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SUBJECT

Contract Task Order (CTO) No. 0145
Literature on Comparative Evaluation of
Groundwater Sampling Pumps
Marine Corps Air Station (MCAS) El Toro RI/FS

PARTICIPANTS: (* DENOTES PART-TIME ATTENDANCE)

ACTION REQ'D. BY	ITEM
	Attached are articles comparing the performance of submersible groundwater sampling pumps to other types of groundwater sampling equipment for the sampling of groundwater containing volatile organic compounds. These articles are being forwarded to representatives from the U.S. Environmental Protection Agency, California Environmental Protection Agency - Department of Toxic Substances Control, and the Santa Ana Regional Water Quality Control Board per their request at the Contract Task Order 145 Remedial Project Managers' Meeting on 17 February 1995.

Nonparticipant Distribution

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Effects of Selected Sampling Equipment and Procedures on the Concentrations of Trichloroethylene and Related Compounds in Ground Water Samples

by Kenneth A. Pearsall and David A.V. Eckhardt

Abstract

Variations in concentrations of trichloroethylene and related compounds in ground water obtained from seven ground water samplers were used to compare the performance of three submersible pumps, a centrifugal pump, two peristaltic pumps, and a bailer. Two- and 4-inch diameter submersible pumps and a centrifugal pump produced samples whose trichloroethylene concentrations, on the average, did not differ significantly from each other. Ground water samples collected by using a peristaltic pump and silicone tubing had significantly lower trichloroethylene concentrations than samples from the submersible pumps. Concentrations of 1,2-dichloroethylene and trichloroethylene in ground water samples collected by using a bailer were indistinguishable from those in samples taken by a submersible pump when the concentrations were as much as 96 and 76 micrograms per liter, respectively, but were 15 and 12 percent lower when concentrations were as low as 29 and 23 micrograms per liter, respectively. Tests of different configurations of sampler placement in observation wells indicate that pump placement, rate of pumping, duration of pumping, and the uniformity of the vertical and lateral distribution of trichloroethylene in ground water near the well screen have a potentially significant influence on trichloroethylene concentrations in ground water samples and that these factors can have a greater effect than the type of sampler used.

Introduction

Frequently, the same monitoring wells, sampling equipment, and procedures that traditionally have been used to sample inorganic constituents in ground water are used to sample synthetic volatile organic compounds (VOCs), although more specialized sampling devices and sampling procedures are usually recommended for this purpose. Pettyjohn et al. (1981) have asserted that "a typical electrical submersible pump attached to plastic pipe or garden hose . . . is entirely inadequate" for sampling for organic compounds and recommend glass and Teflon® as preferable materials for pumps and tubing systems. Scalf et al. (1981) recommend Teflon bailers in preference to pumping systems "because of the possible stripping of VOCs from the sample under the reduced or elevated pressure occurring in systems using pumps."

The purpose of this investigation was to compare the use of conventional sampling methods with more rigorous methods of sampling for VOCs in ground water. This report describes field tests of sampling procedures initiated in 1983 on Long Island, New York, to determine the effects of selected aspects of sample collection on the concentration of trichloroethylene and related VOCs in ground water samples. Several types of samplers, tubing materials, and pump-intake placements in relation to the screened zone of the well were tested under field conditions. The experiments were designed to examine the extent that field methods and sampling procedures directly affect the concentration of trichloroethylene in ground water samples.

Method of Study

Two aspects of sampling were examined to evaluate their effect on VOC concentrations: (1) the type of sampler and its method of use, and (2) the duration of pumping. The sampler comparisons were accomplished by collecting samples simultaneously at frequent intervals from different sampling devices installed in the same well during one-hour pumping tests. Conditions were varied among these tests to examine the influence of well depth, pump placement in relation to the well screen, and VOC concentrations. The types of sampling devices, pump depths, pumping rates, and monitoring wells are summarized in Table 1. To monitor the effect of pumping duration, samples were collected at frequent intervals during three-hour pumping tests to obtain an indication of VOC concentration changes in water entering the well screen.

Trichloroethylene and related compounds were chosen as representative test constituents because of their frequent detection in Long Island ground water (Myott 1980) and because their physical characteristics are typical of volatile chlorinated hydrocarbons. Although the tests were conducted at variable trichloroethylene concentrations, the goal of these experiments was to determine the capability of a sampler to provide reproducible samples at approximately 50 $\mu g/L$ (micrograms per liter) — the

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TABLE 1

Test Design Data for Sampler Comparisons

Test Number	Well	Screened Interval (ft below land surface)	Static Depth to Water (ft)	Drawdown (ft)	Pumps Used	Depth to Pump Intake (ft below land surface)	Pumping Rate (gal/min)
1	A	65–75	4.72	2.75	EPDM[1] submersible pump	50	1.5
					Viton submersible pump	50	.64
					4-inch submersible pump	48	18
					Centrifugal pump	10	3.0
2	B	63–73	5.67	1.99	EPDM submersible pump	61.5	1.4
					Viton submersible pump	61.5	.67
					4-inch submersible pump	60	18
					Centrifugal pump	15	3.6
3	A	65–75	4.89	2.17	EPDM submersible pump	50	1.4
					4-inch submersible pump	48	18
					Viton submersible pump	46	.77
					Centrifugal pump	10	1.1
4	C	20.5–30.5	5.39	.27	EPDM submersible pump	16	1.5
					4-inch submersible pump	14.5	21
					Viton submersible pump	13	.82
					Centrifugal pump	8	3.9
5	D	24–34	10.06	1.95	EPDM submersible pump	21	1.4
					4-inch submersible pump	20	21
					Viton submersible pump	19	.71
					Centrifugal pump	15	3.3
6	C	20.5–30.5	5.84	1.06	EPDM submersible pump	17	1.4
					Centrifugal pump and Teflon pipe	18	90
					Peristaltic pump and Teflon tube	17	.19
					Peristaltic pump and silicone tube	17	.18
					Centrifugal pump	8	22.5
7	D	24–34	10.70	2.42	EPDM submersible pump	17	1.3
					Centrifugal pump and Teflon pipe	17	23
					Peristaltic pump and Teflon tube	17	.18
					Peristaltic pump and silicone tube	17	.25
					Centrifugal pump	14	3.1
8	C	20.5–30.5	6.05	<0.01	EPDM submersible pump	17	1.4
					Centrifugal pump and Teflon tube	17	2.5
					Teflon bailer	17	—
					Centrifugal pump	9	3.7
9	D	24–34	11.70	1.20	EPDM submersible pump	18	1.3
					Viton submersible pump	18	.80
					4-inch submersible pump and PVC pipe	19	14
					Teflon bailer	18	—
					Centrifugal pump	14	3.1
10	D	24–34	12.01	1.37	EPDM submersible pump	18	1.3
					4-inch submersible pump and plastic garden hose	18	16
					Centrifugal pump	14	3.1
11	E	48–53	22.72	1.81	EPDM submersible pump	29	1.2
					Centrifugal pump and Teflon pipe	29	7.2
					Centrifugal pump	27	1.65
12	C	20.5–30.5	5.05	.53	EPDM submersible pump	25	1.40
					4-inch submersible pump	23	26
					Centrifugal pump	21	4
13	C	20.5–30.5	4.95	.62	EPDM submersible pump	25	1.4
					4-inch submersible pump	23	30
					Viton submersible pump	21	.78
					Centrifugal pump	10	3.9

[1] EPDM is an ethylene propylene rubber

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New York State drinking water guideline (most of the volatile organic compounds on the U.S. Environmental Protection Agency "priority pollutant" list.

Monitoring Wells

Monitoring wells used for the tests are screened in sand and gravel in the upper glacial (water table) aquifer of the Long Island aquifer system. The wells are components in existing (in use) ground water monitoring networks and were selected because they offered specifically desired features, including a known history, a small volume of water in the well casing, a shallow screen, and the desired concentration of the specified constituents. All wells have steel casings and stainless steel screens installed less than 80 feet below land surface by either cable tool or auger. Wells A, B, C, and D are 6-inch diameter wells that were drilled in June 1972. Well E is a 4-inch well installed in October 1982. They were not specially designed or installed for monitoring volatile contaminants; thus, special construction techniques, such as steam cleaning of steel pipe before installation, were not used. The depth to water in wells used for sampler comparisons was generally between 5 and 15 feet.

Sampling Equipment

The sampling devices compared included two 2-inch diameter submersible pumps, a 4-inch diameter submersible pump, a centrifugal pump, two peristaltic pumps, and a Teflon bailer. The 4-inch submersible pump and the centrifugal pump are designed for general-purpose pumping and are not intended specifically for sampling.

Both 2-inch submersible pumps were Model SP-81 Keck submersible sampling pumps. The positive-displacement pumping mechanism of the Keck pump consists of a screw or worm gear (rotor) and a flexible rubber sleeve (stator). One pump contained an EPDM (ethylene propylene elastomer) stator, and the other a Viton (fluorocarbon elastomer) stator. These pumps are hereafter referred to as the EPDM submersible pump and the Viton submersible pump. The EPDM submersible pump typically delivered between 1.2 and 1.5 gal/min (gallons per minute) to the surface with 35 feet of pumping head. Viton, although preferable in sampling for organic compounds because it is less reactive than EPDM, is less pliable. The Viton submersible pump typically delivered between 0.5 and 0.7 gal/min to the surface with 35 feet of pumping head. The 2-inch submersible pumps were identical in all other respects. Teflon tubing was used to transmit pumped water to the land surface. The EPDM submersible pump was arbitrarily chosen as the standard against which the other samplers were compared.

The 4-inch submersible pump was a 1-hp, three-stage Goulds Model E-5125 pump that was connected to a 1.25-inch outside diameter (OD) flush-threaded Teflon pipe. The outlet was fitted with a flowmeter and a valve to control flow between 3 and 30 gal/min. The centrifugal pump was a Homelite Model 111S2-1 pump made of cast iron that delivered between 2 and 50 gal/min, depending on the length and diameter of the intake hose. The peristaltic pumps were Horizon Ecology Model 7570 Portable MasterFlex sampling pumps. These pumps were equipped with ⅜-inch OD silicone tubing and delivered 0.2 gal/min with 15 feet of pumping head. The bailer was a 3-foot long, 1.75-inch OD Teflon cylinder with a check valve (Teflon ball and seat) in the bottom.

Test Procedures

Samplers were compared by placing several of them in a well at the same time and obtaining samples from them simultaneously. The intakes of all sampling pumps were placed as close together as possible above the screened zone in the well to ensure that the sample water was withdrawn from the same area within the well casing (Figure 1). A centrifugal pump was additionally used with its intake near the drawdown level in the well to facilitate evacuation of the casing. All pumps were started at the same time, and samples were collected simultaneously from each device six times during the tests. To collect samples with the bailer, it was lowered to the sampling depth and flushed five to 10 times by raising it about 3 feet and allowing it to fall back through the water column. The check ball would lift as the bailer descended, allowing the bailer to fill with water from the correct depth. After the bailer was withdrawn from the well, a bottom-emptying device was fitted to raise the check ball and drain the bailer while minimizing agitation and aeration of the sample. VOC concentrations in samples from

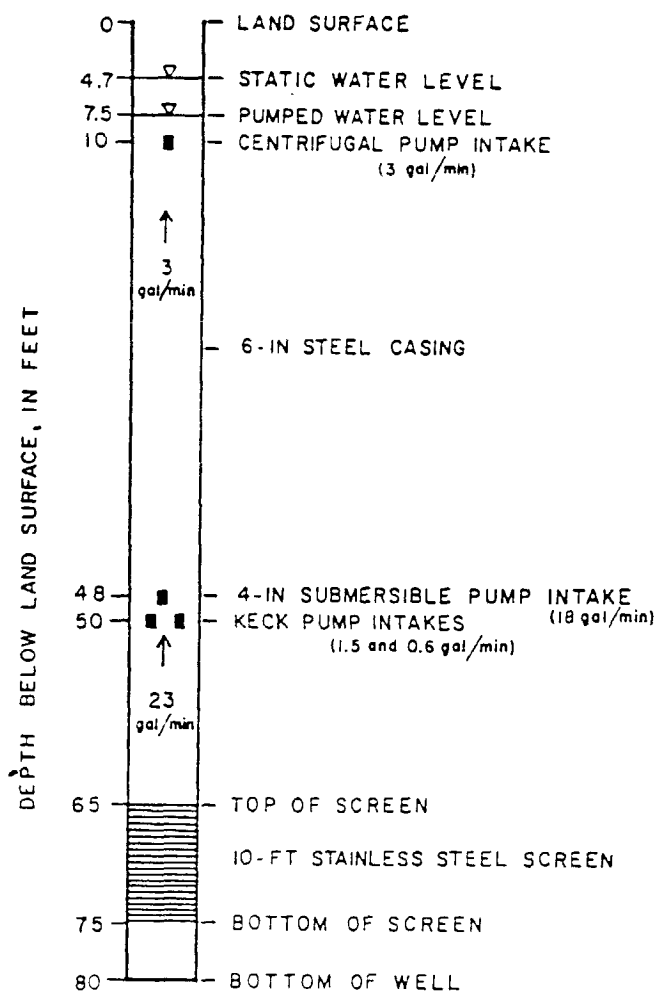

Figure 1. Pump positions in sampling Test 1 (Experimental data are given in Table 2)

each sampling device were compared to rev[illegible] differences among samplers. The experimental desig[illegible] is based on the assumption that VOC concentrations in the test well may change during the course of the experiment and that comparisons between samples from different samplers are valid only when the samples are collected at the same time.

In separate tests to evaluate changes in VOC concentration in monitoring wells during well casing evacuation and pumping, six wells were sampled at various intervals with the EPDM submersible pump during 15 three-hour pumping tests. Trichloroethylene concentrations, pH, specific conductance, and temperature of each sample were compared. The pump intake was placed just above the screened zone in the well for each of these tests, also.

Samples were collected in 40-mL glass vials that were sealed with Teflon-lined septa. The containers were filled in a manner that minimized aeration of the sample. This involved routing a slow, steady stream of sample water through a Teflon tube with the tube outlet below the water surface in the sample container. The 2-inch submersible and MasterFlex pumps were flushed after each sampling with 2 to 5 gallons of clean water. Samples of flush water (flush blanks) were collected and scanned by gas chromatography for VOCs to verify the cleanliness of the sampling equipment after each sampling test. Other equipment was rinsed with clean water and allowed to air dry before reuse. Field data recorded during each sampling experiment included initial water level, drawdown, pump intake depth, pumping time and flow rate. Field pH, specific conductance, and temperature were recorded at each sampling and also at frequent intervals during the initial stages of pumping.

Analytical Methods

Volatile compounds were stripped from water samples and preconcentrated by a Tekmar LSC-2 Liquid Sample Concentrator (purge and trap apparatus). Compounds were analyzed on a Varian Model 3700 Gas Chromatograph with a flame ionization detector (FID). The detector output was quantified with a Hewlett-Packard 3390A Digital Integrator. The use of an FID was the only modification to the analytical procedure described by the U.S. Environmental Protection Agency (Federal Register 1979). Error associated with comparison of samples referenced to differing standards or analyzed on different instruments was avoided by analyzing all samples from each experiment on the same instrument during as short a time as possible (six to 10 hours) and comparing peak areas directly. Samples were analyzed within two days after collection. One-third of all samples from each experiment were collected in duplicate and analyzed by the U.S. Geological Survey National Water Quality Laboratory in Atlanta, Georgia, according to procedures outlined in Wershaw et al. (1982) as a quality-control check on the identification and quantification of volatile compounds.

Statistical Methods

Concentrations of VOCs in samples collected from each of the sampling devices were compared through a paired-difference t-test on p[illegible]rs of concentration values obtained simultaneously [illegible]n different samplers at selected times during the pumping tests (Iman and Conover 1983). The null hypothesis of this statistical test is that no difference exists among concentration values from different samplers. The alternative hypothesis is that a set of concentration values from one sampling device is either larger or smaller than the corresponding set of paired values from a second device. The confidence level for detecting a significant difference in concentrations was set to 95 percent by using two-tailed test statistics from the Student's t-distribution. The paired-concentration differences for each sampler comparison were checked for normality by the Shapiro-Wilk W-statistic (Conover 1980); on the basis of these tests, the paired-data sets were assumed to be normally distributed (alpha = 0.05), which is necessary for the paired t-test.

Results and Discussion

Comparison of Sampling Devices

Submersible Pumps

In Table 2, gas chromatographic peak areas representing trichloroethylene concentrations in water samples collected by using the Viton and 4-inch submersible pumps can be compared to those in samples obtained by the EPDM pump for a representative experiment at well A (Test 1). The paired-difference t-test is used to determine if differences between these peak areas are significant. Figure 1 is a diagram of the arrangement of the pump intakes within the well in Test 1. Samples were obtained from each pump 5, 10, 20, 30, 45, and 60 minutes after the start of pumping. Concentrations of trichloroethylene and 1,2-dichloroethylene in samples from the EPDM submersible pump were 130 and 15 $\mu g/L$, respectively, in the 60-minute sample.

TABLE 2
Gas Chromatographic Peak Areas Representing Concentrations of Trichloroethylene Obtained from Three Sampling Systems in Test 1

Elapsed Time from Start of Pumping (minutes)	Keck SP-81 Pump with EPDM Stator and Teflon Tubing	Keck SP-81 Pump with Viton Stator and Teflon Tubing	Goulds 4-inch Submersible Pump with Teflon Pipe
5	137390	138090	139960
10	138600	145230	139620
20	138940	145320	139280
30	143150	135950	141880
45	138640	142810	139810
60	140010	142820	143250

No significant difference in trichloroethylene concentrations was found among samples from the three pumps in Test 1, but 1,2-dichloroethylene concentrations averaged 2 percent higher in samples from the 4-inch submersible pump than in samples from the EPDM pump, and this difference was statistically significant (α = 0.05).

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The well also contained 13 μg/L of 1,1-dichloroethane and no significant differences were evident among samples from the three pumps for this compound during Test 1. Results from all submersible pump comparison tests are summarized in Table 3.

The three submersible pumps were re-examined in well A during Test 3, with similar results. This time, concentrations of 1,2-dichloroethylene, trichloroethylene, tetrachloroethylene, and 1,1-dichloroethane in samples from the EPDM submersible pump were 41, 140, 14, and 10 μg/L, respectively, at 60 minutes. No statistical differences in concentrations of trichloroethylene, tetrachloroethylene, or 1,1-dichloroethane were evident among samples, but 1,2-dichloroethylene concentrations in samples from the 4-inch submersible pump and the Viton submersible pump averaged 3 and 4 percent higher, respectively, than in samples from the EPDM submersible pump.

