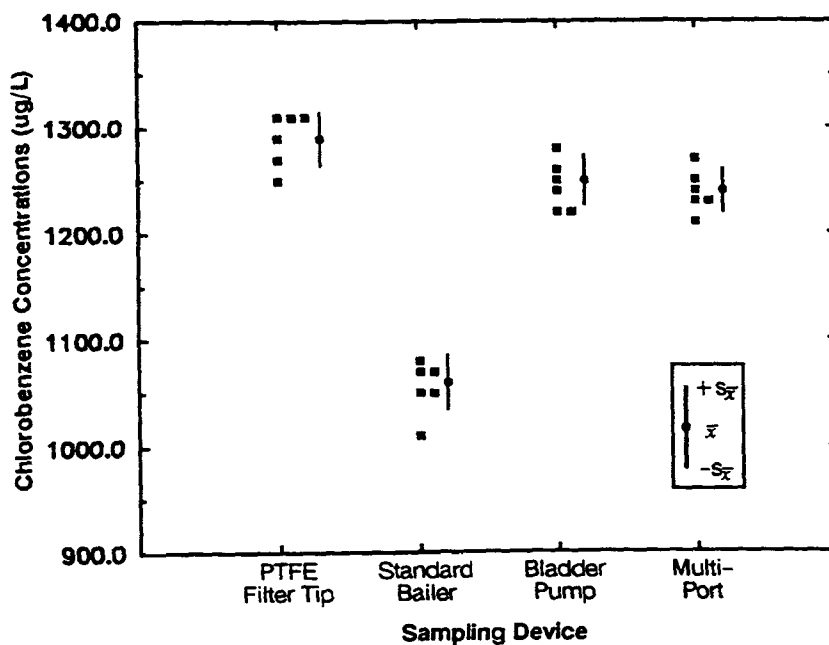


FIGURE D.2 - EXPERIMENT B - CHLOROBENZENE DATA

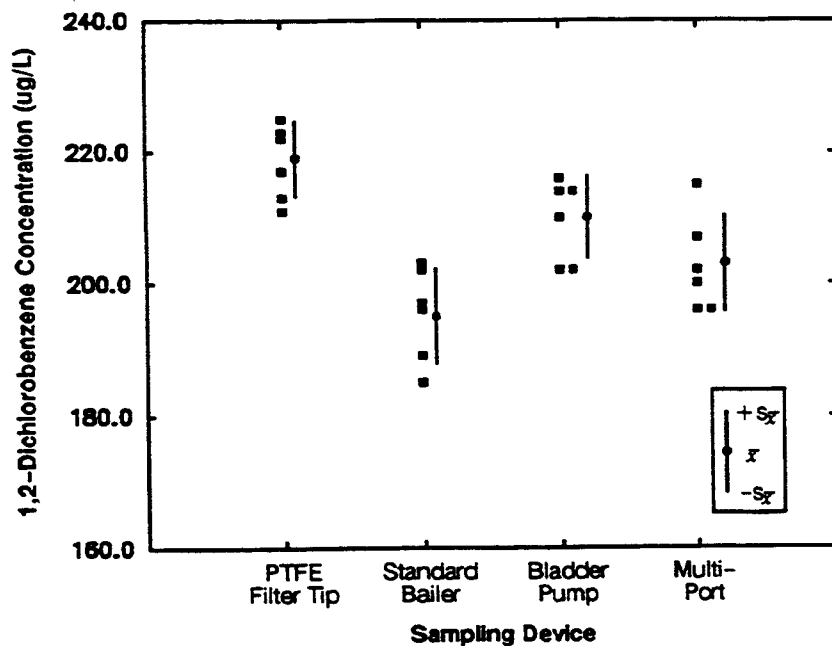


FIGURE D.3 - EXPERIMENT B - 1,2-DICHLOROBENZENE DATA

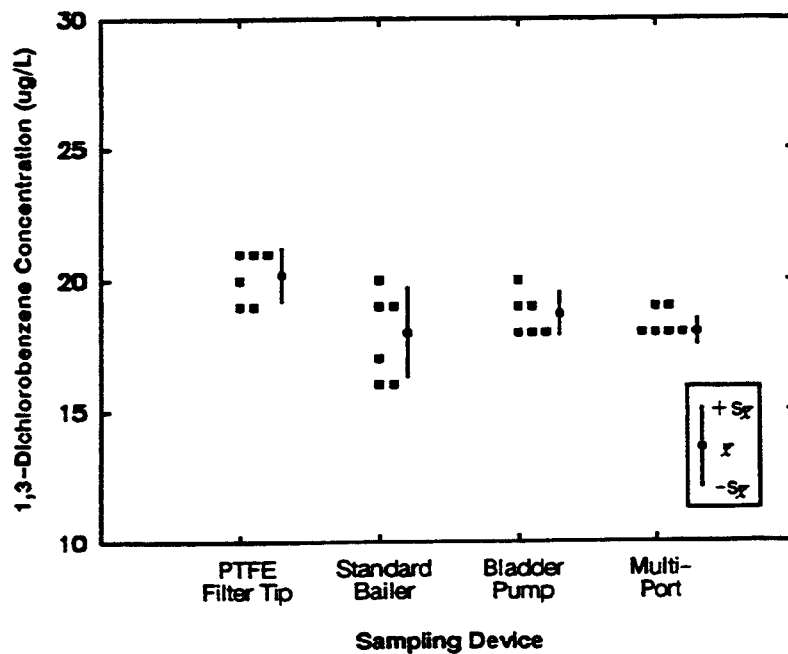


FIGURE D.4 - EXPERIMENT B - 1,3-DICHLOROBENZENE DATA

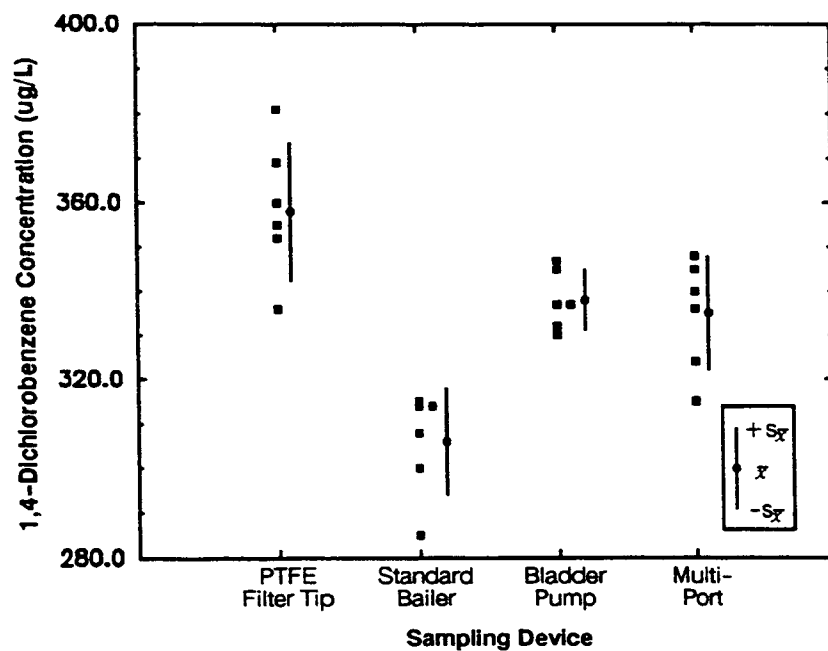


FIGURE D.5 - EXPERIMENT B - 1,4-DICHLOROBENZENE DATA

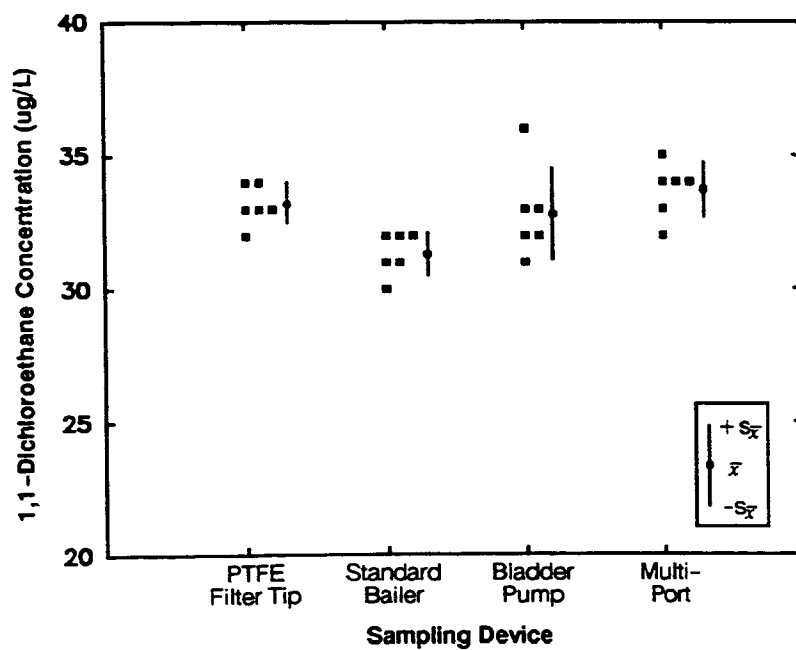


FIGURE D.6 - EXPERIMENT B - 1,1-DICHLOROETHANE DATA

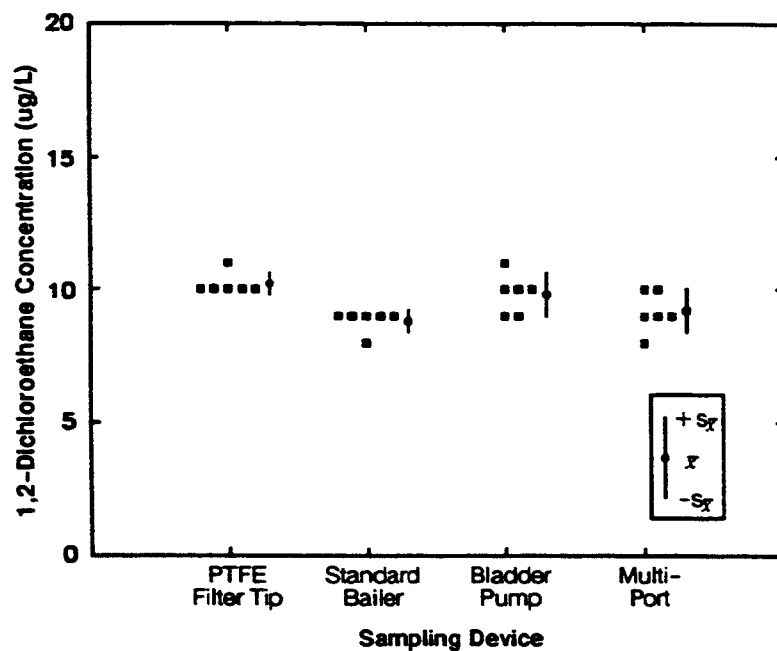


FIGURE D.7 - EXPERIMENT B - 1,2-DICHLOROETHANE DATA

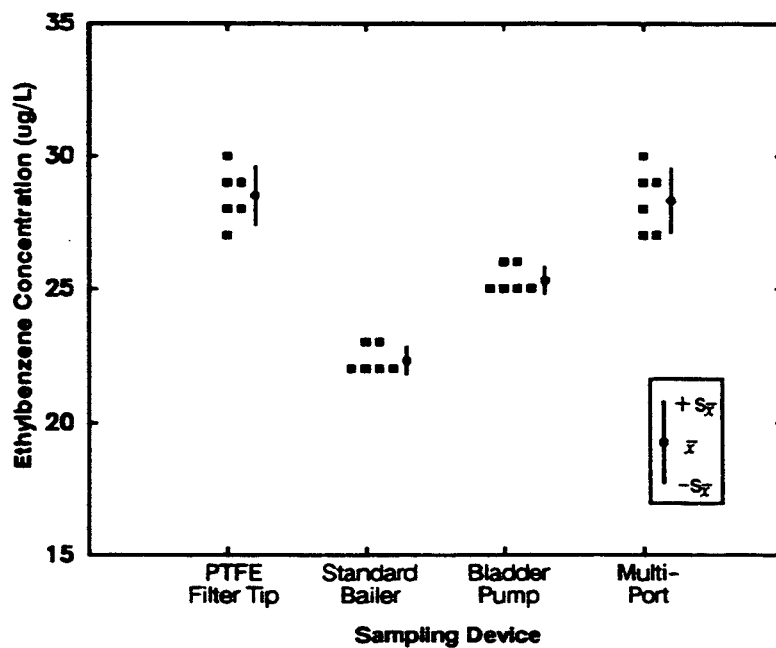


FIGURE D.8 - EXPERIMENT B - ETHYLBENZENE DATA

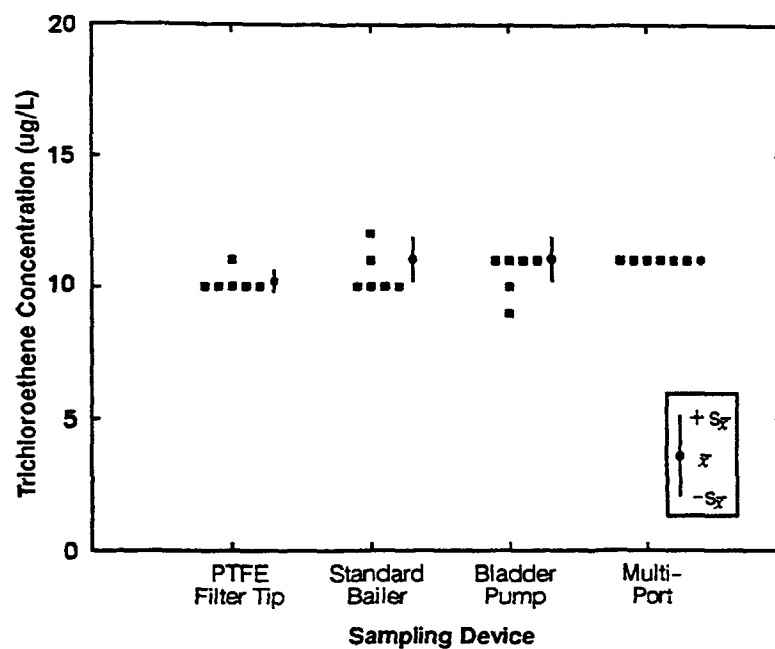


FIGURE D.9 - EXPERIMENT B - TRICHLOROETHENE DATA

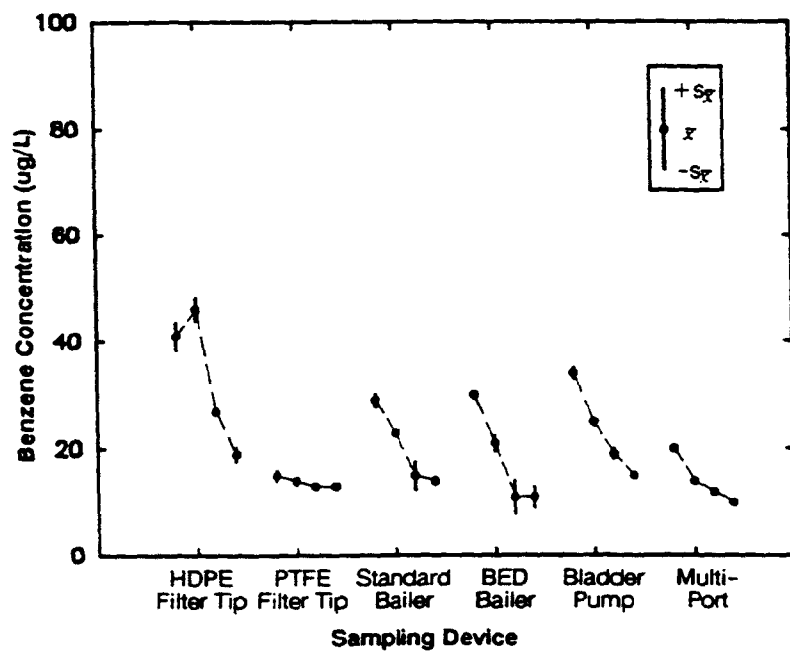