The volume of water in the well casing above the samplers and the concentration of trichloroethylene in the ground water being sampled were varied by conducting sampler comparisons in different wells. In Test 2 (well B), trichloroethylene and tetrachloroethylene concentrations after 60 minutes of pumping were 6 and 37 μg/L, respectively, and no concentration differences were observed among samples from the three pumps. Tests 4 and 5 (wells C and D) were done in shallower wells with lower casing volumes. Test 4, where the 60-minute sample from the EPDM submersible pump contained 72 μg/L 1,2-dichloroethylene and 85 μg/L trichloroethylene, showed no statistical difference among the samplers. In Test 5, where the 60-minute EPDM submersible pump sample contained 36 μg/L 1,2-dichloroethylene and 20 μg/L trichloroethylene, samples from the Viton submersible pump were 16 percent higher in trichloroethylene and 14 percent higher in 1,2-dichloroethylene that those from the EPDM submersible pump, and this difference was statistically significant. Concentrations of

TABLE 3
Comparison of EPDM Submersible Pump with the Viton and 4-inch Submersible Pumps

Test Number	Well	Compound[a]	Sample Concentration After Pumping EPDM Submersible Pump 60 min (μg/L)	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: Viton Submersible Pump	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: 4-inch Submersible Pump and 1.25-inch Teflon Pipe
1	A	DCE	15	0	2
		TCE	130	0	0
		DCA	13	0	0
2	B	TCE	6	0	0
		PCE	37	0	0
3	A	DCE	41	4	3
		TCE	140	0	0
		PCE	14	0	0
		DCA	10	0	0
4	C	DCE	72	0	0
		TCE	85	0	0
5	D	DCE	36	14	0
		TCE	20	16	0
9	D	DCE	29	0	-15[c]
		TCE	23	0	-12[c]
10	D	DCE	17	—	0[d]
		TCE	19	—	0[d]

[a] DCE = 1,2-dichloroethylene; TCE = trichloroethylene; PCE = tetrachloroethylene; DCA = 1,2-dichloroethane.

[b] Zero indicates no statistically significant difference.
Minus sign indicates concentrations were less than those in samples from EPDM submersible pump.
—Indicates no data.

[c] 4-inch submersible pump outlet connected to 1.25-inch OD PVC pipe instead of Teflon pipe

[d] 4-inch submersible pump outlet connected to ⅝-inch OD plastic garden hose

volatiles in samples from the 4-inch submersible pump were not statistically different from those from the EPDM submersible pump, however. A second test at well D (Test 9) showed no statistical difference among samples from the Viton and EPDM submersible pumps.

In Test 9 (well D), the Teflon pipe that was usually used with the 4-inch submersible pump was replaced with 1.25-inch threaded PVC pipe. The resulting samples were 12 percent lower in trichloroethylene and 15 percent lower in 1,2-dichloroethylene than in samples from the EPDM submersible pump (the 60-minute samples from the EPDM submersible pump at this well contained 23 μg/L of trichloroethylene and 29 μg/L of 1,2-dichloroethylene). In Test 10 (well D), ⅝-inch ID plastic garden hose was substituted for the Teflon pipe, and concentrations in the resulting samples were not significantly different from those in samples from the EPDM submersible pump.

In all, six tests (Table 3) were conducted in which the EPDM and Viton submersible pumps were compared. Among 35 pairs of trichloroethylene concentrations, the only significant differences in concentrations were observed in Test 5, and these were not reproduced when the well was retested (Test 9). Twenty-nine pairs of 1,2-dichloroethylene concentrations were obtained in five tests. In three of these tests (Test 1 at well A; Test 4 at well C; and Test 9 at well D), concentrations did not differ significantly, but in the other two tests (Test 3 at well A and Test 5 at well D), concentrations in samples from the Viton submersible pump were 4 and 14 percent higher, respectively, than in those from the EPDM submersible pump. For 1,1-dichloroethane, similar to 1,2-dichloroethylene in physical properties, no differences between the two pumps were indicated by concentrations which ranged from 10 to 13 μg/L. Analyses of nine pairs of tetrachloroethylene samples from two experiments indicated no difference between the EPDM and Viton submersible pumps.

The EPDM and 4-inch submersible pumps were compared in five tests in which Teflon tubing or pipe was used. No significant differences between the samplers were indicated by 29 pairs of trichloroethylene concentrations from these tests. 1,2-dichloroethylene concentrations in 22 pairs of samples from four tests showed no significant differences between the two samplers in two of the tests; the other two indicated significant differences of less than 4 percent. Tetrachloroethylene concentrations in 12 pairs of samples from two tests showed no significant difference in sampling performance between the two samplers.

Centrifugal Pump

Results of four centrifugal-pump tests are summarized in Table 4. In three tests (no. 6 at well C, no. 7 at well D, and no. 11 at well E), the pump was equipped with a 1.25-inch Teflon pipe intake line. Trichloroethylene concentrations in samples from the centrifugal pump were 4 percent greater than those from the EPDM submersible pump in the first test, 8 percent lower in the second test, and not significantly different in the third test. 1,2-

TABLE 4
Results of Comparison Between EPDM Submersible Pump, Centrifugal Pump and Bailer

Test Number	Well	Compound[a]	Sample Concentration After Pumping EPDM Submersible Pump 60 min (μg/L)	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: Centrifugal Pump and 1.25-inch Teflon Pipe	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: Teflon Bailer
6	C	DCE	97	0	—
		TCE	82	4	—
7	D	DCE	60	-9	—
		TCE	36	-8	—
8	C	DCE	96	0[c]	0
		TCE	76	0[c]	0
9	D	DCE	29	—	-7
		TCE	23	—	-7
11	E	DCE	36	0	—
		TCE	58	0	—

[a] DCE = 1,2-dichloroethylene; TCE = trichloroethylene.

[b] Zero indicates no statistically significant difference.
Minus sign indicates concentrations were less than concentrations obtained from EPDM submersible pump.
—Indicates no data.

[c] ½-inch OD Teflon tubing was substituted in place of 1.25-inch OD Teflon pipe.

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dichloroethylene concentrations in samples from the centrifugal pump were the same as those in samples from the EPDM submersible pump in Tests 6 and 11 but were 9 percent less in Test 7. In Test 8 (well C), the centrifugal pump was used with ½-inch OD Teflon tubing, and results indicated no performance differences between the centrifugal and EPDM submersible pumps. Data from the centrifugal-pump tests showed significantly greater variability (larger standard deviations) than data from the other tests.

In Tests 6 (well C), 7 (well D), 8 (well C), and 11 (well E), the depths to water in the well during pumping were 6.9, 13.1, 6.0, and 24.5 feet, respectively. In Test 11, where water was close to the maximum depth at which a centrifugal pump can be effective, no significant differences were discerned between 1,2-dichloroethylene or trichloroethylene concentrations in duplicate samples from the EPDM submersible pump and the centrifugal pump with 1.25-inch Teflon pipe. In Test 8, which repeated the conditions of Test 6 but with a much narrower intake hose to restrict the flow rate and increase the head difference to which the pumped water was subjected, neither compound indicated a significant difference between the two pumps. Thus, a reduction of head to below atmospheric pressure by the centrifugal pump had negligible effect on 1,2-dichloroethylene and trichloroethylene concentrations in these tests.

Peristaltic Pumps

Two peristaltic pumps were tested simultaneously in different configurations in Tests 6 (well C) and 7 (well D); results are given in Table 5. One of the pumps was used with conventional ⅜-inch OD heavy-wall silicone tubing: the other was used with ½-inch Teflon tubing except for 3 feet of silicone tubing at the pump head, where the flexibility of the silicone tubing is required. All tubing was flushed with clean water between tests.

Trichloroethylene concentrations in samples from the peristaltic pump with all-silicone tubing were 16 and 14 percent lower in Tests 6 and 7, respectively, than in duplicate samples from the EPDM submersible pump, and 1,2-dichloroethylene concentrations were 12 and 8 percent lower. Trichloroethylene concentrations in samples from the peristaltic pump with Teflon tubing were 8 percent lower than in EPDM submersible-pump samples in Test 6 but not different from the EPDM submersible pump samples in Test 7; 1,2-dichloroethylene concentrations were the same as those in EPDM submersible-pump samples in both tests. The lower concentrations in samples from the first pump probably can be attributed to contact with the silicone tubing. Apparently, the slow flow rates of the peristaltic pumps and the narrow bore of the silicone tubing provide sufficient contact time for VOC sorption by the tubing material. Ho (1983) also observed significant sorption of organics by silicone tubing.

Bailer

The sampling performance of a Teflon bailer was compared to that of the EPDM submersible pump in Tests 8 (well C) and 9 (well D); results of these tests are given in Table 4. In Test 8, 60-minute samples from the EPDM submersible pump contained 96 μg/L of 1,2-dichloroethylene and 76 μg/L of trichloroethylene, and no significant difference was evident between samples from the EPDM submersible pump and samples from the bailer. In Test 9, in which water collected from the EPDM submersible pump after 60 minutes of pumping contained much lower VOC concentrations than Test 8 — 29 μg/L of 1,2-dichloroethylene and 23 μg/L of trichloroethylene—five samples from the Teflon bailer had 7 percent lower average concentrations of both constituents than the five corresponding duplicate samples from the EPDM submersible pump. This is the only test that indicated a decrease in the effectiveness of a sampling device with decreasing constituent concentrations, possibly indicating a systematic concentration loss that is more apparent at low concentrations.

Effect of Pump-Intake Placement

During initial experiments to compare samplers before the experimental design was finalized, the pump

TABLE 5
Results of Comparison Between EPDM Submersible Pump and Peristaltic Pumps

Test Number	Well	Compound[a]	Sample Concentration After Pumping EPDM Submersible Pump 60 min (μg/L)	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: Peristaltic Pump and Silicone Tubing	Deviation of Concentration from that in EPDM Submersible Pump[b], in Percent: Peristaltic Pump and Teflon Tubing
6	C	DCE	97	-12	0
		TCE	82	-16	-8
7	D	DCE	60	-8	0
		TCE	36	-14	0

[a] DCE = 1,2-dichloroethylene; TCE = trichloroethylene.

[b] Zero indicates no statistically significant difference.
Minus sign indicates concentrations were less than concentrations obtained from EPDM submersible pump.

intakes were located within the 10-foot screened zone of well C with the intention of ensuring minimum contact of sample water with the well casing. The EPDM submersible pump was placed toward the bottom of the well screen, the 4-inch submersible pump next, and either a centrifugal pump intake or the Viton submersible pump was placed above the 4-inch submersible pump, toward the top of the screened zone. In this first test (Test 12), no additional pump was used near the drawdown level in the well to flush the casing volume above the samplers, whereas when the test was repeated (Test 13), a centrifugal pump intake was used at the pumped water level to assist casing evacuation. In both tests, trichloroethylene concentrations in water collected by the pump with an intake at the top of the screen were about 30 percent lower than those from the pump whose intake was at the bottom of the screen. (See Table 6).

In a similar experiment at the same well (Test 4), the pump intakes were set between 5 and 8 feet above the top of the screen, and all samplers delivered identical samples. Apparently, VOC concentrations in the stratified deposits differ along the 10-foot screened zone at this site. The pumps in Tests 12 and 13 sampled different horizons within the screened zone, whereas the pumps in Test 4 were sampling a homogeneous mixture from above the screen. Thus, when a second pump is used above the sampling device to ensure flushing of the casing, the sampler intake must be placed in the casing above the well screen to obtain fully integrated samples at this site.

Changes in Trichloroethylene Concentrations During Pumping

Trichloroethylene concentrations changed considerably as wells were pumped during 15 three-hour pumping tests at three wells screened within a plume of trichloroethylene-contaminated ground water. Representative plots of the concentration changes during one test at each of these wells are shown in Figure 2.

Trichloroethylene concentrations increased continuously at well F, a 2-inch diameter well screened at 35 to 36 feet below land surface. Trichloroethylene concentrations increased most rapidly during the first 15 minutes of pumping, presumably because stagnant water in the casing was mixing with more highly contaminated aquifer water, and increased to a maximum of about 180 μg/L when pumping ceased after three hours. Field measurements of ground water temperature, pH, and specific conductance were stable after 20 minutes of pumping. At the pumping rate of 0.32 gal/min with the Viton submersible pump, three hours of pumping corresponds to a borehole evacuation of 20 casing volumes.

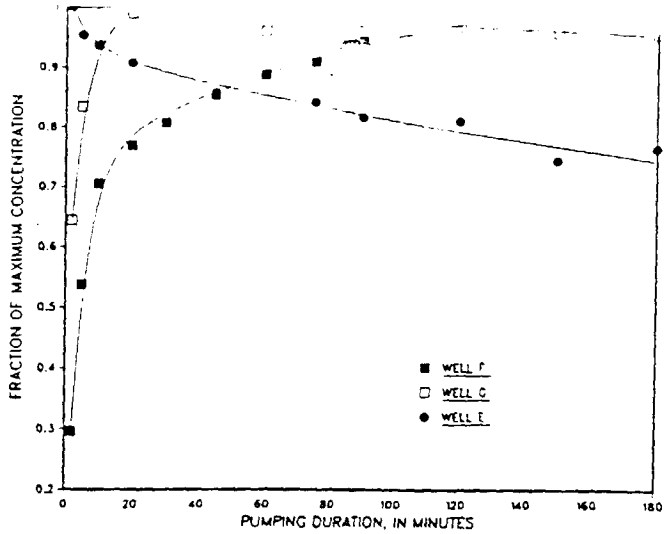

Figure 2. Changes in trichloroethylene concentrations during three-hour pumping tests at selected wells

Trichloroethylene concentrations at well G — another 2-inch well screened 35 to 36 feet below land surface —reached a maximum of 250 μg/L after 30 minutes of pumping and declined slightly thereafter. Field measurements of ground water temperature, pH, and specific conductance during this test stabilized after 10 minutes of pumping. At a pumping rate of 1.40 gal/min with the EPDM submersible pump, three hours of pumping corresponds to evacuation of 126 casing volumes.

Trichloroethylene concentrations at well E, a 4-inch

TABLE 6
Comparison of Trichloroethylene Concentrations in Samples from Well C Taken by the EPDM Submersible Pump with Those Taken by a Pump with Intake Placed Above the EPDM Submersible Pump

Test Number	Concentration in Samples from EPDM Submersible Pump After 60 Minutes of Pumping (μg/L)	Average Concentration Normalized to Concentration in Samples from EPDM Submersible Pump: EPDM Submersible Pump	Average Concentration Normalized to Concentration in Samples from EPDM Submersible Pump: Upper Pump
12	120	1.00[a]	0.68[b]
13	83	1.00[a]	.69[b]
4	85	1.00[c]	1.00[c]

[a]Pump intake at bottom of well screen
[b]Pump intake at top of well screen
[c]Pump intakes above well screen

well screened 48 to 53 feet below land surface, declined sharply in the first 20 minutes of pumping with the EPDM submersible pump (1.35 gal/min), and the decline continued through the end of the test, when a minimum concentration of 81 μg/L was recorded after 14 casing volumes had been evacuated.

Results of several sampling tests at well E indicate that the pattern of trichloroethylene concentrations during pumping may not be duplicated each time the well is sampled (Figure 3). The sampling procedures, equipment, and flow rate in these tests were identical, and ground water temperature, pH, and specific conductance were generally stable within 20 minutes of the start of pumping. One reason for the differing concentration trends (Figure 3) is that this well is influenced by periodic discharges of trichloroethylene-contaminated water at a recharge basin located hydraulically upgradient. In all 15 three-hour tests, the trichloroethylene concentration after 60 minutes of pumping was within 15 percent of the concentration reached after three hours of pumping.

The variability of trichloroethylene concentrations during pumping at these wells is an important consideration in designing a sampling protocol. A typical procedure for collecting representative samples of ground water is to evacuate a specified number of casing volumes, such as three, five, or 10, and to establish that field measurements of pH, specific conductance, and temperature have stabilized. These procedures are intended to ensure the sampling of fresh aquifer water. Yet, in each of the 15 tests above, field measurements were stable within 30 minutes of the start of pumping, after more than 10 casing volumes had been evacuated, and trichloroethylene concentrations were still changing after three hours of pumping. Thus, accepted practices of pumping a specific number of well casing volumes and obtaining stable field measurements before sampling did not ensure stable VOC concentrations in these monitoring wells. These concentration changes are not due to continued mixing with standing water from the casing. Casing water from wells A and B contained significant amounts of visually apparent oxidized iron particulate matter. When these wells were pumped, the turbidity cleared within about 10 minutes. These changes more likely were caused by local spatial and vertical variations in the trichloroethylene distribution and variations in hydraulic characteristics within the aquifer. Sampling protocols for wells that are sampled frequently should be designed to detect this variability.

Summary and Conclusions

Water samples collected by using the 2- and 4-inch diameter submersible pumps with Teflon tubing or Teflon pipe had similar concentrations of 1,2-dichloroethylene, trichloroethylene, and tetrachloroethylene. Small differences in sample concentrations sometimes noted between pumps were not reproducible but represent unexplained random variability. Samples collected by using a 4-inch submersible pump with PVC tubing averaged 12 percent lower in trichloroethylene and 15 percent lower in 1,2-dichloroethylene than samples collected by using an

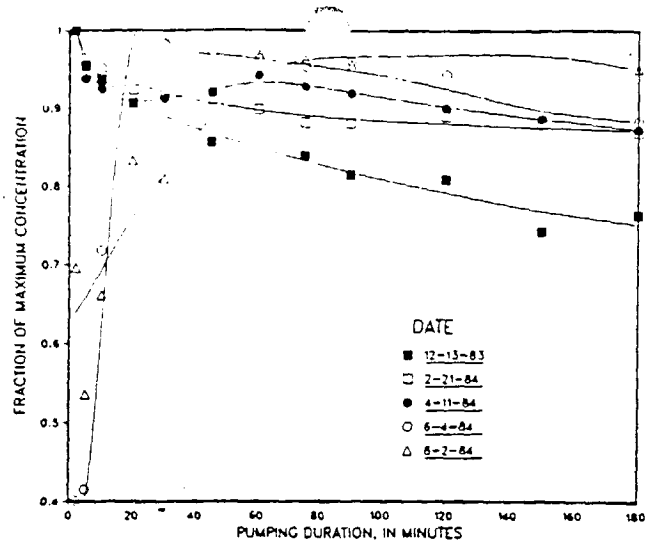

Figure 3. Changes in trichloroethylene concentrations during pumping tests at bimonthly intervals at well E

EPDM submersible pump and Teflon tubing, which indicates systematic bias. Thus, PVC tubing may be unsuitable for this type of sampling.

Concentrations in samples taken by a centrifugal pump and Teflon pipe or tubing were more variable (larger standard deviations) than in tests of other samplers. Statistically, however, concentrations in samples from a centrifugal pump were not significantly different from concentrations in samples taken by the submersible pumps. The effect of suction pumping (reduction of head to below atmospheric pressure) on VOC concentrations in samples was negligible in tests where depth to ground water was as much as 24.5 feet below land surface — close to the maximum that a centrifugal pump can lift — and when the flow to the centrifugal pump was restricted by small-diameter Teflon tubing.

Samples collected by using a peristaltic pump and silicone tubing contained significantly lower concentrations of 1,2-dichloroethylene and trichloroethylene than those taken by the EPDM submersible pump with Teflon tubing. When the silicone tubing was replaced with Teflon tubing (except for 3 feet of silicone tubing at the pump head), these losses were reduced. In one test where Teflon tubing was substituted for silicone tubing, trichloroethylene concentrations were reduced 8 percent, but in a second test, no differences in sample concentrations were detected. In both tests, 1,2-dichloroethylene concentrations in samples taken with the peristaltic pump were indistinguishable from concentrations in samples collected using the EPDM submersible pump.

Concentrations of 96 μg/L 1,2-dichloroethylene and 76 μg/L trichloroethylene in samples collected by using a Teflon bailer were the same as those in samples obtained by using the EPDM submersible pump. At lower levels (29 and 23 μg/L), however, concentrations in samples collected by bailer were 15 and 12 percent lower than those in samples from the EPDM submersible pump. This was the only clear indication of a concentration effect (loss at low concentrations that is not reproduced at higher concentrations) observed in the study.

Some erratic or non-reproducible concentrations

were observed in isolated samples from each sampling device. The unexplained va ility emphasizes the importance of repetitive sampling with careful control of all aspects of the sampling procedure to obtain reliable data.

In several tests of wells with short screens, field measurements of drawdown, specific conductance, pH, and temperature stabilized within five to 20 minutes of pumping, yet trichloroethylene concentrations failed to stabilize after one hour of pumping (the equivalent of five to 42 casing volumes). The changing concentrations were caused, in part, by mixing of fresh aquifer water with water standing in the well casing early in the test. However, local variations in the trichloroethylene distribution in the aquifer and in hydraulic characteristics of the aquifer near the well screen probably account for the changing concentrations later in the test.

Sample concentrations may be affected by pump-intake placement, pumping rate, and pumping duration, as well as VOC distribution in the aquifer system, which indicates a need to standardize sampling procedures for monitoring wells that are sampled repeatedly for trend analyses. Careful duplication of pump depth, flow rate, and pumping time are needed each time a well is sampled if trend data are to be reliable. A standardized system of sampling equipment and technique for each monitoring well will reduce the variability in concentration that results from pumping effects.

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Disclaimer

The use of brand and trade names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

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Volatilization Losses of Organics During Ground Water Sampling from Low Permeability Materials

by T.A. McAlary and J.F. Barker

Abstract

Volatilization biases that can affect a ground water sample before its collection from a monitoring well were evaluated in this study. Previous studies showed that volatilization losses during sampling of high permeability materials do not introduce unacceptable bias, except for the most volatile compounds. In low permeability materials, however, ground water must normally accumulate for hours to days after flushing before a volume sufficient for sampling is available. During this period, the ground water sample is open to the atmosphere and volatilization can lower the oncentration of volatile compounds in solution.

Laboratory simulations were conducted to evaluate this bias using four chlorinated, one- and two-carbon compounds. Two distinct conditions of headspace exposure were investigated: (a) the water standing in the well casing, and (b) formation water entering the screen of a well that has been dewatered during purging.

Water standing in the well was depleted in volatile organics by exponential decay with a half life of about four days. Volatilization losses will be less than 10 percent if the standing time is less than about six hours. In wells that have been purged dry, volatilization losses of 10 percent are likely in as little as five minutes as the recovering formation water trickles through the headspace in the dewatered sand filter pack. Losses may reach 70 percent for recovery periods of one hour. When the sand filter pack is drained by the purging procedure, the sample should not be analyzed for volatile constituents since volatilization biases are likely to be substantial.

Conventional open system monitoring wells should be used to collect volatile organic samples only if fresh formation water can be drawn into the well with minimal turbulence and exposure to the atmosphere. One should therefore avoid drawing the water level down into the sand pack when the well is purged. Specialized sampling methods should be developed and evaluated for volatile organics where sample integrity is critical.

Introduction

Contamination of ground water resources is an increasingly important concern from the viewpoint of water supply and public health. In geochemical investigations, care must be taken to ensure that sample collection methods do not excessively bias the chemical composition of the sample. This paper discusses volatilization biases that may affect a ground water sample during its residence in the monitoring well in low permeability materials prior to sample collection.

Organic compounds are being analyzed more frequently in geochemical investigations because of their increasing occurrence in ground water and their threat to public health. Volatile organics partition into the vapor phase whenever they are exposed to the open atmosphere or headspace. In a monitoring well, any exposure of the sample to headspace or to the open atmosphere has the potential to bias the sample chemistry. Volatilization biases can have significance if the losses result in an analysis that shows that an organic contaminant is not present or is present below a specified concentration criterion (Reynolds 1985).

Background

Dilling et al. (1975) studied the evaporation rates of several chlorinated hydrocarbons in continuously stirred, open containers. The compounds studied evaporated to the extent of 50 percent in less than 30 minutes. They concluded that 1.0 mg/L concentrations of low-molecular-weight, chlorinated hydrocarbons would not persist in agitated natural water bodies due to evaporation. Lyman et al. (1982) estimated environmental half lives between three and five hours for chlorinated one-and two- carbon compounds. They noted that the volatilization process depends on turbulence and duration of exposure to the gas phase. Many organics evaporate so quickly that any exposure to headspace must be considered a threat to the sample integrity until proven otherwise.

The standard monitoring well referred to in this paper consists of a 2-inch (5cm) diameter casing installed in a 7-inch (17.5cm) diameter hollow-stem auger hole. The bottom segment of the casing is slotted to allow water influx, and the borehole annulus in the slotted interval is filled with clean, coarse sand to keep fine-grained soil particles out of the well. The interval above the screen is sealed with swelling clay (bentonite) or similar material to hydraulically isolate the well screen from the remainder

of the borehole. The top of the well is open to the atmosphere to allow the formation water to rise in the casing to the piezometric surface (Figure 1).

Many authors, including Scalf et al. (1981), recommend that the standing water in a monitoring well be purged or flushed before the well is sampled. This induces the influx of fresh formation water into the well. Provided that suitable flushing methods are used, removal of two to three well volumes is sufficient to reach background conditions (Gillham et al. 1985). In materials of low hydraulic conductivity, the flow of ground water into a well is slow. Either the well and sand pack will be drained by purging or the well will only be drained to some level above the sand pack. If the sand pack is drained, the formation water will flow into the well by cascading through the headspace in the dewatered sand filter pack and some volatilization can be expected to affect the ground water even before a sample can be collected. This study was designed to determine the effects of such volatilization on the integrity of ground water samples.

Experimental Methods and Results

Contaminated ground water was simulated by mixing Trichloromethane (TCM), Trichloroethylene (TCE), 1,1,1-Trichloroethane (TCA) and Tetrachloroethylene (PER) in distilled and charcoal-deactivated (organic-free) water. These are among the most common ground water contaminants according to Westrick et al. (1984). Except where otherwise stated, the initial concentrations were about 500 +g/L for each test, a level chosen for ease of analysis. The typical ground water is not so chemically sterile but the stock solution is nonetheless expected to model real ground water fairly well. As Mackay (1983) noted, no interactions occur when solutes volatilize simultaneously.

All of the chemical analyses were performed by gas chromatography on the HP 5840A GC with a 10-foot long, 0.125-inch outside diameter column with a stationary phase of 3 percent SP1500 on a Carbopack B packing. The samples were analyzed by direct aqueous injection of 3+L. An external standard was used and the relative concentrations were determined by comparison of the peak areas integrated by the HP 5840A GC terminal. A flame ionization detector was used with a carrier gas of 5 percent methane and 95 percent argon. The column temperature was 185 C with a carrier gas flow rate of 30 mL per minute. A series of four to six replicates of the chromatographic analysis were performed on both the standards and the samples in order to provide statistically significant data.

The analytical variability was generally in the 5 percent to 10 percent range, expressed by the coefficient of variation (standard deviation divided by the mean). TCM showed the greatest analytical variability, averaging 7 percent, while PER showed the least variability, averaging 3 percent.

Volatilization from a Standing Column

An experiment was conducted to determine whether the water standing in a piezometer is likely to lose signifi-

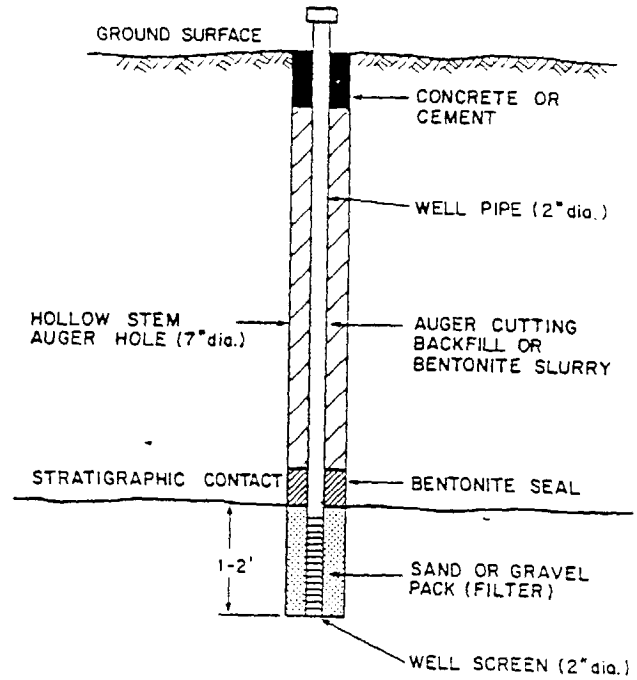

Figure 1. A conventional ground water monitoring piezometer

water stagnant in the piezometer pipe was modeled by a standing column made from a section of glass pipe, 4 feet (1.22m) long and 2 inches (5cm) in diameter. Glass was used to minimize adsorption. Sample ports were emplaced at various depths by fusing small screw-cap vials onto the side of the glass pipe. The sample ports were fitted with Teflon®-lined septa and plastic screw caps to enable sampling by microliter syringe with immediate analysis. The only exposure of the simulated ground water to the atmosphere during this test was at the surface area at the top of the water column. There were no bubbles in the system acting as a headspace sink.

Before the experiment, the glass pipe was cleaned using Extran (BDH Chemicals), nitric acid and organic-free water. The pipe was then filled using a Teflon tremie tube with the contaminant spike solution at about 500 +g/L concentrations that were allowed to volatilize for one month. The water in the column was tranquil with a calm surface. The ambient temperature was about 20 C, though Lyman et al. (1982) noted that volatilization is relatively temperature insensitive.

Samples were collected daily for 10 days and again after 32 days. All of the sampling ports were used intermittently during the experiment in order to determine the distribution of the volatile organics with depth. Calibration standards were prepared by volumetric dilution to match the initial concentration in the standing column and fresh standards were prepared every second day even though they did not change concentration by more than 10 percent over several days.

The standing column volatilization test showed first-order exponential decay of aqueous concentrations with approximately the same rate for all four of the compounds studied. These observations can be explained by reference to Lyman et al. (1982) and the two-layer theory of volatilization. Where the Henry's law constant (H) is greater than 0.001 atm*m^3/mol and the atmospheric concentration is negligible, the liquid-phase exchange

coefficient is independent of the value of .nd the volatilization proceeds by first-order decay. Diffusion in the liquid phase was apparently fast enough so that no significant concentration gradients developed in the column, which is consistent with Lyman's model. Figure 2 shows the depth-integrated average data graphically in a semilog plot. The slope is constant and equal to the first-order decay coefficient, k, as shown in Equation 1.

first-order decay:

$$N = Kl*C \quad (1)$$

where:

N = flux (g/cm^2*s)
kl = liquid-phase exchange coefficient (cm/s)
C = concentration in solution

which, for the initial condition C=Co integrates to:

$$C(t) = Co*e^{kt} \quad (2)$$

where:

C(t) = concentration in solution as a function of time
Co = initial concentration in solution
e = exponential log function
k = first-order decay coefficient (inverse time)
t = Time (in consistent units)

For the 2-inch (5cm) diameter standing column volatilization test, the first-order decay coefficient was:

$k = -1.27*10^{-4}\ min^{-1}$
$k = -0.18\ day^{-1}$

The results of the standing column volatilization test show that losses will reach 10 percent within about 12 hours and 99 percent in about one month (a common monitoring interval). The standing water in the well should therefore be thoroughly purged prior to sampling since it will not be representative of the in situ ground water chemistry. In the context of a sampling event, it may be acceptable for moderately low permeability materials to return for sampling of volatile organics several hours after purging a well, providing the calm surface of the water in the casing was the only exposure of the sample to headspace.

Volatilization During Recovery of Wells Drained by Evacuation

A second series of experiments, termed recovery tests, was conducted to quantify the mass losses resulting from volatilization during ground water flow into a drained well. The laboratory apparatus shown in Figure 3 was designed to model the screened interval of the well. All materials were selected to minimize adsorption. A 7-inch (17.5cm) diameter glass cylinder was used to simulate the standard hollow-stem auger borehole. A 2-inch (5cm) Teflon casing, with 2-feet (61cm) slotted and 1-foot (30.5cm) solid casing, was used as the well. Medium-grained quartz sand was used as the filter pack material. A 4-liter Teflon bag was used as a reservoir for the simulated ground water. It was connected via 3/16-inch Teflon tubing through a glass and Teflon valve to an

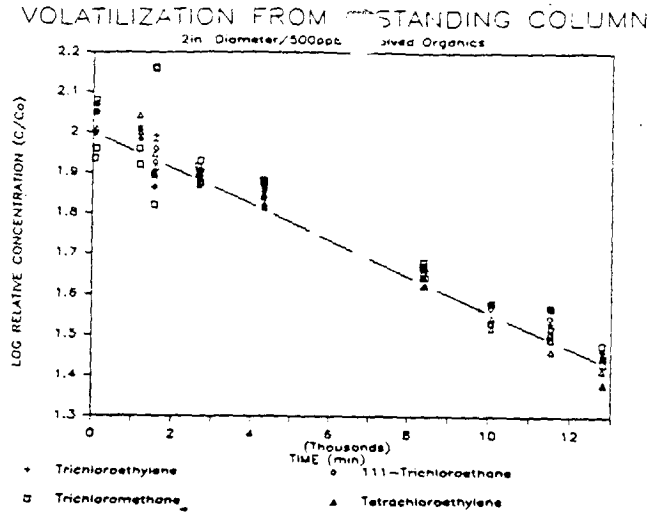

Figure 2. Volatilization from a standing water column

intake manifold inside the glass cylinder. The intake manifold was made of 3/16- inch Teflon tube, perforated every ¼ inch to allow uniform inflow around the perimeter of the model borehole.

All of the apparatus was cleaned before each test to remove traces of the organics using Extran, nitric acid and organic-free water. The filter sand was baked dry to drive off traces of organics.

A contaminated solution was prepared by volumetric dilution of the stock solution in organic-free water in the Teflon bag reservoir. After one hour of equilibration, the solution was allowed to flow into the well. Halfway through the recovery period, the reservoir standard was sampled by laminar flow into a vial with a Teflon septa for analysis. After complete refilling or recovery, the well

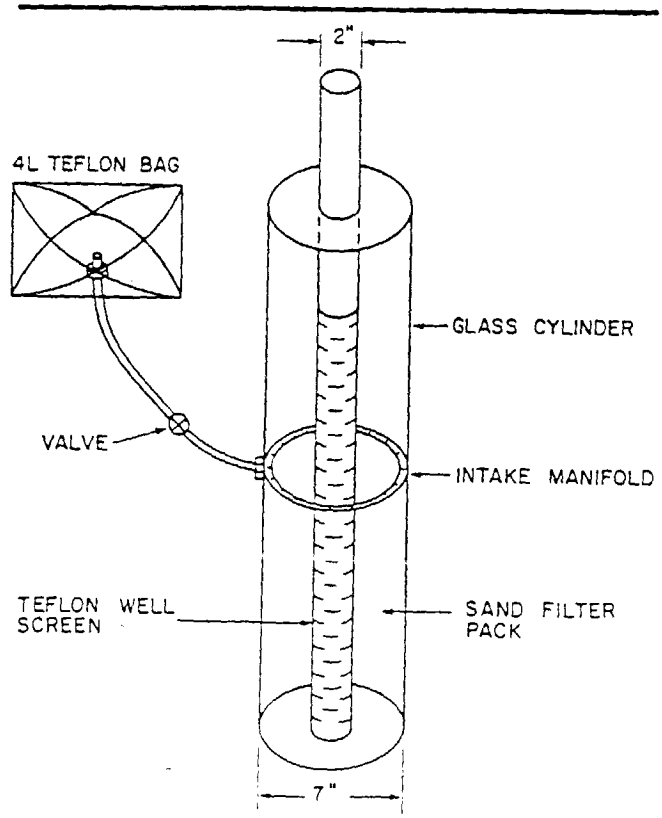

Figure 3. Laboratory model of the piezometer tip, 2-inch diameter, 50-+g/L dissolved organics

was sampled by siphoning through a Teflon tube. The first 10 mL of the sample were discarded because it was exposed to negative pressures during siphoning. The rest of the sample was drawn into an evacuated Teflon bag in a closed system to minimize volatilization. A vial sample was collected from the Teflon bag using the same method as for the standard. The sampling losses were subsequently measured in a sampling control test.

A total of seven recovery tests were performed to determine the effect of the inital concentration and the recovery duration on the rate of volatilization. Five tests were performed at the 500 +g/L level. The recovery durations were 4, 6, 30, 30, and 64 minutes. Two tests were performed at the 50 +g/L level, both for 70 minutes duration.

Experimental Controls

Experimental control tests were conducted to isolate each process contributing to the loss of volatiles in the recovery tests. To model the in situ well accurately, the raw recovery test data were corrected for biases that were relicts of the laboratory procedure. The principal processes examined were adsorption and volatilization; degradation was not considered important because of the short duration of the tests.

A batch test was conducted to estimate the degree of adsorption of each compound onto the sand filter pack adjacent to the well screen. The batch test was designed to match the recovery test as closely as possible in terms of the ratio of the volume of solution to the surface area of the solids. The test was conducted by filling two 150 mL vials with the 500 +g/L solution, adding clean sand to one of these vials and sealing both with Teflon-lined septa. Subsequent analysis of the solutions by chromatography showed that adsorption was 4 percent for TCM, 5 percent for TCA, 6 percent for TCE and 8 percent for PER, over 70 minutes. Similar relative losses were assumed to occur during the recovery tests. A conservative estimate of the volatilization losses was then calculated by subtracting the sorptive losses from the gross mass loss data.

A second batch test was conducted to correct the recovery test data for the losses resulting from adsorption onto the tubing (FEP Teflon) and the well casing (TFE Teflon). Although Teflon is extremely non-reactive, Reynolds (1985) found that some chemicals (particularly PER) will adsorb significantly onto the surface. The manufacturers reported no difference in the reactivities of the two types of Teflon, so the batch test results were assumed to provide similar adsorptive losses for both cases. Adsorption onto the Teflon tubing ranged from -3 percent to +9 percent over 70 minutes. The negative value probably represents analytical variability since the tubing was cleaned thoroughly before testing and is not expected to have leached any chemicals. The adsorptive losses for TCM, TCE and TCA were smaller than their respective analytical variabilities so their adsorption onto the Teflon tubing was neglected. PER was more strongly sorbed, so the recovery test data were corrected for its adsorption onto the Teflon by subtracting 9 percent from the gross recovery test losses.

A third test was performed to measure the loss of volatiles during sampling of the laboratory well. This test used all the same materials and procedures as the sampling of a standard recovery test, with the exception that the recovery process was omitted and the sample was taken directly from the Teflon bag reservoir. The results showed negative biases in the range of 10 percent to 14 percent. The sampling procedure was the least repeatable part of the recovery tests so the sampling control test results cannot be applied uniformly to each recovery test. The major source of variability was the amount of headspace to which the sample was exposed. The sample was collected in an evacuated Teflon bag but it was not possible to completely prevent air from entering the bag. Estimates of the volume of the air bubble were used to calculate the sampling losses using the equilibrium headspace equations of Pankow (1985) as shown below.

$$C/Co = 1 - \frac{1}{(H/RT * Vg/Vs) + 1} \qquad (3)$$

where:

C/Co = Relative concentration (dimensionless)
H = Henry's law constant (atm*m^3/mol)
R = Ideal gas constant (L*atm/mol*K)
T = Temperature (K)
Vg = Volume of headspace (mL)
Vs = Volume of solution (mL)

Pankow's headspace equation assumes equilibrium conditions so the sample was mixed mechanically to expedite equilibrium before the aliquot was drawn. The sampling losses ranged from 0 percent to 5 percent for TCM, 0 percent to 11 percent for TCE, 4 percent to 30 percent for TCA, and 9 percent to 27 percent for PER.