FIGURE D.10 - EXPERIMENT C - BENZENE DATA

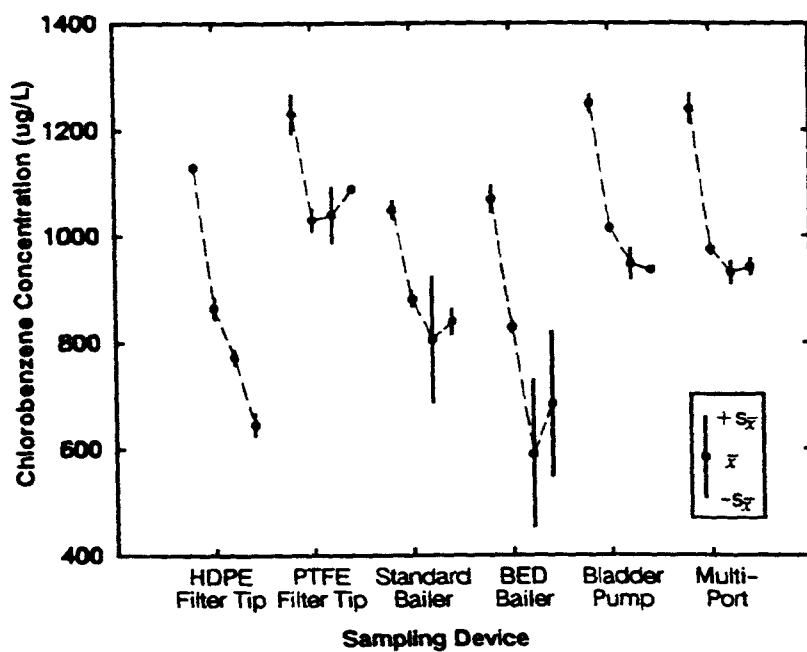


FIGURE D.11 - EXPERIMENT C - CHLOROBENZENE DATA

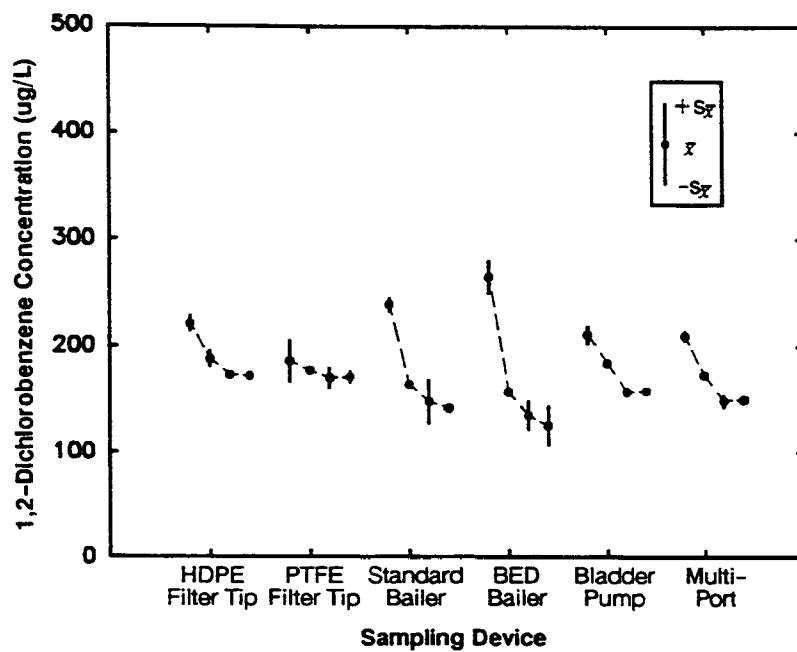


FIGURE D.12 - EXPERIMENT C - 1,2-DICHLOROBENZENE DATA

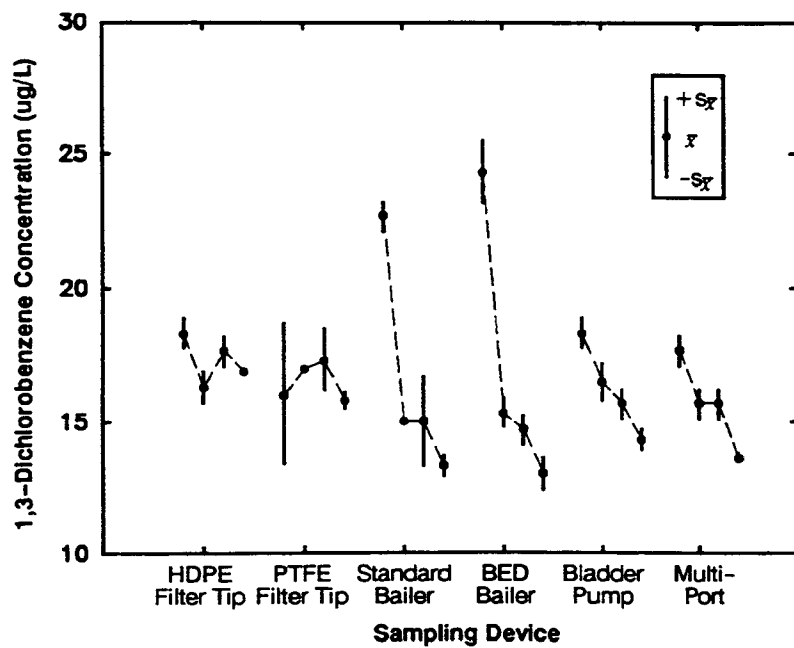


FIGURE D.13 - EXPERIMENT C - 1,3-DICHLOROBENZENE DATA

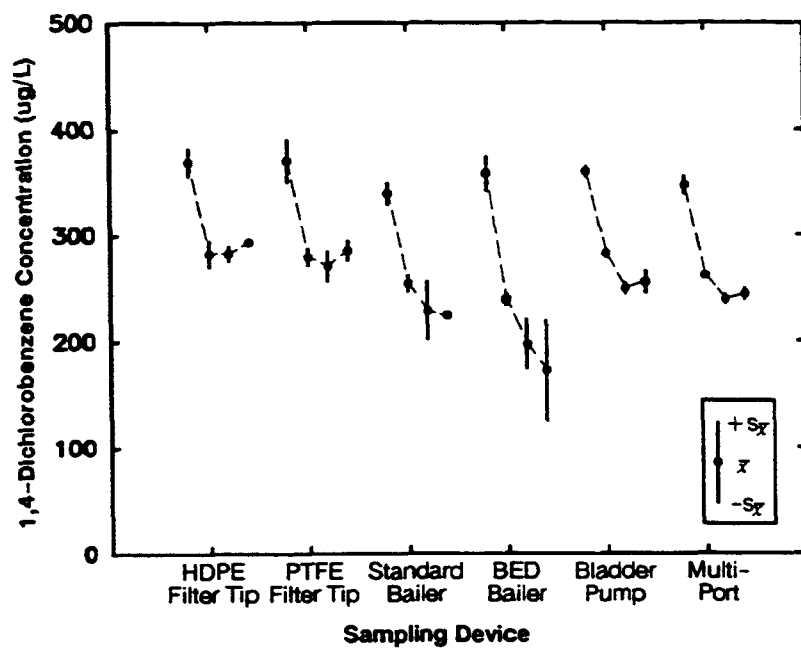


FIGURE D.14 - EXPERIMENT C - 1,4-DICHLOROBENZENE DATA