Two recovery tests were performed with presoaked conditions to determine whether the field conditions can be accurately modeled by recovery into a dry-well. The laboratory recovery tests were performed using a piezometer that was initially completely dry, but this is no strictly the case in wells in the field, because surface tension will always hold some residual water saturation after drainage. The procedure for the presoaked recovery tests was the same as for the dry recovery tests except that the contaminated solution was first poured slowly into the model well, allowed to equilibrate for about one hour and then withdrawn into the Teflon reservoir bag. The solution was then allowed to refill as usual. After being corrected for the dilution by the residual water, the losses are consistent with the other recovery tests so the laboratory method is presumed to be valid.

After conducting the control tests, the net volatilization losses during recovery were calculated by subtracting both the best estimates of the adsorptive losses, based on the sand and Teflon batch tests and the results of Reynolds (1985), and the sampling losses, as previously described. The estimates have been made conservatively so that the corrected recovery test data show minimum values of the expected volatilization losses. The results of the recovery tests are shown in Figure 4.

Significant volatilization l s can occur during ecovery if the piezometer tip is drained before sampling. The net losses ranged from 2 percent to 68 percent for recovery periods of five to 70 minutes. The corrections from the control tests ranged from about 5 percent to 20 percent, depending on the compound, but were generally less than half the magnitude of the net volatilization losses. The spread in the net loss data is most likely caused by both the analytical variability and variations in the amount of turbulence and exposed surface area during recovery. This was uncontrollable in the laboratory and will undoubtedly have a similarly variable effect on field monitoring data. The magnitudes of volatilization losses were ordered in the same sequence as predicted by Lyman et al. (1982), which supports the results of the recovery tests.

Conclusions and Recommendations

Volatilization losses from the standing water in a two-inch (5cm) diameter well casing can affect the concentration of dissolved organics in the monitoring well. For compounds with Henry's law constants greater than 0.001 atm*m^3/mol, the losses follow a first-order decay where the decay constant is about 0.18 inverse days. Diffusion of low molecular weight organics in the liquid phase is rapid enough that the effect of volatilization losses will spread throughout the well.

If a monitoring well is drained completely during the purging process, the formation water will encounter exposure to the atmosphere as it cascades through the headspace in the sand filter pack during recovery. This may cause 10 percent losses of highly volatile compounds in as little as five minutes and losses of up to 70 percent in about one hour. Accurate modeling of the volatilization losses for different recovery durations is not practical because of unpredictable hydrodynamics of the recovery event, but it is important to be aware that they are very likely to occur.

Sampling methods, particularly well flushing or purging, can affect the concentrations of volatile organic contaminants in ground water samples. Protocols should avoid draining the well and any unnecessary exposure of the sample to the atmosphere, especially when combined with turbulence. A new sampling method should be developed if this objective cannot be met with current methods, especially for sampling of low permeability materials.

Acknowledgments

Many thanks to the following people for their assistance in this study: Ralph Dickhout for his assistance in the laboratory, Dave Smyth and Denys Reades of Golder Associates for advice and encouragement, and John Cherry for editing and coordinating NSERC and Golder Associates with the University of Waterloo.

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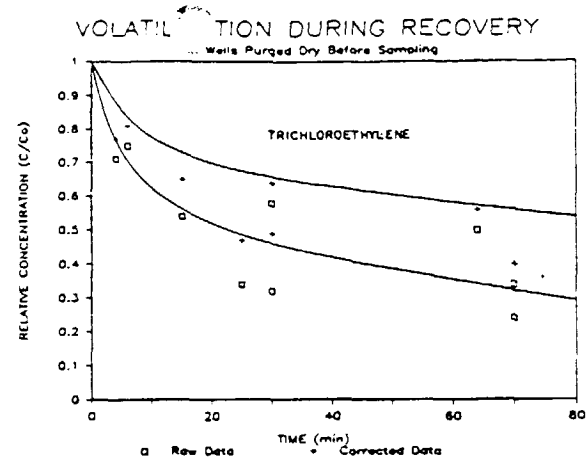

Figure 4a. Trichloroethylene

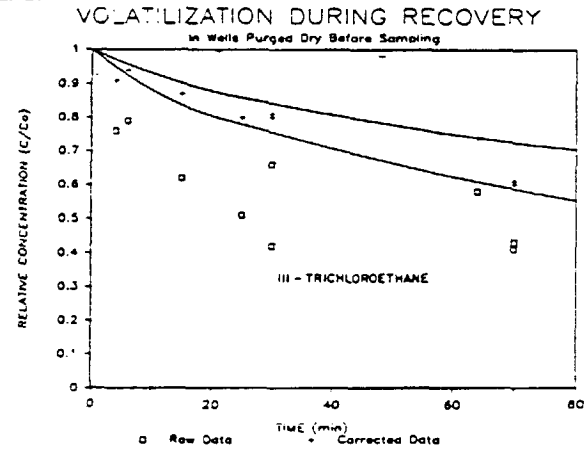

Figure 4b. 1,1,1-Trichloroethane

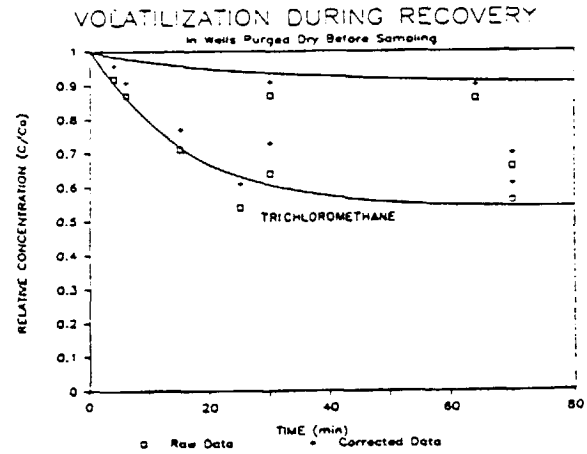

Figure 4c. Trichloromethane

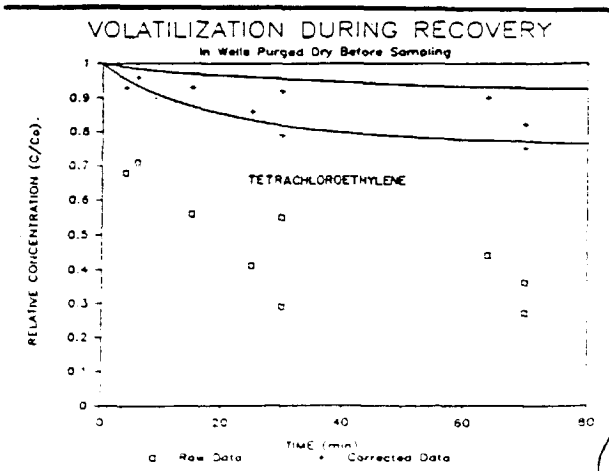

Figure 4d. Tetrachloroethylene

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Biographical Sketch

T.A. McAlary is a student pursuing a master's degree in hydrogeology from the Earth Sciences Department, University of Waterloo. He received his B.A.Sc. in geological engineering from Waterloo in April 1986, having completed this study as his undergraduate thesis. He has two years work experience in hydrogeology from undergraduate cooperative work. terms. He is continuing research in the area of volatile organics in ground water for his master's project.

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DAVE MARK

The Use of a Standpipe to Evaluate Ground Water Samplers

by Doreen Y. Tai, Kenneth S. Turner, and Lisa A. Garcia

Abstract

A standpipe system was developed for testing the reliability of ground water samplers. The unit consists of a stainless steel pipe 5 inches (13 centimeters) in diameter and 100 feet (30.5 meters) in height. It has 14 sampling ports from which control samples can be withdrawn at the same time and position as the samples are collected by a sampler lowered to that position. Test solutions were made in two mixing tanks, totaling 260 gallons (980 liters), by diluting the concentrate of five volatile chlorohydrocarbons in water at two levels of concentration: 10-to-30 and 100-to-200 parts per billion (micrograms per liter).

A gas chromatograph interfaced with a purge-and-trap system was used to perform the analyses. Comparisons of the control samples with the sampler-collected samples have indicated that the three non-pumping samplers had recoveries in the range of 92.4 to 103.5 percent and the three pumping samplers had recoveries ranging from 97.7 to 101.5 percent.

Introduction

Many kinds of sampling devices are available for collecting ground water samples for the determination of volatile organic compounds (VOCs) (Pohlmann and Hess 1988). A frequent concern has been the ability of these devices to obtain samples representative of the actual in situ ground water quality with good precision. This concern is especially important when samples are taken from ground water monitoring wells because no means are available to obtain information on the actual in situ concentration. Many investigations of the performance of sampling devices have been based on the precision of sampling in existing wells (Imbrigiotta et al. 1988, Nielsen and Yeates 1985, Pearsall and Eckhardt 1987). Barker and Dickhout 1988, have reported on the evaluation of several samplers for gas-charged ground water. The use of a standpipe has been previously reported by Barcelona et al. (1984) and Schalla et al. (1988).

This paper describes a standpipe system that was developed for testing the ability of samplers to deliver representative ground water samples. The standpipe has sampling ports from which samples can be withdrawn at the same time and at the same position as those collected by the sampler. Comparison of the results of analyses for the control samples and the collected samples makes possible the evaluation of not only the precision through repetitive sampling, but also the accuracy as indicated by the percent recovery values of the sample collection.

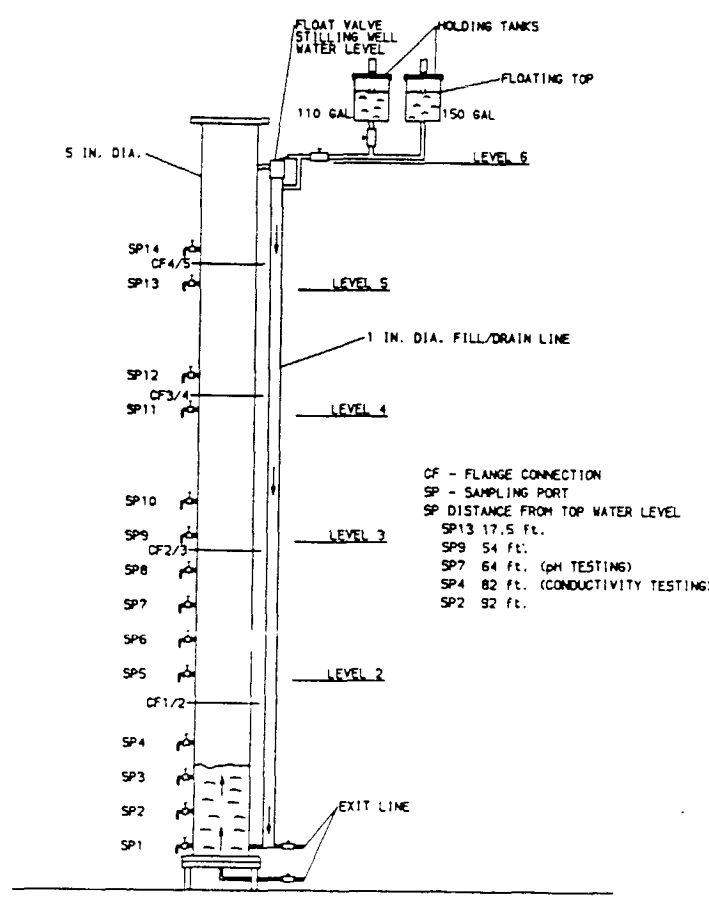

Figure 1. The standpipe system.

Standpipe

The standpipe system (Figure 1) consists of three

parts: the standpipe, the fill-drain line, and the mixing tanks. All the materials in contact with the test solution in this system are stainless steel. A description of these parts follows:

The standpipe is a stainless steel pipe (316, Schedule 10), 5 inches (13cm) in diameter and 100 feet (30.5m) in height, installed vertically inside a six-story building. The standpipe consists of five 20-foot (6m) sections with flange-bolt connections. Along the length of the pipe are 14 sampling ports for collecting control samples at various water depths. Each sampling port consists of a 1/4-inch (6mm) needle valve with a piece of right-angle tubing attached to the end for draining the water sample into a vial. A stilling well is attached to the standpipe at 30 inches (75cm) from the top. A floating valve is installed inside the well and connected by a tee to the fill-drain line for controlling the water level in the standpipe.

The fill-drain line, a 1-inch (2.5cm) diameter stainless steel pipe, is installed alongside the standpipe. The bottom end is connected by a tee to the drain valve on the bottom of the standpipe. The top end is connected by a tee to the mixing tanks and stilling-well floating valve at the sixth-floor level.

The mixing tanks are two stainless steel tanks with a total capacity of 260 gallons (980L). Each tank is equipped with a variable speed mixer, a floating top, and a cover. The tanks are connected to each other by a 1-inch (2.5cm) line. The floating top is made of a thin sheet of stainless steel with a 2-inch (5.0cm) lip welded around the outer rim of the sheet. This top, which floats on the surface of the test solution, eliminates the headspace and prevents the loss of volatile organics. The top has a 4-inch (10cm) diameter opening for introducing stock solution into or collecting water samples from the tank. This opening is covered with a piece of aluminum foil.

Samplers

Three non-pumping samplers and three pumping samplers were evaluated in this study. These samplers represented several major types of sampling devices.

Non-Pumping Samplers:

- Teflon® bailer — double check valve, point-source sampler, length 14 inches (35cm), with controlled-flow bottom-emptying device, manufactured by Norton Inc., Wayne, New Jersey
- Manual-driven piston sampler — U.S. Geological Survey prototype sampler (Ficken 1988)
- Motor-driven piston sampler — U.S. Geological Survey prototype sampler (Ficken 1988).

Pumping Samplers:

- Submersible pump — stainless steel helical rotor submersible Keck pump Model SP-81 with stainless steel rotor and Viton stator, manufactured by Keck Geophysical Instruments Inc., Williamston, Michigan
- Peristaltic pump — Cole Parmer MasterFlex variable speed pump, marketed by Cole-Parmer Instrument Co., Chicago, Illinois
- Bladder pump — ISCO series 3600, manufactured by ISCO Inc., Lincoln, Nebraska.

Test Solutions

The five volatile organic chemicals selected for this study were methylene chloride (MCL), 1,1-dichloroethene (1,1-DCE), 1,2-dichloroethane (1,2-DCA), trans-1,2-dichloroethene (t-1,2-DCE) and 1,1,1-trichloroethane (1,1,1-TCA). These are among the chemicals most frequently detected in ground water (Plumb 1987). A 30-fold concentrate stock solution of these compounds was prepared in the laboratory one day before an experiment. Aliquots of each desired chemical solution were injected into a 13L carboy containing natural-quality ground water. The artesian well from which the ground water was taken was 1500 feet deep; the ground water was analyzed by gas chromatography and found to be free of the five compounds.

The solution with the five compounds was poured through the opening of the floating top into the mixing tank containing dilution water. The solution was further stirred for one hour by a mixer (300 rpm) before being released to the standpipe. Concentrations of the stock solutions were such that two concentration levels were produced in the mixing tank, depending upon how the stock solution was made. The low concentration level was in the range of 10 to 30 micrograms per liter (μg/L) and the high concentration level was in the range of 100 to 200 μg/L of each compound.

Analytical Method

A gas chromatograph (GC), Hewlett Packard Model 5890 with a flame ionization detector interfaced with a Tekmar LSC-2 (liquid sample concentrator) purge-and-trap system, was used for the analyses of water samples. The GC column was a coiled stainless steel tubing, 6 feet (1.8m) long and ⅛ inch (3mm) in diameter, packed with SP-1000 on Supelcoport. Temperature programming from 60 C to 100 C (140 F to 212 F) at a rate of 5 C (9 F) per minute was used. Helium was used as the carrier gas, at a flow rate of 30 mL/min (0.008 gal/min). The analytical methodology was essentially based upon Environmental Protection Agency Method #601 (U.S. Environmental Protection Agency 1984).

Water samples of 5 to 10mL were used for the analyses. Samples were collected in 40mL vials sealed with Teflon-faced septa and plastic screw caps. Samples were stored in a refrigerator at a temperature of 5 C (41 F) until analysis, which usually was completed within one week.

Precision and recovery of the purge-and-trap system were determined. The recoveries ranged from 83 to 89 percent for the five compounds. Precision was determined from a set of 20 samples collected from sampling port No. 2 (depth 28m [92 feet]) and stored in a refrigerator. Duplicate analyses (two vials) were conducted daily for 10 days. The percent relative standard deviations of all 20 samples ranged from 0.38 to 1.06 percent for the five compounds. These results also indicated that the samples could be stored for 10 days with no apparent changes in concentrations.

Tests and Discussions

Standpipe System Test

The standpipe system was tested for two factors: (1) the uniformity with depth of the chemical concentration in the standpipe, because there was no mixing mechanism in the standpipe, and (2) the stability with time of the chemicals in the standpipe and the mixing tanks.

The standpipe was filled with well-mixed test solution by gravity flow from the mixing tanks through the fill-drain line to the bottom of the standpipe. The float valve automatically shut off when the test solution reached the set level in the upper part of the standpipe. Filling the standpipe took about 15 to 18 minutes. About 30 minutes was allowed for the solution to reach equilibrium in the standpipe. Samples were then collected at 12 water depths through the appropriate sampling ports. The first 20mL of the solution was discarded; then the samples were collected in 40mL glass vials with Teflon-faced septa and plastic screw caps. Samples were collected with care so that no air bubbles were allowed in the vials. Four sets of samples were collected at one, three, five, and 24 hours after the 30-minute equilibrium period. The samples were refrigerated until analysis. Table 1 presents the detailed results at various depths of one set and Table 2 gives a summary of all four sets.

The concentration of methylene chloride, trans-1,2-dichloroethene and 1,2-dichloroethane were quite uniform. However, 1,1-dichloroethene and 1,1,1-trichloroethane showed a slight decrease in concentration with decreasing depth. This means that it is important to take the control samples at the same position and time with the sampler. As shown in Table 2, the percent relative standard deviations ranged from 0.33 to 2.48 for the five compounds. The results indicated that the standpipe system was enclosed well with no obvious decrease in chemical concentration in 24 hours.

Twelve of the 14 sample ports were used for sampling

TABLE 1
Vertical Distribution of the Compounds in the Standpipe 1 Hour After Equilibrium

Water Depth (ft)	MCL (μg/L)	1,1-DCE (μg/L)	t-1,2-DCE (μg/L)	1,2-DCA (μg/L)	1,1,1-TCA (μg/L)
97	132.7	172.9	165.5	135.0	210.8
92	132.5	174.8	165.8	135.7	208.3
87	131.1	170.6	163.8	133.9	208.3
72	131.7	171.1	163.8	135.5	205.3
68	129.1	164.7	160.5	132.7	202.5
59	131.2	165.4	161.8	135.3	202.4
54	132.5	164.9	163.3	135.8	204.5
49	131.2	161.9	161.1	135.3	201.9
35	128.6	157.2	157.0	133.4	193.8
31	130.9	158.5	160.2	134.8	198.8
17.5	129.1	149.7	155.6	133.9	189.4
13	129.1	147.6	154.4	134.0	187.0
Mean	130.8	163.3	161.1	134.6	201.01
S	1.48	8.74	3.75	1.00	7.54
% RSD	1.13	5.35	2.33	0.74	3.75

S = Standard deviation.
% RSD = Percent relative standard deviation.

TABLE 2
Stability of the Compounds in the Standpipe

Time (Hour)	MCL (μg/L)	1,1-DCE (μg/L)	t-1,2-DCE (μg/L)	1,2-DCA (μg/L)	1,1,1-TCA (μg/L)
1	130.8	163.3	161.1	134.6	201.1
3	130.8	163.6	160.2	134.4	200.2
5	131.7	154.1	158.4	136.2	190.8
24	130.9	163.4	161.1	134.7	200.5
Mean	131.1	161.1	160.2	135.0	198.2
S	0.44	4.7	1.3	0.83	4.91
% RSD	0.33	2.9	0.8	0.61	2.48

* Values are means from 12 sampling ports.
S = Standard deviation.
% RSD = Percent relative standard deviation.

and the other two ports (ports Nos. 4 and 7, respective depths at 25 and 19.5 m [82 and 64 feet]) were used to monitor the pH and conductivity of the test solution in the standpipe. The pH and conductivity were stable at a pH of about 8.5 and a conductivity of about 400 microsiemens per centimeter (μS/cm).

The stability of the chemical concentrations in the mixing tanks was also tested. Both tanks were filled with water and then the concentrated chemical solutions were added. The tanks were covered, and the solutions were mixed at a mixer speed of 300 rpm for about one hour. Samples were collected in 40 mL glass vials by siphoning with a stainless steel siphon tube from about mid-depth of the tank through the opening of the floating top. After mixing, samples were collected at zero, one, three, and 22 hours. The analytical results of the mixing tank samples are presented in Table 3. The percent relative standard deviation ranged from 0.31 to 1.54 percent, indicating that the chemicals were stable over a 22-hour period in the tanks. The floating cover and the tank cover were apparently sufficient to prevent the escape of these volatile organic compounds from the water.

This well-enclosed system allowed enough time to conduct the sampler test without having to consider the possible loss of organic concentration during the test period. The results established that a competent test for the sampling devices could be performed with this system.

Non-Pumping Sampler Test

Each of the non-pumping samplers was lowered with a Teflon-coated cord into the standpipe to the desired position. Samples were taken with the sampler, and at the same time and same position, a control sample was collected through the sampling port with a 40 mL glass vial. For each sampler, samples were collected at depths of 5.3, 16.5 and 28 m (17.5, 54, and 92 feet). The sampler was lowered five times to the same position to take five replicate samples. Two concentration levels were used for these tests.

Concentrations of the five compounds with five replicate samplings showed percent relative standard deviation ranging from 1.42 to 3.38 percent for the bailer, 0.43 to 2.07 percent for the manual-driven sampler, and 0.74 to 1.70 percent for the motor-driven sampler. The precisions of the five replicate samplings were considered adequate; therefore, a mean value of each set of five replicates was used as the value for the evaluation of the samplers. Table 4 is an example of the detailed results for the low concentration test at three depths for the three non-pumping samplers.

The performance of each sampler was evaluated by percent recovery values, which are calculated using the following formula:

$$\text{Percent Recovery} = \frac{\text{Concentration } (\mu g/L) \text{ using Sampler}}{\text{Concentration } (\mu g/L) \text{ of Control}} \times 100$$

The percent recovery values of the low concentration are listed in Table 4. The overall averages ($\bar{X}$) of percent recovery values for five compounds are also listed in Table 4. The average of percent recovery values for two levels of concentrations and at three depths for the three non-pumping samplers are listed in Table 5. A set of samples was not collected with the manual-driven piston

TABLE 3
Stability of the Compounds in the Mixing Tanks

Time Hour	MCL (μg/L)	1,1-DCE (μg/L)	t-1,2-DCE (μg/L)	1,2-DCA (μg/L)	1,1,1-TCA (μg/L)
Tank A					
0	132.8	185.8	172.3	138.1	218.9
1	133.8	184.8	173.8	138.6	223.3
3	133.9	184.8	173.7	139.8	223.7
22	133.1	184.5	173.4	138.6	222.5
Mean	133.4	185.0	173.3	138.8	222.1
S	0.54	0.57	0.69	0.72	0.99
% RSD	0.37	0.31	0.40	0.52	0.99
Tank B					
Time Hour	**MCL (μg/L)**	**1,1-DCE (μg/L)**	**t-1,2-DCE (μg/L)**	**1,2-DCA (μg/L)**	**1,1,1-TCA (μg/L)**
0	133.4	170.2	165.3	134.7	208.9
1	134.0	172.9	166.1	135.0	208.0
3	134.5	172.5	166.6	136.4	208.5
22	131.7	167.1	162.8	133.8	205.8
Mean	133.4	170.7	165.2	135.2	207.8
S	1.22	2.64	1.69	1.20	1.38
% RSD	0.92	1.54	1.02	0.88	0.67

S = Standard deviation.
% RSD = Percent relative standard deviation.

TABLE 4
Evaluation of Non-Pumping Samplers, Low Concentration Study, μg/L*

Compound	Bailer	Control	Recovery %	Manual Driven	Control	Recovery %	Motor Driven	Control	Recovery %
				Water Depth 17.5 Feet					
MCL	10.6	11.9	89.1	10.9	10.9	100.0	10.5	11.5	91.3
1,1-DCE	18.3	19.3	94.8	19.8	19.4	102.1	17.8	19.2	92.7
t-1,2-DCE	19.0	19.6	96.9	20.3	19.8	102.5	18.7	19.7	94.9
1,2-DCA	12.3	13.3	92.5	13.6	12.9	105.4	14.6	13.2	110.6
1,1,1-TCA	23.9	24.8	96.4	25.1	24.9	100.8	23.9	24.6	97.2
$\bar{X}$			93.9			102.2			97.4
				Water Depth 54 Feet					
MCL	10.6	11.8	89.8	11.6	12.0	96.7	11.2	11.8	94.9
1,1-DCE	19.5	21.2	92.0	22.2	21.3	104.2	20.5	21.1	97.2
t-1,2-DCE	19.8	21.3	93.0	22.0	21.1	104.3	20.5	21.0	97.6
1,2-DCA	12.8	13.7	94.1	14.1	13.4	105.2	15.0	13.4	111.9
1,1,1-TCA	25.1	27.0	93.0	27.6	27.0	102.2	25.9	26.6	97.4
$\bar{X}$			92.4			102.5			99.8
				Water Depth 92 Feet					
MCL	10.6	11.2	94.6	11.7	11.2	104.5	11.4	11.3	100.9
1,1-DCE	20.3	22.4	90.6	22.6	22.4	100.9	22.0	22.4	98.2
t-1,2,-DCE	20.3	21.5	94.4	22.0	21.6	101.8	21.7	21.7	100.0
1,2-DCA	13.1	13.8	94.9	14.1	13.5	104.4	14.4	13.6	105.9
1,1,1-TCA	25.8	27.6	93.5	27.9	27.9	100.0	27.6	27.8	99.3
$\bar{X}$			92.7			102.3			100.9

* Each value is the average of the five replicate samples in terms of mg/L.
$\bar{X}$ = average percent recovery of five compounds.

TABLE 5
Percent Recoveries of Non-Pumping Samplers

Sample	Water Depth 17.5 Ft Recovery %	Water Depth 54 Ft Recovery %	Water Depth 92 Ft Recovery %
	Low Concentration (10 to 30 μg/L)		
Control	100.0	100.0	100.0
Bailer	93.9	92.4	92.7
Manual-Driven Piston	102.2	102.5	102.3
Motor-Driven Piston	97.4	99.8	100.9
	High Concentration (100 to 200 μg/L)		
Control	100.0	100.0	100.0
Bailer	96.3	93.9	91.4
Manual-Driven Piston	—	101.1	103.5
Motor-Driven Piston	96.8	98.4	100.7

sampler at high concentrations due to the lack of supply of sampler cylinders at the time of collection. This value is, therefore, missing in Table 5.

As shown in Table 5, the bailer consistently gave lower concentrations than the control for all five compounds, with percent recoveries ranging from 92.4 to 93.9 percent. Samples collected by the bailer also showed more variation for the five replicate sample analyses. During the sample transfer from the bailer to the sample vials, a flow-controlled bottom-emptying device was used. However, air bubbles introduced into the bailer during insertion of the bottom-emptying device may have caused degassing of the volatiles. This and the operator's technique may have contributed to the lower concentrations and poorer precision. These present observations agree with the results reported by

Pearsall and Eckhardt (1987) and Sonntag (1987).

The manual-driven piston sampler gave slightly higher sample concentrations than the control (101.1 to 103.5 percent recovery). This sampler had an attached stainless steel sample cylinder that could easily be sealed and detached. A water sample was kept in the cylinder and refrigerated until analysis. The water sample could be transferred into a syringe through a septum by a screw press device. The sample could be injected into the GC with a syringe without going through the glass sample vial. This operation saves one step of sample transferring; thus, there was less chance of losing the volatiles. The water sample in the cylinder was also under water-column pressure. This may have caused a slightly higher concentration than the concentration determined in the control samples.

When the motor-driven piston sampler was used, the water sample was transferred by a pressure device

TABLE 6
Evaluation of Pumping Samplers, High Concentration Study, μg/L*

Compound	Submersible Pump	Control	Recovery %	Peristaltic Pump	Control	Recovery %	Bladder Pump	Control	Recovery %
				Water Depth 17.5 Feet					
MCL	104.4	103.9	100.5	103.8	103.6	100.2	105.0	103.6	101.4
1,1-DCE	109.6	111.4	98.4	108.9	113.5	96.0	113.3	111.7	101.3
t-1,2,-DCE	123.7	124.2	99.6	123.1	124.7	98.7	125.7	124.8	100.7
1,2-DCA	107.6	107.1	100.5	106.8	106.6	100.2	108.0	106.6	101.3
1,1,1-TCA	141.6	142.0	99.7	140.3	142.8	98.3	145.6	141.8	102.7
$\bar{X}$			99.7			98.7			101.5
				Water Depth 54 Feet					
MCL	107.2	107.3	99.9	107.1	107.6	99.5	108.0	107.3	100.7
1,1-DCE	126.3	130.8	96.5	129.5	132.7	97.6	133.0	132.7	100.2
t-1,2-DCE	133.0	135.4	98.2	133.6	136.2	98.1	136.4	136.4	100.0
1,2-DCA	108.5	108.5	100.0	109.0	109.0	100.0	108.8	108.4	100.4
1,1,1-TCA	157.8	160.9	98.1	158.0	162.1	97.5	163.9	161.7	101.4
$\bar{X}$			98.5			98.5			100.5
				Water Depth 92 Feet					
MCL	108.3	107.7	100.3	107.7	106.7	100.0	107.4	106.7	100.7
1,1-DCE	137.8	138.6	99.4	135.7	137.2	98.9	135.0	137.1	98.5
t-1,2-DCE	138.8	138.6	100.1	137.3	137.1	100.2	136.7	137.9	99.1
1,2-DCA	109.7	109.1	100.6	108.9	108.3	100.6	108.6	108.3	100.3
1,1,1-TCA	166.0	165.2	100.2	163.6	163.1	100.3	165.4	164.0	
$\bar{X}$			100.1			100.0			99.9

* Each value is the average of the five replicate samples.
$\bar{X}$ = average percent recovery for five compounds.

TABLE 7
Percent Recoveries of Pumping Samplers

Sampler	Water Depth 17.5 Ft Recovery %	Water Depth 54 Ft Recovery %	Water Depth 92 Ft Recovery %
	Low Concentration (10 to 30 μg/L)		
Control	100.0	100.0	100.0
Submersible pump	97.8	99.5	100.1
Peristaltic pump	97.7	98.7	97.9
	High Concentration (100 to 200 μg/L)		
Control	100.0	100.0	100.0
Submersible pump	99.7	98.5	100.1
Peristaltic pump	98.7	98.5	100.0
Bladder pump	101.5	100.5	99.9

into a gas-tight, minivalved syringe through a septum on the sampler. The syringe, which contained the water sample, was refrigerated until analysis. This sampling method also saved one step of sample handling. However, the dead volume in the needle could have introduced air bubbles into the syringe, and the pressure device could have failed to maintain a constant pressure during sample transfer. These might have caused the variations in the analytical results from the five replicate samples; that is, they may have produced lower concentrations than the control and, consequently, lower recoveries.

Pumping Sampler Test

Three pumping samplers were tested at depths of 5.3, 16.5, and 28m (17.5, 54, and 92 feet). Teflon tubing was used for all pumping samplers to convey the water samples to sample bottles. When the bladder and peristaltic pumps were used, a stainless steel sample head (a weighted strainer), was attached to the end of the Teflon tubing. The tubes with sample head or submersible pump were lowered into the standpipe to the desired position, and five replicate samples were taken at five-minute intervals. The controlled samples were collected at the corresponding times and positions. The concentrations in samples taken at three depths using three pumping samplers are listed in Table 6. The percent recovery values of two concentration levels at three depths for the three pumping samplers are listed in Table 7.

The pumps gave good precision for the five replicates. The average percent relative standard deviation of the five compounds ranged from 0.43 to 0.82 for the submersible pump, 0.07 to 0.74 for the peristaltic pump, and 0.78 to 0.90 for the bladder pump. The pumping sampler concentrations were very close to the control sample concentrations. All pumping samplers gave good recoveries, ranging from 97.7 to 101.5 percent.

The submersible pump produces a uniform continuous flow without agitation. The pump used for this study was at a fixed rate of about 3.79 liters per minute (1 gallon per minute). This made it difficult to transfer the sample into the sample vial. A variable flow control would help in collecting samples with this pump.

The peristaltic pump cannot pump water samples when the lift exceeds 24 feet (7.6m). In this study, the standpipe was full of water, the lift was about 5 feet (1.5m), and the peristaltic pump was able to pump water from a depth of 28m (92 feet). It is interesting to note that the peristaltic pump performed well under low-lift conditions during this study. The percent recoveries were close to those of the submersible pump.

The bladder pump can be operated at a high pumping rate, which allows the user to quickly purge a well. However, collecting a sample at a high flow rate with a pulse delivery of water could cause volatilization of organic compounds and introduce air bubbles in the sample vial. One set of samples at the low concentration level was lost due to this. For samples at the high concentration level, it was necessary to use manual control and low gas pressure to achieve an acceptable flow rate.

Summary and Conclusion

The design of the standpipe system described in this paper has been indicated to be versatile and reliable for testing and evaluating ground water samplers used to collect samples of volatile organic compounds. This system can accommodate a variety of samplers and a variety of volatile organic compounds. Test results indicated that the standpipe system was well enclosed with no apparent decrease in control chemical concentration in 24 hours. The unique feature of this system is that a control sample and a test sample can be obtained simultaneously. This arrangement enables a convenient and direct comparison of sampling accuracy and reproducibility, which produces reliable testing results.

Experiments were performed in testing non-pumping and pumping samplers. For non-pumping samplers, the bailer showed less precision and the lowest recoveries, 91.4 to 96.3 percent. The manual-driven piston sampler gave good precision and good recoveries (101.1 to 103.5 percent). The higher recoveries may result from the water-column pressure in the sample cylinders. The motor-driven piston sampler showed some variation in sampling due to sample storage in syringes, but the recoveries, in the range of 96.8 to 100.9 percent, were satisfactory. This sampler is bulky and requires some skill to operate. Comparison of the percent recovery also indicated that the sample transfer step could be the main cause of sample loss.

The three pumping samplers gave good recoveries, ranging from 97.7 to 101.5 percent. The submersible pump produced continuous flow, but a variable flow-rate controller would improve the sampling precision. The peristaltic pump gave results comparable to the submersible pump. For the bladder pump, it was necessary to use a manual control to obtain samples of volatile organic compounds.

Both non-pumping samplers and pumping samplers, with the bailer as the only exception, showed more variations and less recoveries for samples taken at the shallow depth of 17.5 feet (5.33m).

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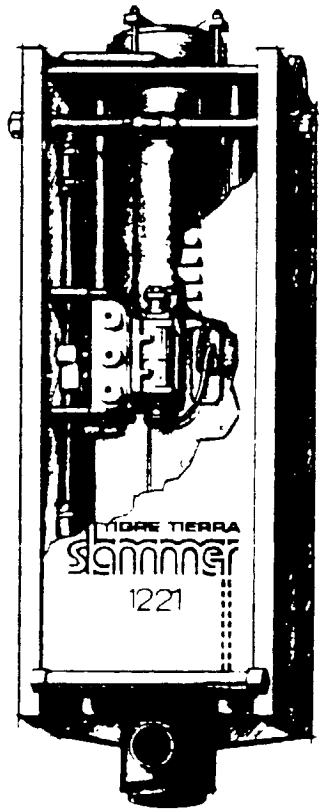

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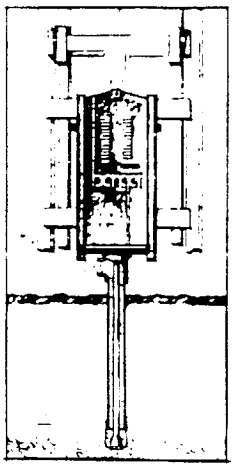

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Sampling for Purgeable Organic Compounds Using Positive-Displacement Piston and Centrifugal Submersible Pumps: A Comparative Study

by LeRoy L. Knobel and Larry J. Mann

Abstract

Positive-displacement piston pumps that minimize sample agitation have no apparent advantage over centrifugal submersible pumps when used to collect ground water samples for analysis of low concentrations of purgeable organic compounds. Analytical uncertainties inherent in laboratory environments appear to influence analytical results of low-concentration purgeable organic compound samples more than either pump type or sampling team. Centrifugal submersible pumps are at least equally efficient as positive-displacement piston pumps in the recovery of carbon tetrachloride, 1,1,1-trichloroethane, trichloroethylene, and chloroform after sampling and analytical influences are made constant.

Introduction

The U.S. Environmental Protection Agency's (U.S. EPA) Resource Conservation and Recovery Act ground water monitoring technical enforcement guidance document (1986) recommends that the technique used to withdraw a ground water sample from a well should (1) be selected on the basis of the constituents to be analyzed in the sample; (2) ensure the ground water sample is representative of the formation or aquifer; and (3) minimize physically altering or chemically contaminating the sample during the withdrawal process. Equipment and procedures that minimize sample agitation and contact with the atmosphere during sample transfer are required. Acceptable sampling devices for both inorganic and organic constituents are constructed of fluorocarbon resin or stainless steel and include (1) gas-operated squeeze or bladder pumps; (2) double-check valve, bottom-emptying bailers; (3) syringe bailers; and (4) single-check valve bailers (U.S. EPA 1986).

Investigations have been designed to evaluate sampling devices such as bladder pumps, helical-rotor and gear-driven submersible pumps, bailers, and peristaltic pumps. Gibs et al. (1990) and Dumouchelle et al. (1990) provide a comprehensive list of references on sampling ground water for organic compounds. Conclusions drawn by

the investigators differ as to best sampling devices, but most agree that the use of suction, air-lift, and peristaltic pumps, and pumps that allow sample contact with air, should be avoided. However, most investigations were done in areas where the depths to water were relatively shallow, less than 100 feet below land surface.

In places where the depth to ground water is several hundreds of feet below land surface and purgeable organic compounds are the constituents of interest, the acceptable sampling devices (U.S. EPA 1986) often are not practical because of the long time required to purge the well and obtain water samples representative of the aquifer. Centrifugal submersible pumps are not recommended by the U.S. EPA, Region X, or Idaho Department of Health and Welfare, Hazardous Materials Bureau, for collecting samples for determinations of purgeable organic compounds (Lane 1990). A field experiment was done to determine whether comparability of analytical results for low concentrations of purgeable organic compounds in water is markedly affected by the type of pump used to collect the samples. The pump types selected for comparison were centrifugal submersible pumps and positive-displacement piston pumps. The evaluation was done utilizing deep wells at the Idaho National Engineering Laboratory. No attempt was made to evaluate the accuracy of analytical results; only comparability of data was evaluated.