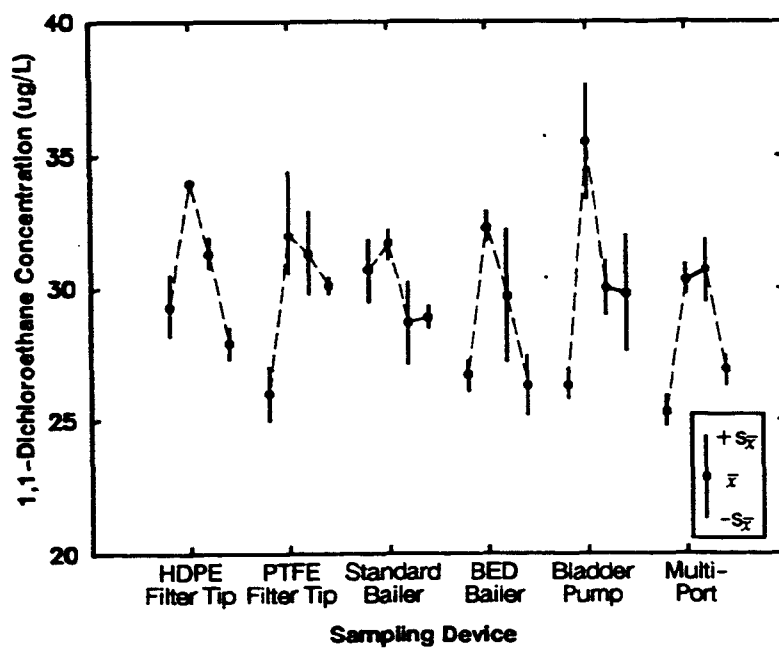


FIGURE D.15 - EXPERIMENT C - 1,1-DICHLOROETHANE DATA

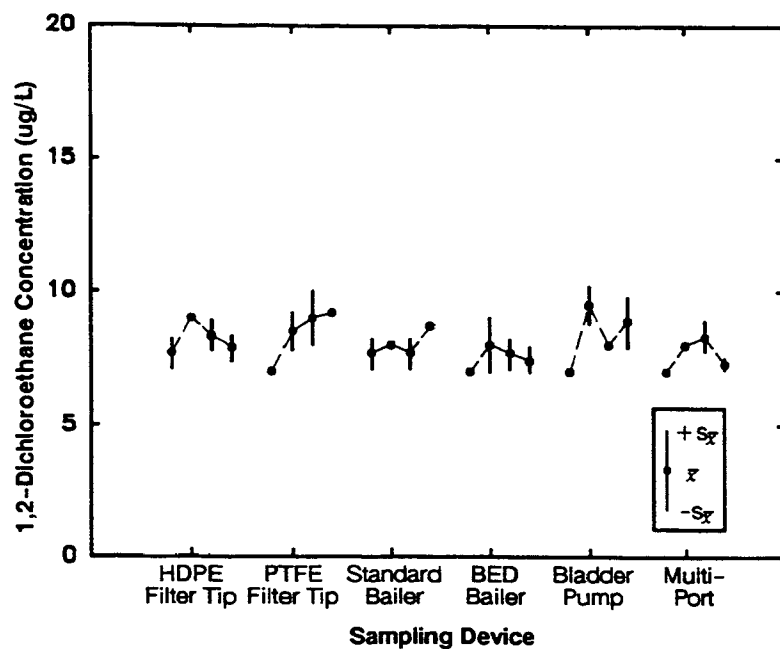


FIGURE D.16 - EXPERIMENT C - 1,2-DICHLOROETHANE DATA

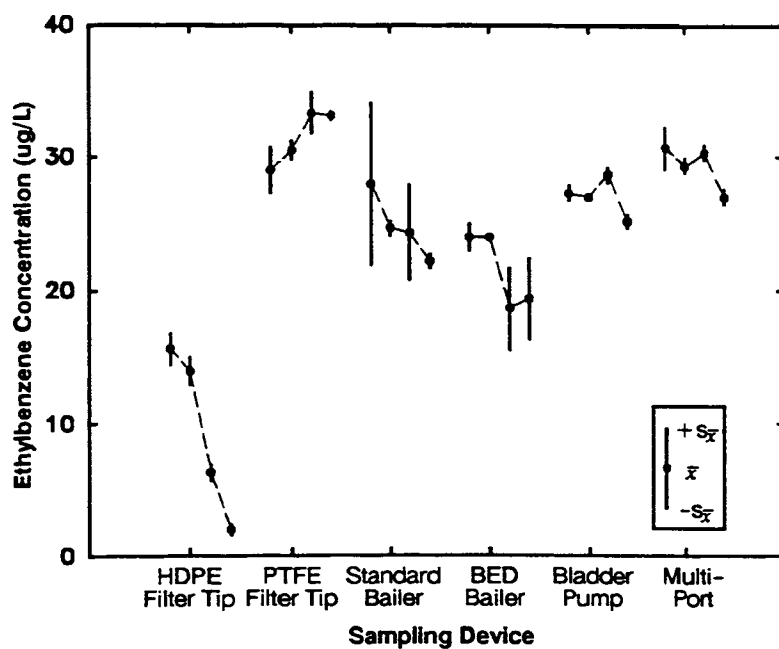


FIGURE D.17 - EXPERIMENT C - ETHYLBENZENE DATA

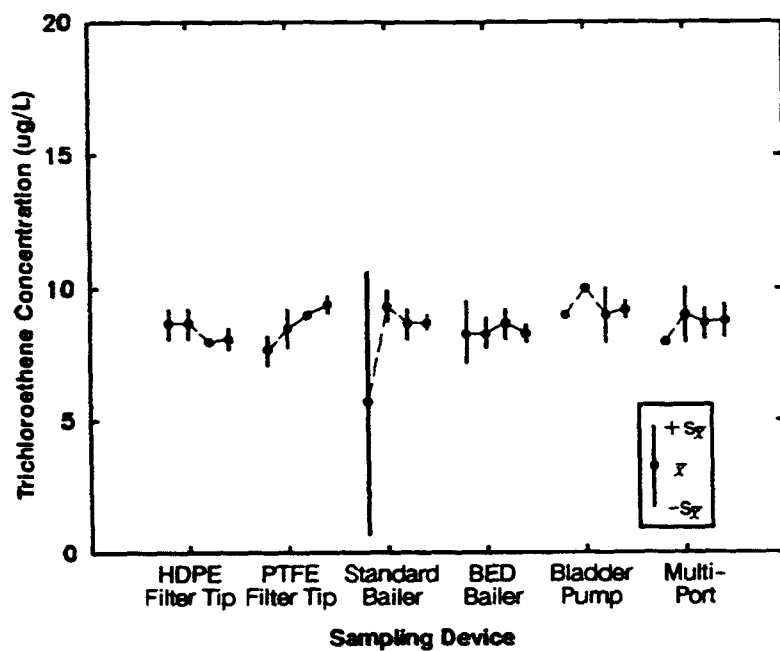


FIGURE D.18 - EXPERIMENT C - TRICHLOROETHENE DATA