Approach

Three deep wells at the U.S. Department of Energy's Idaho National Engineering Laboratory were selected for the experiment. Water from wells 88 and 120 (Figure 1) consistently contained detectable concentrations of carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene (Mann and Knobel 1987; Mann 1990). Carbon tetrachloride has been the most prevalent constituent, generally detected at concentrations between 1 and 3 μg/L. Water from well 117 (Figure 1) has not contained detectable concentrations of purgeable organic compounds.

Each well was equipped with a dual pumping system. The original electrically operated centrifugal submersible pumps were removed and then replaced along with commercially available, pneumatically operated stainless steel piston pumps. Although centrifugal submersible pumps deliver water to the surface at pressures higher than atmospheric, the impellers are not specifically designed to minimize agitation of the water. Piston pumps are positive-displacement pumps that minimize agitation of the water. They meet material construction standards recommended by the U.S. EPA and lift about 2 gal/min of water from a depth of about 600 feet. Construction of the wells and descriptions of the pumps used in the experiment are included in Table 1.

Both the piston and the submersible pumps were used simultaneously to purge water from the wells prior to collection of water samples. Wells 88, 117, and 120 were purged at total combined rates of 4.0, 10.5, and 26.0 gal/min, respectively. Subsequent to purging and

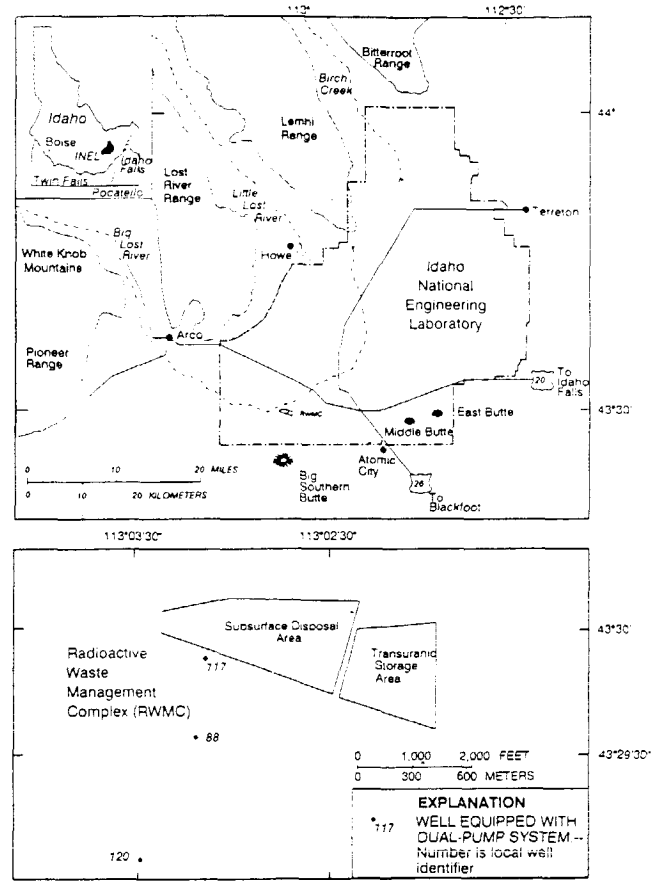

Figure 1. Location of the Idaho National Engineering Laboratory, Radioactive Waste Management Complex, and wells with dual-pump systems.

prior to sample collection, the total combined discharge from well 88 remained the same, 2 gal/min from the sample port of each pump. The sample port discharge from well 117 was reduced to about 3 gal/min; 2.5 gal/min from the submersible pump and 0.5 gal/min from the piston pump (the piston pump would not produce more than 0.5 gal/min). The sample port discharge from well 120 was reduced to about 4 gal/min; 2 gal/min from each pump. The excess discharge from wells 117 and 120 was diverted away from the sampling ports using an apparatus described by Mann and Knobel (1987). To determine whether the wells had been thoroughly purged, they were pumped until at least three wellbore volumes had been removed and water temperature, pH, and specific conductance were stable (Wood 1981).

In August 1990, 15 pairs of water samples from wells 88 and 120 were collected for determinations of 36 purgeable organic compounds that were tabulated by Pritt and Jones (1989). Five pairs of water samples were also collected at well 117. Previous samples from well 117 collected using the submersible pump did not contain detectable concentrations of purgeable organic compounds. Each pair of samples was collected from each pump in the well within two minutes of one another. In each pair, the submersible pump sample was collected first. One trip blank accompanied samples from each well to the laboratory for analysis. Trip blanks consisted of deionized water that was boiled for one

Table 1
Description of Wells and Pumps[1]

Well Number	Depth of Well (feet)	Open Interval (feet)	Casing: Type of Openings	Casing: Type of Material
88	662	587-662	open hole	—
117	653	550-653	perforations	stainless steel
120	705	638-705	perforations	stainless steel

Well number	Pump Setting: Piston (feet)	Pump Setting: Submersible (feet)	Static Water Level Below Land Surface (feet)	Type of Steel in Pump Column: Piston	Type of Steel in Pump Column: Submersible
88	627	634	587-589	stainless	galvanized
117	625	635	585	stainless	stainless
120	665	678	615	stainless	stainless

Well Number	Pump Power Source: Piston	Pump Power Source: Submersible	Type of Pump: Piston	Type of Pump: Submersible	Principle Type of Pump Construction Material: Piston	Principle Type of Pump Construction Material: Submersible
88	generator & compressor	generator	Hydrostar	1.5 hp Pacific	stainless steel	steel
117	generator & compressor	generator	Hydrostar	5 hp Grundfos	stainless steel	stainless steel
120	generator & compressor	generator	Hydrostar	5 hp Grundfos	stainless steel	stainless steel

[1]Dual-pump installation precluded measurement of pumping level. On the basis of specific capacity data presented by Ackerman (1991), pumping levels were at least 15 feet above the pump intakes at the time water samples were collected. Any use of trade, product, or firm names in this report is for descriptive purposes only and does not imply endorsement by the U.S. government.

hour and purged with ultra-high purity nitrogen gas.

The water samples were analyzed by the U.S. Geological Survey's National Water Quality Laboratory (NWQL) in Arvada, Colorado, by using a method that conforms to U.S. EPA method 524.2 (Schroeder 1991). The reporting level — 0.2 μg/L in this instance — is the lowest measured concentration of a constituent that may be reliably reported using a given analytical method (Pritt and Jones 1989). The NWQL routinely uses internal standards and surrogates to monitor recovery and improve quantification (Wershaw et al. 1987). In general, the analytical precision of this method for most compounds at the NWQL under routine conditions is ± 30 percent. Better precision can be achieved by the NWQL for individual compounds. For example, single-operator precision for carbon tetrachloride, chloroform, 1,1,1-trichloroethane, and trichloroethylene ranges from ± 10 to ± 20 percent (Schroeder 1992).

Results

The 15 pairs of water samples collected from the piston and submersible pumps in well 88 contained four purgeable compounds: carbon tetrachloride, chloroform, 1,1,1-trichloroethane, and trichloroethylene (see Round 1 results on Table 2). Water from well 117 did not contain reportable concentrations of the 36 compounds, and water from well 120 contained only carbon tetrachloride (Table 2). Trip blanks did not contain reportable concentrations of any compound.

At well 88, water samples collected during Round 1

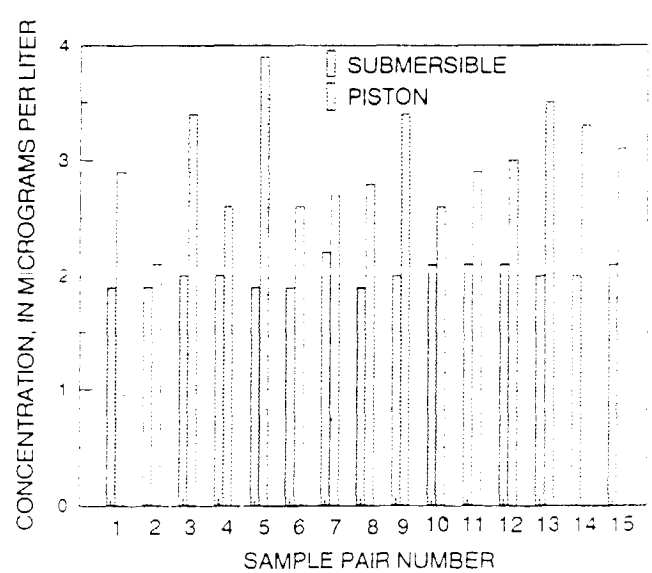

Figure 2. Comparison of carbon tetrachloride concentrations in water from piston and submersible pumps at well 88, August 1990.

Table 2
Concentrations of Selected Purgeable Organic Compounds
(Concentrations in Micrograms per Liter)

Sample Pair	Carbon Tetrachloride		Chloroform		1,1,1-Trichloroethane		Trichloroethylene	
Number	Submersible	Piston	Submersible	Piston	Submersible	Piston	Submersible	Piston
Well 88:	Round 1; August 1990							
1	1.9	2.9	0.7	0.4	0.4	0.5	0.8	1.0
2	1.9	2.1	0.6	0.3	0.4	0.3	0.8	0.7
3	2.0	3.4	0.7	0.5	0.4	0.5	0.9	1.2
4	2.0	2.6	0.7	0.4	0.4	0.4	0.9	0.9
5	1.9	3.9	0.6	0.5	0.4	0.6	0.7	1.3
6	1.9	2.6	0.6	0.3	0.4	0.4	0.8	0.9
7	2.2	2.7	0.6	0.4	0.4	0.4	0.9	1.0
8	1.9	2.8	0.6	0.4	0.4	0.4	0.8	1.0
9	2.0	3.4	0.6	0.4	0.4	0.5	0.8	1.2
10	2.1	2.6	0.5	0.4	0.4	0.4	0.8	0.9
11	2.1	2.9	0.6	0.4	0.4	0.4	0.8	0.9
12	2.1	3.0	0.6	0.4	0.4	0.5	0.9	1.1
13	2.0	3.5	0.6	0.4	0.4	0.5	0.9	1.2
14	2.0	3.3	0.6	0.5	0.4	0.5	0.8	1.2
15	2.1	3.1	0.6	0.4	0.4	0.5	0.8	1.1
	Round 2; March 1991							
1	2.2	2.0	0.5	0.3	0.3	0.3	0.9	0.8
2	2.0	2.0	0.6	0.3	0.3	0.3	0.9	0.8
3	2.1	2.0	0.5	0.3	0.3	0.3	0.9	0.8
4	2.0	2.0	0.5	0.3	0.3	0.2	0.9	0.8
5	2.0	2.0	0.5	0.3	0.3	0.3	0.8	0.8
6	2.0	1.9	0.6	0.3	0.3	0.3	0.9	0.8
7	2.0	1.9	0.6	0.3	0.3	0.2	0.9	0.7
8	2.0	1.8	0.5	0.3	0.3	0.3	0.9	0.7
9	2.1	2.1	0.5	0.3	0.3	0.3	0.9	0.8
10	2.0	1.8	0.5	0.3	0.3	0.3	0.9	0.7
Well 117:	Round 1; August 1990							
1	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
3	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
4	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
Well 120:	Round 1; August 1990							
1	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
2	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
3	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
4	0.5	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
5	0.5	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
6	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
7	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
8	0.5	0.7	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
9	0.5	0.5	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
10	0.4	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
11	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
12	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
13	0.5	0.6	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
14	0.6	0.7	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2
15	0.5	0.7	<0.2	<0.2	<0.2	<0.2	<0.2	<0.2

from the piston pump consistently contained greater concentrations of carbon tetrachloride (see Figure 2 and Table 2) and trichloroethylene (Table 2) than water from the submersible pump. The 95 percent confidence limits of the mean concentrations of carbon tetrachloride were 3.0 ± 0.9 μg/L from the piston pump and 2.0 ± 0.2 μg/L from the submersible pump. The 95 percent confidence limit of the mean concentration, $\bar{C}$, is $\bar{C} \pm 1.96$ s, where s is the standard deviation about the mean concentration. The confidence limits of the mean concentrations

of trichloroethylene were 1.0 ± 0.4 μg/L from the piston pump and 0.8 ± 0.2 μg/L from the submersible pump. However, confidence limits of the mean concentration of chloroform were 0.4 ± 0.2 μg/L from the piston pump and 0.6 ± 0.1 μg/L from the submersible pump; the confidence limits for 1,1,1-trichloroethane were 0.5 ± 0.1 μg/L from the piston pump and 0.4 ± 0.0 μg/L from the submersible pump. Confidence limits of the mean concentrations of carbon tetrachloride in water at well 120 were 0.6 ± 0.2 μg/L from the piston pump and 0.5 ± 0.05 μg/L from the submersible pump.

Round 1 samples independently collected by state of Idaho personnel and analyzed by the Bureau of Laboratories, Idaho Department of Health and Welfare, Boise, are shown in Table 3. An analysis of those data was provided by Barrash (1991). Carbon tetrachloride concentrations in water samples from well 88 were 1.89 and 1.91 μg/L from the piston pump, and 1.53 and 1.49 μg/L from the submersible pump. Concentrations of trichloroethylene were 0.67 and 0.66 μg/L in water from the piston pump and 0.71 and 0.68 μg/L in water from the submersible pump. At well 117, neither carbon tetrachloride nor trichloroethylene was detected. At well 120, 0.53 and 0.51 μg/L of carbon tetrachloride were detected in two water samples from the piston pump, and 0.46 and 0.43 μg/L were detected in two water samples from the submersible pump.

Discussion

Round 1 determinations of carbon tetrachloride concentrations in water from the piston and submersible pumps at well 88 were statistically compared using the paired t-test as described by Iman and Conover (1983). For fewer than 30 pairs of samples, the paired t-test assumes the data are normally distributed. The Lilliefors test (Iman and Conover 1983) indicated the data could reasonably be assumed to have come from a normal distribution. Because the paired-t value was 8.061, compared with $t_{0.01,14}$ = 2.624 (where 0.01 is the level of significance and 14 represents the degrees of freedom), the mean concentrations of carbon tetrachloride in the samples from the piston and submersible pumps were concluded to be statistically different.

An alternative statistical test that was applied by state of Idaho personnel (Barrash 1991) assumed that samples collected from each well — 88 and 120 — were 30 random samples from two populations. Calculated F-statistic values indicated that population variances were different, and sample population means were compared with a modified t-test. The modified t-test used pooled sample variance to calculate the t′-statistic values. This statistical test indicated the sample population mean concentrations for carbon tetrachloride, trichloroethylene, and chloroform in water from well 88 were different. The sample population mean concentrations for carbon tetrachloride in water from well 120 were also different. The sample population mean concentrations for 1,1,1-trichloroethane in water from well 88 were the same (Barrash 1991).

On the basis of the greater mean concentration of carbon tetrachloride in water from the piston pump at well 88, it initially was concluded that the piston pump might be more effective in recovering small concentrations of purgeable organic compounds in water from deep wells. However, at least four variables could cause the mean concentrations of carbon tetrachloride to differ by 1.0 μg/L: (1) two teams were involved in collecting the 15 pairs of samples; (2) one person from the NWQL analyzed the 15 samples from the submersible pump as a group, whereas three people from the NWQL analyzed the 15 samples from the piston pump; (3) each analyst used a different gas chromatograph-mass spectrometer; and (4) a systematic error (bias) in the performance of either pumping mechanism may have existed. If bias existed in the pumping mechanisms, the current study could not account for it because field spikes were not done. However, the magnitude of potential bias is likely to have been small because in no case did the piston pump detect carbon tetrachloride when the centrifugal pump did not.

Table 3
Concentrations of Carbon Tetrachloride and Trichloroethylene in Water Samples Collected and Analyzed by the State of Idaho, August 1990[1]
(Concentrations in Micrograms per Liter)

Well Number	Sample Pair Number	Carbon Tetrachloride		Trichloroethylene	
		Piston	Submersible	Piston	Submersible
88	1	1.89	1.53	0.67	0.71
	2	1.91	1.49	0.66	0.68
117	1	<0.2	<0.2	<0.2	<0.2
120	1	0.53	0.46	<0.2	<0.2
	2	0.51	0.43	<0.2	<0.2

[1]Data from the report by Barrash (1991, Table 5). Additional data are available in that report.

An analysis of samples collected by each team (odd-numbered pairs were collected by Team 1 and even-numbered pairs were collected by Team 2) indicated the mean concentrations for carbon tetrachloride in water from the piston pump in well 88 were different. For example, the 95 percent confidence limit of the mean concentration in samples collected from the piston pump by Team 1 was $3.2 \pm .08$ μg/L and, by Team 2, was 2.7 ± 0.7 μg/L; mean concentrations from the submersible pump were 2.0 ± 0.2 μg/L for both teams. Given differences in mean concentrations in water samples collected from the piston pumps by the two teams and the differences in concentrations between the NWQL and the state of Idaho's laboratory, 10 pairs of samples were collected from well 88 during a second round of sampling in March 1991.

The March 1991 samples were collected by one sampling team and the laboratory agreed to dedicate one analyst and one gas chromatograph-mass spectrometer to analysis of the samples. Single-operator precision of ± 10 to ± 20 percent was obtained for compounds detected during this round of analyses. Pump discharge rates were about 2 gal/min from each pump. Concentrations of the four purgeable organic compounds in water from well 88 are shown in Table 2; a comparison of the carbon tetrachloride concentrations is presented in Figure 3. Mean concentrations of carbon tetrachloride, trichloroethylene, and 1,1,1-trichloroethane in water from the piston and submersible pumps were virtually identical. The 95 percent confidence limits of mean concentrations of carbon tetrachloride in water from the piston and submersible pumps were 2.0 ± 0.2 and 2.0 ± 0.1 μg/L, respectively, and the mean concentrations of 1,1,1-trichloroethane were both 0.3 μg/L. Confidence limits of mean concentrations of trichloroethylene in water from the piston and submersible pumps were 0.8 ± 0.1 and 0.9 ± 0.1 μg/L, respectively. Mean concentrations of chloroform, however, were relatively consistent with those for the August 1990 samples, although the mean concentration differed in water for the piston pump; the mean concentration in water from the submersible pump was 0.6 μg/L, but that for the piston pump was 0.3 μg/L, compared with 0.4 μg/L in August 1990. A paired t-test was not conducted on carbon tetrachloride concentrations in Round 2 samples at well 88 because the 95 percent confidence limits of the mean concentrations were virtually identical and the reliability of the test decreases with a decreasing number of samples.

Conclusions

For aquifers containing low concentrations of carbon tetrachloride, as demonstrated by data from Rounds 1 and 2 for well 88, laboratory analytical uncertainties from different analysts and equipment appear to influence analytical results more than pump type or sampling team.

Based on sampling and analytical conditions tested in this study, centrifugal submersible pumps recovered higher average concentrations of chloroform than positive-displacement piston pumps.

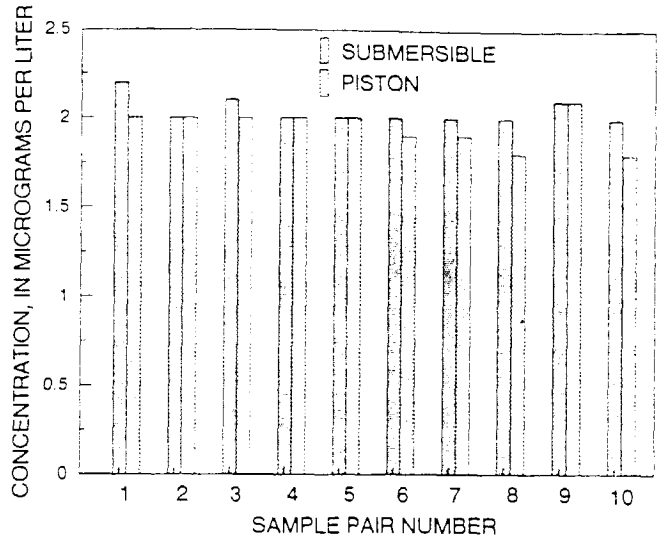

Figure 3. Comparison of carbon tetrachloride concentrations in water from piston and submersible pumps at well 88, March 1991.