TABLE D.1 - EXPERIMENT C - TUKEY TEST RESULTS FOR ROUND 1

| Rank* | Benzene | Chlorobenzene | 1,2-Dichlorobenzene |
|-------|---------------------|---------------------|---------------------|
| 1 | HDPE Filter Tip | Bladder Pump | BED Bailer |
| 2 | Bladder Pump | Multi-Port | Bailer |
| 3 | BED Bailer | PTFE Filter Tip | HDPE Filter Tip |
| 4 | Bailer | HDPE Filter Tip | Bladder Pump |
| 5 | PTFE Filter Tip | BED Bailer | Multi-Port |
| 6 | Multi-Port | Bailer | PTFE Filter Tip |
| Rank* | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane |
| 1 | BED Bailer | PTFE Filter Tip | Bailer |
| 2 | Bailer | HDPE Filter Tip | HDPE Filter Tip |
| 3 | Bladder Pump | Bladder | BED Bailer |
| 4 | HDPE Filter Tip | BED Bailer | Bladder Pump |
| 5 | Multi-Port | Multi-Port | PTFE Filter Tip |
| 6 | PTFE Filter Tip | Bailer | Multi-Port |
| Rank* | 1,2-Dichloroethane | Ethylbenzene | Trichloroethene |
| 1 | HDPE Filter Tip | Multi-Port | Bladder Pump |
| 2 | Bailer | PTFE Filter Tip | HDPE Filter Tip |
| 3 | PTFE Filter Tip | Bailer | BED Bailer |
| 4 | BED Bailer | Bladder Pump | Multi-Port |
| 5 | Bladder Pump | BED Bailer | PTFE Filter Tip |
| 6 | Multi-Port | HDPE Filter Tip | Bailer |

*Ranked from highest to lowest concentration

TABLE D.2 - EXPERIMENT C - TUKEY TEST RESULTS FOR ROUND 2

| Rank* | Benzene | Chlorobenzene | 1,2-Dichlorobenzene |
|-------|---------------------|---------------------|---------------------|
| 1 | HDPE Filter Tip | PTFE Filter Tip | HDPE Filter Tip |
| 2 | Bladder Pump | Bladder Pump | Bladder Pump |
| 3 | Bailer | Multi-Port | PTFE Filter Tip |
| 4 | BED Bailer | Bailer | Multi-Port |
| 5 | Multi-Port | HDPE Filter Tip | Bailer |
| 6 | PTFE Filter Tip | BED Bailer | BED Bailer |
| Rank* | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane |
| 1 | PTFE Filter Tip | Bladder Pump | Bladder Pump |
| 2 | Bladder Pump | HDPE Filter Tip | HDPE Filter Tip |
| 3 | HDPE Filter Tip | PTFE Filter Tip | BED Bailer |
| 4 | Multi-Port | Multi-Port | PTFE Filter Tip |
| 5 | BED Bailer | Bailer | Bailer |
| 6 | Bailer | BED Bailer | Multi-Port |
| Rank* | 1,2-Dichloroethane | Ethylbenzene | Trichloroethene |
| 1 | Bladder Pump | PTFE Filter Tip | Bladder Pump |
| 2 | HDPE Filter Tip | Multi-Port | Bailer |
| 3 | PTFE Filter Tip | Bladder Pump | Multi-Port |
| 4 | Bailer | Bailer | HDPE Filter |
| 5 | BED Bailer | BED Bailer | PTFE Filter Tip |
| 6 | Multi-Port | HDPE Filter Tip | BED Bailer |

*Ranked from highest to lowest concentration

TABLE D.3 – EXPERIMENT C – TUKEY TEST RESULTS FOR ROUND 3

| Rank* | Benzene | Chlorobenzene | 1,2-Dichlorobenzene |
|-------|---------------------|---------------------|---------------------|
| 1 | HDPE Filter Tip | PTFE Filter Tip | HDPE Filter Tip |
| 2 | Bladder Pump | Bladder Pump | PTFE Filter Tip |
| 3 | Bailer | Multi-Port | Bladder Pump |
| 4 | PTFE Filter Tip | Bailer | Multi-Port |
| 5 | Multi-Port | HDPE Filter Tip | Bailer |
| 6 | BED Bailer | BED Bailer | BED Bailer |
| Rank* | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane |
| 1 | HDPE Filter Tip | HDPE Filter Tip | HDPE Filter Tip |
| 2 | PTFE Filter Tip | PTFE Filter Tip | PTFE Filter Tip |
| 3 | Bladder Pump | Bladder Pump | Multi-Port |
| 4 | Multi-Port | Multi-Port | Bladder Pump |
| 5 | Bailer | Bailer | BED Bailer |
| 6 | BED Bailer | BED Bailer | Bailer |
| Rank* | 1,2-Dichloroethane | Ethylbenzene | Trichloroethene |
| 1 | PTFE Filter Tip | PTFE Filter Tip | PTFE Filter Tip |
| 2 | HDPE Filter Tip | Multi-Port | Bladder Pump |
| 3 | Multi-Port | Bladder Pump | Multi-Port |
| 4 | Bladder Pump | Bailer | Bailer |
| 5 | Bailer | BED Bailer | BED Bailer |
| 6 | BED Bailer | HDPE Filter Tip | HDPE Filter Tip |

*Ranked from highest to lowest concentration

TABLE D.4 - EXPERIMENT C - TUKEY TEST RESULTS FOR ROUND 4

| Rank* | Benzene | Chlorobenzene | 1,2-Dichlorobenzene |
|-------|---------------------|---------------------|---------------------|
| 1 | HDPE Filter Tip | PTFE Filter Tip | HDPE Filter Tip |
| 2 | Bladder Pump | Multi-Port | PTFE Filter Tip |
| 3 | Bailer | Bladder Pump | Bladder Pump |
| 4 | PTFE Filter Tip | Bailer | Multi-Port |
| 5 | BED Bailer | BED Bailer | Bailer |
| 6 | Multi-Port | HDPE Filter Tip | BED Bailer |
| Rank* | 1,3-Dichlorobenzene | 1,4-Dichlorobenzene | 1,1-Dichloroethane |
| 1 | HDPE Filter Tip | HDPE Filter Tip | PTFE Filter Tip |
| 2 | PTFE Filter Tip | PTFE Filter Tip | Bladder Pump |
| 3 | Bladder Pump | Bladder Pump | Bailer |
| 4 | Multi-Port | Multi-Port | HDPE Filter Tip |
| 5 | Bailer | Bailer | Multi-Port |
| 6 | BED Bailer | BED Bailer | BED Bailer |
| Rank* | 1,2-Dichloroethane | Ethylbenzene | Trichloroethene |
| 1 | PTFE Filter Tip | PTFE Filter Tip | PTFE Filter Tip |
| 2 | Bladder Pump | Multi-Port | Bladder Pump |
| 3 | Bailer | Bladder Pump | Multi-Port |
| 4 | HDPE Filter Tip | Bailer | Bailer |
| 5 | BED Bailer | BED Bailer | BED Bailer |
| 6 | Multi-Port | HDPE Filter Tip | HDPE Filter Tip |

*Ranked from highest to lowest concentration