When sampling and analytical differences are removed and the associated biases are neglected, mean concentrations at the 95 percent confidence limits indicate that the centrifugal submersible pump is at least equally efficient for recovery of carbon tetrachloride, 1,1,1-trichloroethane, and trichloroethylene as the positive-displacement piston pump.

In this study, positive-displacement piston pumps had no apparent advantages over centrifugal submersible pumps.

Round 2 data for well 88 suggested that under the conditions tested, stainless and galvanized steel sample-delivery systems have no discernible effect on concentrations of carbon tetrachloride and 1,1,1-trichloroethane.

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A Field Study of Various Sampling Devices and Their Effects on Volatile Organic Contaminants

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ABSTRACT

A common concern in any ground-water sampling program is the type of sampling device used to collect the sample. Different sampling devices, commonly used in Region V, were tested on several wells that had different levels of volatile organic contaminants (VOC's). The samples were collected and sent to the U.S. Environmental Protection Agency's Contract Laboratory Program for analysis. The devices were: a teflon bailer, with and without a bottom emptying device; a bladder pump; an air-activated piston pump; and two different types of electric submersible pumps.

In most cases, the levels of VOC's found did not vary significantly between the sampling devices. However, the levels of VOC's were statistically lower in several samples obtained with the bailer. The lack of consistency between samples taken with a bailer and those taken with the pumps may be attributed to different sampling personnel. Any variations of VOC concentrations between different sampling pumps were within the margin of error indicated by duplicate samples. Clean decontamination blanks indicated that cross contamination of VOC's was not present. Bailing for samples appears to be dependent on sampling technique and is prone to variability in the levels of VOC's.

INTRODUCTION

A primary concern in the investigation of any hazardous waste site is the collection of data that best represents the ground-water quality. An integral part of any sampling program is the device used to collect the ground-water samples. When collecting ground-water samples, care is taken to minimize the possible changes in ground-water chemistry by the collection device. This is especially important when sampling for compounds that are prone to alteration or destruction because of sampling methods, such as volatile organic compounds (VOC's).

This study will be one of many that will investigate possible sampling bias that can be introduced during ground-water investigations. Future studies will generate a larger data base in order to complete a statistical analysis of the techniques, as well as, to develop a quantification on the relative importance of the sampling techniques in obtaining a "representative" ground-water sample.

BACKGROUND

The objective of this sampling program was to obtain water samples for VOC analysis using sampling devices that are commonly used within the six state area of the U.S. EPA, Region V (Illinois, Indiana, Ohio, Michigan, Minnesota and Wisconsin). The program was to determine the variability between the levels of VOC's obtained by the different sampling devices. The sampling devices included a teflon bailer which was sampled by pouring from the top and sampled using a bottom emptying device. Also used were an air-activated piston pump, two different electric submersible pumps and a bladder pump. A detailed description of each of these devices is given by Nelson and Yeates (1985). Many of the VOC's found during this study are included in the list of the most frequent ground water contaminants detected on Superfund sites nationwide (Plumb, 1987).

Barcelona and others (1984) showed the possible effects sampling mechanisms may have on various Trihalomethanes (THM's) under stringent laboratory conditions. They concluded that the bladder pump yielded the most consistent levels of THM's. Unwin (1984) completed a laboratory study of several devices using several different VOC's with different Henry's Law Constants. These tests using the bailer, the squeeze type submersible pump (bladder pump) and the Johnson-Keck submersible electric pump (helical, submersible electric pump) showed little, if any, statistical variation between the devices. Pearsall and Eckhardt (1987) studied several pumps and their effects of some VOC's in the field. Their study compared a Keck submersible electric pump, a bailer, a peristaltic pump, a centrifugal pump and a 4-inch submersible pump. Very little statistical difference was noted between the devices, except for the peristaltic pump.

The sampling devices were used on two sites that had different geologic environments. The first site was in Northwestern Indiana (MSWF) where the wells were set within a sandy aquifer. The depth to water ranged from 15 to 25 feet. The second site was in Northern Illinois (BSY) and had wells set in fractured dolomite. The depth to water ranged from 30 to 85 feet on this site. All of the wells tested, except one, were composed of stainless steel risers and screens. The exception was an open borehole within fractured rock at the BSY site, which had a very low hydraulic conductivity and was pumped dry twice during sampling.

PROCEDURES

The teflon bailer was used and sampled by either pouring from the top of the bailer (BTE), or by using a bottom emptying device (BBE). Nylon chord that was wound on a reel, was used so that raising and lowering of the bailer was done at an even rate, which would reduce the rate of

volatilization during the sampling process. The nylon chord was changed between sampling locations.

The two submersible electric pumps were of two different designs. The first was an impeller, submersible electric pump (ISEP) and the second was a helical, submersible electric pump (HSEP). The ISEP was composed of stainless steel and teflon, and had a teflon discharge line. The HSEP was composed of stainless steel with an ethylene-propylene stator, and had nylon reinforced vinyl tubing for the discharge line. The bladder pump (Blad) was composed entirely of teflon, including the discharge line. The air-activated piston pump (AAPP) was composed of stainless steel, but the discharge line was composed of polypropylene.

Three well volumes were purged using one of the sampling pumps prior to sampling. The exception to this was the open borehole with low hydraulic conductivity which was pumped dry prior to sampling and allowed to recover overnight. While the pumps were purging, a flow-through cell described by Garske and Schock (1985) was used, which allowed simultaneous measurements of pH, temperature and conductivity of the groundwater. These parameters were allowed to stabilize prior to sampling for each of the sampling devices, except for the bailer. These parameters were allowed to stabilize prior to sampling so that we were assured that aquifer water was being sampled.

The bailer was lowered down the well five to ten times prior to sampling, which acclimated the bailer to the groundwater. The devices were lowered down the wells, one at a time, in order to minimize cross contamination between devices. At many of the wells, the first and last samples were taken with the same sampling device, in order to determine if any change in concentrations were time dependent.

The sampling devices were decontaminated using soapy water, followed by a clean water rinse, and concluded by a distilled water rise. The soapy water and clean water rinses were completed in PVC tubes, while the distilled water rinses were completed in a teflon tube. Field blanks were taken following the decontamination of the devices after sampling, during the distilled water rinse.

The samples were sent to the U.S. Environmental Protection Agency's Contract Laboratory Program (CLP) for the chemical analyses. For the set of samples obtained on the MSWF site, several different laboratories were used for the analyses. Therefore, several samples from the same sampling device and well location were sent to each of the laboratories involved, in order to qualitatively determine the variability between the laboratories.

For most of the wells, the same people would generally obtain the samples from the same sampling device. This was done to try and minimize variations between samplers.

DISCUSSION

The sampling effort took place at two different times of the year. The first sampling effort acquired the MSWF series of samples in late June. The second effort (the BSY series) obtained the balance of the samples in

mid August. Unfortunately, the second effort was to have been more extensive, but mechanical (3 pumps malfunctioned) and physical (~3 inches of rain) problems prevented the collection of the balance of the samples.

The results of the sampling effort are given in Table 1. Generally, the results show very little difference in the levels of VOC's found between the sampling devices. Two exceptions to this conclusion are evident. The most notable exception is that the results for the samples that were bailed have lower values for VOC's at some wells. This is especially evident in the results for the wells MSWF-W#1, MSWF-W#4 and BSY-W#1. The contrast between the sampling results for these three wells can be seen by comparing the range of values and means of the sampling pumps versus the range and means of the bailed samples (Table 2).

The second exception to this general conclusion is shown by the results of BSY-M#2. However, this well was pumped dry twice during the sampling effort because of the low recharge rates, indicating other factors may be more important than the sampling device used.

Interestingly, the same field person was used for sampling with the bailer at MSWF-W#3, and -W#4, but with different results. The results for MSWF-W#3 show very little difference between sampling devices. However, the results for MSWF-W#4 show much lower concentrations for Trans-1,2-Dichloroethene when sampled with the bailer, as opposed to the other sampling devices. This would tend to indicate variability not only exists between different field personnel, but also each person would tend to have some variability in the handling of the bailers. No notable differences were seen with the bailer samples when they were sampled with the bottom emptying device as opposed to pouring from the top. This may indicate the controlling factor may not be due to the actual emptying to the device, but perhaps to the way the bailer is brought to the surface.

Also, very little difference was noted between samples taken first and last with the same sampling device (see results for MSWF-W#1 and -W#4). This indicates that the concentrations of the ground-water contaminants remained constant during the sampling.

The blanks generally showed that adequate decontamination procedures were being followed. The only exception to this is shown in the BSY-Bladder blank which showed trace levels of TCE. The TCE levels in the well sampled immediately prior to obtaining the blank were approximately 240 ppb. We noted that the bladder pump is one of the more difficult sampling mechanisms to decontaminate between wells because the pump needs pressure on the bladder in order for the bladder to collapse during the recharge cycle on the pump. This pressure is hard to generate on the surface without having a long tube filled with water. The other sampling devices were much easier to decontaminate, which is illustrated by the essentially clean field blanks. The methylene chloride, acetone and toluene found in the blanks are all attributed to lab contamination, because none of these compounds were present during the sampling process.

The samples from the MSWF series that were sent to different CLP laboratories showed very little variability, which eliminated one possible

Table 1
Summary of Sampling Results

Well Identification /Sample Code	TCE	PCE	VC	Trans 1,2-DCEE	1,2-DCEA	1,1-DCEE	1,1-DCEA
MSWF-W#1/ ISEP L#2	21/22			11/12			
" BTE L#1	2J			5			
" " L#2	2J			6			
" " L#3	5U			6			
" BBE L#2	5U			6			
" HSEP "	21			9			
" Blad "	24			11			
" AAPP "	22			11			
" ISEP/L "	23			11			
MSWF-W#2/ ISEP L#1			8J	61			3J
" ISEP L#2			12	75			5U
" BTE L#1			4J/7J	52/70			3J/4J
" BTE L#3			10U/10U	56/59			5U/5U
" BBE L#1			6J/6J	63/61			4J/4J
" HSEP "			10/9J	65/62			4J/4J
" Blad "			7J	69			4J
" AAPP "			9J	61			4J
MSWF-W#3/ ISEP L#1	49			14			
" BTE L#1	43			12			
" BTE L#2	38			13			
" BTE L#3	36			11			
" BBE L#1	39			11			
" HSEP "	37			5			
" Blad "	41			9			
" AAPP "	45			14			
MSWF-W#4/ ISEP L#2	4J			99			
" BTE "	2J			26			
" BTE L#3	5U/5U			24/27			
" BBE L#2	2J			26			
" HSEP "	3J			99			
" Blad "	3J			100			
" AAPP "	3J			110			
" ISEP/L "	4J/4J			100/110			
BSY-W#1/ BTE	6			2J			
" BBE	6			2J			
" Blad	16			4J			
" AAPP	17/16			4J/3J			
BSY-W#2/ ISEP	4J	2J	4J	12			
" BTE	20	2J	4J	85	14	5	
" BBE	19/18	2J/2J	38/40	77/73	15/15	5/5	5U/2J
" Blad	7	1J	11	24	5	2J	

Sample Codes: ISEP/L = ISEP sampled after all other devices were completed. L#1 = CLP Lab #1, L#2 = Lab #2, etc.
TCE = Trichloroethylene; PCE = Perchloroethylene; VC = Vinyl Chloride; Trans-1,2-DCEE = Trans-1,2-Dichloroethene; 1,2-DCEA = 1,2 Dichloroethane; 1,1-DCEE = 1,1-Dichloroethene; 1,1-DCEA = 1,1-Dichloroethane.
ALL CONCENTRATIONS ARE IN PARTS PER BILLION

Table 2
Ranges and Means of Wells Showing Large Variations Due to Sampling Devices

		MSWF Well #1	MSWF Well #4	BSY Well #1
TCE	Range of Sampling Pumps	21-24		3-4
	Mean	22.2		3.7
	Range of Bailers	2-<5		2
	Mean	<3.5		2
Trans-1,2-DCEE	Range of Sampling Pumps	9-12	99-110	16-17
	Mean	10.8	103	16.3
	Range of Bailers	5-6	24-27	6
	Mean	5.8	25.8	6

Note: All concentrations are in parts per billion. TCE= Trichloroethylene; Trans-1,2-DCEE = Trans-1,2-Dichloroethylene.

problem. This also increased the confidence in the data obtained during this study.

Implications

Certain implications need to be considered based on the evaluation of our data. Because many decisions are made on data obtained during hydrogeologic investigations on CERCLA and RCRA sites, the quality of this data is extremely crucial. In many cases, the water quality samples are obtained only with bailers. Many health risk based criteria, such as MCL's, are set near limits of analytical reproducibility. Therefore, the margins of error produced in both the field and laboratory must be minimized, whenever possible. However, when the water quality samples are obtained with a technique that can induce large degrees of variability, health risk based decisions become more untenable.

For example, in Region V, the Field Investigation Team (FIT) QAPP requires the FIT field crews to only use bailers. In the case of data obtained at MSWF-W#1, if bailers were the only sampling device used, FIT crews would conclude that no release of contaminants has occurred at that location. In the case of the remedial program, the conclusion would be made that the MSWF-W#1 location would not be of concern because the levels found were below MCLs, which in many cases, drives the need to remedy or respond to a site. However, when we compare the results of the other sampling devices to the results from the bailers, we note that a different interpretation could be drawn based on the other sampling devices.

Considerations

One consideration in any sampling program is the ease of operation of the sampling device used. Conceptually, the bailer is perhaps one of the easiest sampling devices to use. However, the variability in the results shown in this study do show a major drawback to this device. The bailer is also prone to one type of physical breakdown, and that is being lost down a well, as this is what happened while sampling BSY-W#2.

Another criteria in any sampling program, is the ability to repair sampling devices in the field. The ISEP and HSEP devices broke down while sampling at the BSY site and could not be repaired because of the complexity of the systems. However, duplication of systems could prevent the loss of field time, although it is an expensive option.

Future Work

Additional work is planned to use some of these same sampling devices on additional sites to develop a greater data base. Different contaminants with different degrees of volatility are planned to be studied. Additional sampling devices, such as an in-situ device, will be used in order to better quantify the variability of sampling devices on VOC concentrations. Also, the effects of different sampling devices on a larger range of concentrations of contaminants will be studied.

Also planned is additional work on fractured rock systems. The well at BSY-W#2 was an open borehole and had high levels of the VOC's when

sampled with the bailer. Perhaps, since the bailer is open on the top and cascading within open boreholes in fractured rock systems is common, bailers may be more appropriate under these circumstances. Additional sampling in open boreholes with low hydraulic conductivities is planned.

CONCLUSIONS

The sampling showed that there was very little variation of VOC concentrations between sampling devices, except for the bailer samples. Sampling by the use of a bailer, is intrinsically dependent on the operator. Most of the other sampling devices are fairly simple to operate, and are somewhat independent of operator error.

This study tends to support what the general literature states, in that sampling by bailers could produce variable results. Most of the previous studies (Barcelona, et al., 1984, Unwin, 1984) were limited to laboratory studies. The limitations of bailers under laboratory conditions would be expected to be minimized because of the short travel times up the laboratory "casing" (Barcelona, et al., 1984).

The degree of variability when sampling with bailers, will need to be studied further. With additional data, variations between sampling pumps can also be determined. Other controlling factors on the sampling of ground water also need to be qualified. However, the data collected thus far, does show a need for field personnel involved in ground-water sampling programs to question the use of bailers when sampling for volatile organic contaminants.

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DISCLAIMER

Although this article was written by the employees of the U.S. Environmental Protection Agency, it has not been subjected to Agency review, and therefore does not necessarily reflect the views of the Agency. The mention of trade names does not constitute endorsement of any kind.

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DAVE MARK

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Field Evaluation of Seven Sampling Devices for Purgeable Organic Compounds in Ground Water

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ABSTRACT: Seven different sampling devices—(1) a bladder pump, (2) a helical-rotor submersible pump, (3) a gear submersible pump, (4) an open bailer, (5) a point-source bailer, (6) a syringe sampler, and (7) a peristaltic pump—were evaluated to determine their ability to recover purgeable organic compounds (POCs) from ground water under field conditions. Significant differences among the mean concentrations obtained with each sampler were found for selected POCs at each of three sites. The overall order of the sampling devices from highest to lowest recovery using data from all three sites yielded the following: (1) gear submersible pump, (2) point-source bailer, (3) open bailer, (4) helical-rotor submersible pump, (5) bladder pump, (6) syringe sampler, and (7) peristaltic pump. The overall standardized mean concentrations of Samplers 1 through 5 were closely grouped, indicating these devices were very similar in their ability to recover POCs. A similar overall order of the coefficients of variation indicated no clear difference between the sampling devices in the precision with which they recovered POCs. However, the three samplers with the lowest coefficients of variation (highest precision) were all positive-displacement pumping devices whereas the three samplers with the highest coefficients of variation (lowest precision) were all grab-sampling devices.

KEY WORDS: ground-water sampling, purgeable organic compounds, volatile organic compounds, sampling techniques, water quality, water chemistry

Increased emphasis on the need to sample wells for analysis of organic compounds has triggered the development and production of a wide variety of ground-water sampling devices. Environmental investigators have questioned the ability of all these devices to obtain equally representative samples for the analysis of purgeable organic compounds (POCs). Such compounds present special sampling and analytical difficulties because of their low molecular weights, low solubilities in water, low boiling points, and natural tendency to degas in open systems.

Most of the previous evaluations of sampler recovery efficiency for POCs have been conducted under controlled laboratory conditions. Ho [*1*] tested a peristaltic pump in the laboratory and found significant losses, particularly for highly volatile POCs (Henry's law constants >0.01 atm-m³/mol), with sample lifts more than 4.8 m (16 ft) and pumping rates greater than 2.6 L/min (0.7 gpm). Unwin [2] found that a peristaltic pump had significantly higher losses of five POCs from a spiked solution than those of a bailer, a bladder pump, and a helical-rotor submersible pump.

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Barcelona and others [3] carried out a comprehensive laboratory comparison of 14 commercially available sampling devices for their performance in collecting dissolved gases and POCs. They found significant bias and poorer precision in sampling with gas-displacement, mechanical positive-displacement, and suction-lift pumping mechanisms. Bladder pumps were rated best for most applications, whereas bailer performance was rated satisfactory but heavily dependent on the expertise of the sampling personnel.

Houghton and Berger [4] conducted a field comparison of several types of sampling devices but did not evaluate POC recovery. They did observe increased losses of volatile inorganic species, such as dissolved carbon dioxide, ammonia, mercury, molybdenum, and selenium, using air-lift, submersible centrifugal, and peristaltic pumps. They rated the bladder pump best in avoiding these problems.

Recently, Pearsall and Eckhardt [5] completed a field comparison of seven sampling devices for recovery of trichloroethylene and 1,2-dichloroethylene. They found no significant difference in paired comparisons between the concentrations of these two compounds recovered by two types of helical-rotor submersible pump, an impeller submersible pump, and a centrifugal pump. However, reduced trichloroethylene concentrations were obtained with a peristaltic pump. Bailer recoveries of trichloroethylene and 1,2-dichloroethylene concentrations in the 76 to 96 µg/L range did not differ significantly from those of a helical-rotor submersible pump. However, significantly reduced bailer recoveries were observed for these compounds in the 23 to 29 µg/L concentration range.

The objective of this study was to conduct a comprehensive statistical comparison of commercially available ground-water sampling devices for the recovery of purgeable organic compounds in a field environment. Seven different samplers were compared at each of three field sites for a wider diversity of purgeable organic compounds than in any of the previously mentioned investigations.

Methods

Sampling Devices Evaluated

The sampling devices evaluated in this study included (1) a bladder pump, (2) a helical-rotor submersible pump, (3) a gear submersible pump, (4) an open bailer, (5) a point-source bailer, (6) a syringe sampler, and (7) a peristaltic pump. These samplers represent three general classes of commercially available and commonly used sampling devices in ground-water monitoring: positive-displacement pumps (1–3), grab samplers (4–6), and suction-lift pumps (7).

The bladder pump tested is a noncontact gas-driven pump constructed completely of polytetra fluoroethylene (Teflon[2]) and Teflon-coated materials. It uses compressed gas to alternately expand and contract a flexible bladder to force successive pump volumes past a check valve and up through a discharge line [6]. This pump produces a noncontinuous flow at a maximum rate of approximately 3.8 L/min (1.0 gpm).

The helical rotor submersible pump employs an electric motor to turn a helical stainless-steel rotor against a semi-flexible Viton stator to create a progressing-cavity pumping head [7]. This pump is capable of delivering a continuous stream of water yielding 2.3 L/min (0.6 gpm) at 16 m (52 ft) of static lift head. The samples contact only stainless-steel, Viton, and Teflon surfaces in this pump.

The gear submersible pump has a set of meshing Teflon gears that form the basis of the pumping system [8]. The gears, driven by an electric motor, act as paddle wheels which push the water along the internal pump walls from the intake point to the pump discharge. The close tolerance of the Teflon gears prevents water from passing back between them. The sample contacts only the

[2] Use of commercial or brand names is for identification purposes only and does not constitute endorsement by the U.S. Geological Survey.

stainless steel pump body and the Teflon gears and discharge tubing. A pump rate of 1.9 L/min (0.5 gpm) is attained at 16 m (50 ft) of static lift head.

The open bailer used in this study is constructed entirely of Teflon. This device cylinder with a one-way valve on the bottom that allows water to pass through w downward [6]. After the bailer is lowered to the desired sampling depth, the directi reversed and a slug of water is retained by the one-way valve. The bailer volume is 0.7 L (0.2 gal). The retrieved sample is transferred from the bailer to the sample means of a Teflon bottom emptying device which opens the one-way valve.

The point-source bailer differs from the open bailer only in that a second one positioned at the top of the bailer barrel [6]. The top one-way valve effectively seals in the bailer as it is retrieved. This prevents exchange with water higher in the well potential for POC degassing during upward travel, and prevents contamination of th particulates scraped from the well casing. The volume of the point-source bailer is 0.7 L (0.2 gal). The top one-way valve is dislodged with a small rod to allow di the sample with air during sample transfer using a bottom-emptying device.

The syringe sampler tested in this study consists of a sliding Teflon piston in a barrel [9]. The piston is machined to very close tolerances that create a seal with th syringe sampler is lowered to the desired sampling depth with the piston positioned of the stainless-steel barrel. The space above the piston is evacuated through the atta tubing. As the piston is drawn toward the top of the barrel, the sample is drawn thro past a one-way valve, and into the bottom of the barrel. After retrieving the syrin pressure is applied to drive the piston downward and force the sample out a diffe valve into a sample container. The volume of the sample retrieved is approximate gal).

The peristaltic pump creates a vacuum to draw water up from a well to the colle the surface [8]. The system evaluated in this study consists of Teflon intake tu Erlenmeyer receiving flask, and a peristaltic pump with silicone tubing in the pu peristaltic pump evacuates the system and draws water up the intake line into the re When filled, the flask is opened and the sample is transferred to a sample container was used so that the samples would contact only Teflon and glass surfaces and no tubing in the pump head, which has been found by Ho [1] and Barcelona and other POCs from solution. The peristaltic pump has a relatively low pumping rate of abo (0.2 gpm) and is limited by atmospheric pressure and pump losses to a lift of about

A final pump used in this study, though not evaluated for purgeable organic compo was an impeller submersible pump. This pump was used at one of the test sites to flu prior to the sampler evaluation because of an interest in determining the effect of on the recovery of POCs. The impeller pump used was a 10-cm diameter (4 in.) in submersible pump of the type commonly found in domestic wells. It pumped at an rate of 38 L/min (10 gpm) at a static head lift of 2 m (6 ft). Water-contact surfaces in system included stainless steel, various rigid plastics, and flexible polyvinyl chlorid

Experimental Design

Three wells with water known to contain POCs were chosen for intensive field sam one in Cape Cod, Massachusetts, one in northern New Jersey, and one in southern All three wells are screened in shallow, unconfined aquifers consisting mainly of un sands and gravels, and had hydrostatic pumping heads of approximately 2 m (6 ft) recovery depths were 15 m (50 ft) in the Cape Cod well, 4 m (12 ft) in the northern well, and 6 m (19 ft) in the southern New Jersey well.

At each site, 15 to 28 replicate samples were collected with each sampler. The rep

prevent bias. For example, in the first round at Cape Cod, four replicates were taken with the open bailer, four replicates with the helical-rotor submersible pump, four replicates with the gear submersible pump, and so on until all seven samplers were used. The second round was conducted similarly, this time with seven replicates obtained successively with the seven samplers in a different randomly picked order. Table 1 summarizes the experimental design and also lists the POCs detected at each of the three test sites.

Field and Laboratory Methods

At all sites a submersible pump was used to flush standing water from the well casing. In accordance with the procedures outlined in Wood [*11*] and Claassen [*12*], temperature, pH, specific conductance, and dissolved oxygen concentrations were monitored at 5 or 10-min intervals to determine the inorganic chemical stability of the water being pumped from the well. Chloride concentration was measured, using a specific ion electrode, as an additional indicator of the inorganic water quality. Ultraviolet absorbance at 254 nm (nanometres) was also measured in the field using a Hitachi Model 100-20 single-beam UV-VIS (ultraviolet-visible) spectrophotometer. Absorbance at this wavelength is characteristic of unsaturated aliphatic and aromatic organic compounds. Therefore, this measurement was used as an indicator of organic water quality.

Chemical stability was deemed to have been achieved when all measurements varied within 5% for three successive readings. The time needed to attain chemical stability always far exceeded the time necessary to flush the recommended minimum of three casing volumes (D. A. Rickert, U.S. Geological Survey, written communication, 1985).

TABLE 1—*Experimental design and purgeable organic compounds detected*

Site	Round	Day	Replicates	Flushing Pump*	Sampling Order*	Purgeable Organic Compounds Detected
Cape Cod, Massachusetts	1	1	4	B	E B G A F D C	1,1-dichloroethylene
	2	2	7	B	C B D G E F A	trans-1, 2-dichloroethylene
	3	2	4	. .	D A B C E G F	trichloroethylene
						tetrachloroethylene
Northern New Jersey	1	1	8	B	B A F C D E G	1,1-dichloroethane
	2	2	8	H	E D F A C B G	1,1 dichloroethylene
						trans-1, 2 dichloroethylene
						1,1,1 trichloroethane
						trichloroethylene
						tetrachloroethylene
Southern New Jersey	1	1	14	B	B G A C D F E	vinyl chloride
	2	2	14	B	B A D C E G F	1,1 dichloroethane
						trans-1,2-dichloroethylene
						chloroform
						trichloroethylene
						benzene
						toluene
						ethylbenzene
						chlorobenzene
						o-1,2-dichlorobenzene
						m-1,3-dichlorobenzene

* A = peristaltic, B = helical-rotor submersible; C = bladder, D = syringe; E = open bailer; F = point-source bailer, G = gear submersible, H = impeller submersible.

Samplers were cleaned prior to sampling and between rounds with distilled deionized was sparged in the field with high-purity helium to remove any remaining purgeable co Samples of the wash water were collected before each sampler use to check for PO contamination.

All samples were concentrated by purge and trap and analyzed for purgeable priority concentrations by gas chromatography with the following detectors: a Hall electrolytic co detector (GC/HALL) in series with a photoionization detector (GC/PID), and a mass spe (GC/MS). This corresponds to U.S. Environmental Protection Agency Methods 601, 624, respectively [*13*].

Statistical Methods

For each purgeable organic compound detected at a site, a mean concentration for each was determined. Unforseen nonrandom effects other than those due to sampler were ob these results. The effect of round was particularly notable. This effect, which presumably to the use of differing well flushing rates prior to each round, will be discussed in m later. Inasmuch as round was not one of the effects being tested in the experiment, it was e from the statistical analyses by standardizing the concentration data using the following

$$X(\text{std}) = X - \bar{X}(\text{round})/s(\text{round})$$

where

$X(\text{std})$ = standardized concentration,
X = observed concentration,
$\bar{X}(\text{round})$ = mean concentration for a compound in a round, and
$s(\text{round})$ = standard deviation of the concentration for a compound in a round [*14*].

Using this formula, the standardized data for each round has a mean of zero and a deviation of one.

The standardized data were compared using a simple one-way analysis of variance to e if the sampling devices exhibited significantly different standardized mean concentratio 95% confidence level. If so, this was attributed to differences in their ability to rec purgeable organic compound. If the analysis of variance showed there was a significant d between samplers for a compound, the Tukey's multiple comparison test was employed to e which standardized means differed. The Tukey's test was used because it is one of effective multiple comparison tests at preserving the chosen significance level and mi Type I errors [*14*]. The Tukey's test resulted in groupings of samplers whose standardi concentrations did not differ at the 95% confidence level for a particular compound. All tests were conducted using a software package called SAS [*15,16*].

The use of standardized data facilitated the combination of results from compounds wi different concentrations. To summarize the results for a sampling site, the standardized all compounds that exhibited a significant difference between sampling devices were in a one-way analysis of variance. For example, at Cape Cod, 10 to 13 replicates for each samplers for each of the 4 compounds were included. The associated Tukey's test re comparison of overall standardized means for each sampler and groupings of sample overall performances were similar at the site. The standardized mean concentrations were to a 1 to 7 scale for ease of understanding and presentation in the tables.

Experimental Results and Discussion

Because this was a field study, the true concentrations of purgeable organic compounds at each well were not known and percent recoveries could not be calculated as in a l

study. It was therefore assumed the highest mean POC concentration obtained with a sampler was the most accurate. This assumption was not unreasonable because (1) losses of POCs would be more likely than increases simply because of their physical and chemical properties, and (2) all samplers tested were constructed of generally inert materials (Teflon, stainless steel, Viton and glass), so contamination from the pumps was minimized.

Averages of field water-quality measurements and POC concentrations for all samplers by round at the three test sites are given in Table 2. Several general characteristics of the ground-water quality at each of the sites should be noted.

First, water from the well in Cape Cod, which was situated in a plume of contamination caused by sewage effluent [17], represents the simplest POC matrix sampled; only four chlorinated solvent purgeables were identified by GC/MS.

Water from the northern New Jersey well, which was contaminated by wastewaters from a metal plating/degreasing operation (E. F. Vowinkel, U.S. Geological Survey, written communication, 1986), is a slightly more complex POC matrix; six purgeable organic compounds were

TABLE 2—*Steady-state field properties or constituents and mean POC concentrations by round at the test sites. [Concentrations are expressed in micrograms per litre unless otherwise noted.]*

	Date, Round No., and Site						
	7-17-84 1	7-19-84 2	7-19-84 3	8-14-84 1	8-15-84 2	12-5-84 1	12-6-84 2
	Cape Cod, MA			Northern NJ		Southern NJ	
Steady-state field properties or constituents							
pH (units)	7.0	7.0	7.0	6.5	6.4	6.1	6.1
water temperature (°C)	12.5	12.0	12.0	18.4	18.9	15.5	16.0
specific conductance (μS/cm @ 25 °C)	227	228	223	805	865	1780	1780
Dissolved oxygen (mg/L)	0.2	0.6	0.3	0.5	0.3	0.2	0.2
chloride (mg/L)	NM[a]	NM	NM	140	145	560	640
ultraviolet absorbance (units)	NM	NM	NM	0.014	0.035	0.404	0.559
Purgeable organic compounds							
vinyl chloride	<1[b]	<1	<1	<1	<1	64	70
1,1-dichloroethane	<1	<1	<1	51	79	11	11
trans-1,2-dichloroethylene	180	170	170	6.5	9.8	76	100
1,1-dichloroethylene	5.8	5.8	5.4	37	53	<1	<1
chloroform	<1	<1	<1	<1	<1	10	15
1,1,1-trichloroethane	<1	<1	<1	700	940	<1	<1
benzene	<1	<1	<1	<1	<1	66	66
trichloroethylene	89	84	82	41	60	27	28
tetrachlorethylene	79	75	72	180	270	<1	<1
toluene	<1	<1	<1	<1	<1	20	21
ethylbenzene	<1	<1	<1	<1	<1	25	27
chlorobenzene	<1	<1	<1	<1	<1	220	200
1,2 dichlorobenzene	<1	<1	<1	<1	<1	15	14
1,3-dichlorobenzene	<1	<1	<1	<1	<1	16	21
Number of measurements	25	31	28	55	40	50	82

[a] NM = not measured.
[b] <1 = lower limit of quantitation.

identified by GC/MS. This water had the highest total concentration of purgeable or levels exceeding 1 mg/L. The data presented show significant differences between the concentrations obtained for each of the rounds at this site. These differences were caused by the different pumping rates used during well flushing. The overall effect of t pumping rates will be discussed in more detail later.

Water from the southern New Jersey well, which was contaminated by a chem recycling facility (J. J. Hochreiter, U.S. Geological Survey, written communication, by far the most complex POC matrix of the three sampled. Eleven POCs were identi MS at this site. This water contained a diverse mixture of purgeable organic compou from the very volatile vinyl chloride (Henry's law constant = 0.08 atm-m³/mol) to the dichlorobenzenes (Henry's law constants = 0.002–0.004 atm-m³/mol). Ground w southern New Jersey site was the only one of the three sampled which contained concentrations of aromatic POCs (benzene, toluene, ethylbenzene, chlorobenzene, benzene, and 1,3-dichlorobenzene). The presence of aromatic compounds is reflected higher ultraviolet absorbance measurements given in Table 2.

Cape Cod, Massachusetts Site

Statistical analysis of the Cape Cod results was done on 10 to 13 replicate sample co for each of the 7 samplers for each of 4 POCs. The difference in numbers of replicates by the loss of a few data values due to analytical difficulties.

Analysis of variance of the Cape Cod data indicated that the standardized mean co of the samplers differed significantly (at $p \leq 0.05$) for all four compounds identified. The Tukey's test results are given in Table 3. The samplers are shown in order from lowest standardized mean concentrations for each purgeable organic compound. Samp the same grouping bracket are not significantly different at the 95% confidence level in t to recover the particular POC from the samples. The range of the actual mean concen given for each compound to indicate the levels at which these groupings occurred.

The bladder pump, the open bailer, and the helical-rotor submersible pump consisten the highest concentrations of all four purgeable organic compounds at the Cape Cod t

TABLE 3—*Tukey's test results: individual purgeable organic compound and overall orders an of samplers for the Cape Cod site.*

	Individual Compounds[a,b]				Overall	
Order	1,1-dichloro-ethylene	Trans-1,2-dichloro-ethylene	Tri-chloro-ethylene	Tetra-chloro-ethylene	Order	Samp
1	BLAD	BLAD	HR	HR	1.52	BLA
2	OB	OB	OB	BLAD	1.87	HR
3	HR	HR	BLAD	OB	2.02	OB
4	PSB	GEAR	GEAR	GEAR	3.77	GEA
5	GEAR	SYR	PSB	PSB	5.05	PSB
6	SYR	PSB	SYR	SYR	5.81	SYR
7	PER	PER	PER	PER	7.00	PER
Range (μg/L)	6.4–4.7	190–160	95–68	91–8		

[a] BLAD = bladder pump; OB = open bailer; HR = helical-rotor submersible pump; PSB = bailer; GEAR = gear submersible pump; SYR = syringe sampler; PER = peristaltic pump.
[b] Sampling devices within a bracket do not differ significantly at the 95% confidence level in their mean POC concentration.

peristaltic suction-lift pump recovers the lowest concentrations of all compounds and is the only pump not grouped with the two top samplers in any of the comparisons. However, for all four compounds there is considerable overlap in the groupings within each sampler comparison. For example, for 1,1-dichloroethylene and trichloroethylene, all samplers except the peristaltic pump are grouped together. The groupings are useful in comparing the relative performance of pairs of samplers.

To summarize the data for the Cape Cod site, a one-way analysis of variance was done on the standardized data as described earlier in the "Statistical Methods" subsection. The overall site order and grouping of the samplers given by the Tukey's test are given in the last two columns of Table 3. There is more differentiation between samplers when all four POCs are considered together rather than separately. This overall site order and grouping corroborates the previous general observations that the bladder pump, the helical-rotor submersible pump, and the open bailer are the most effective samplers and that the peristaltic pump is the least effective sampler at recovering POCs.

The point-source bailer ranking is probably low because of an operational problem encountered in emptying this sampling device at this first test site. Initially, the bailer was not equipped with a deflecting rod to displace the top ball check valve and allow the sample to drain out. Consequently, this bailer could not be emptied from the bottom so samples were poured from the top into the 40-mL sample vials. Aeration of the samples with associated degassing of the purgeable organics probably took place during this sample transfer. Prior to any further field testing, the bailer was returned to the manufacturer and the deflecting rod was installed. At the final two test sites, the point-source bailer was properly drained using the bottom-emptying device, and the standardized means were equal to or higher than those of the open bailer.

Northern New Jersey Site

Statistical analysis of the northern New Jersey results was done on 7 to 16 replicate concentrations for each of the 7 samplers for each of 6 POCs. The difference in numbers of replicates was caused by analytical difficulties and the effects of sampler order and pumping rate which resulted in the elimination of the data from one round for each of two samplers. As mentioned previously, the well flushing rate affected the results at this site. A detailed discussion of these results will be deferred to the "Effect of Pumping Rate" subsection.

Analysis of variance of the remaining northern New Jersey data showed that the standardized mean concentrations of the samplers differed significantly (at $p \leq 0.05$) for five of the six purgeable organic compounds identified at this site. The sixth POC was not significantly affected by sampling device primarily because its concentrations were near the detection limit of the gas chromatographic analysis procedure. At low concentrations, analytical variation makes up a much greater portion of the total variation in the results, causing greater overlap in the mean concentrations of all the samplers. At this site, the average coefficient of variation for the five significantly affected compounds was 20%, compared to 51% for the low concentration compound.

The Tukey's test results for the five POCs significantly affected by sampling device are given in Table 4. The point-source bailer and the gear submersible pump are the two most effective samplers for all compounds at the northern New Jersey site. The bladder and the peristaltic pumps consistently recovered the lowest standardized mean concentrations for all five compounds. As with the first test site, there is considerable overlap in all the groupings for all five compounds.

The overall site order and grouping of the samplers are shown in the final two columns of Table 4. These groupings do not overlap. They confirm the observations made on the individual compound comparisons, that the point-source bailer and the gear submersible pump are the most effective samplers and the bladder and peristaltic pumps are the least effective samplers for POCs at this site.

TABLE 4—*Tukey's test results: individual purgeable organic compound and overall orders and of samplers for the northern New Jersey site*

	Individual Compounds[a,b]					Ov
Order	1,1-dichloroethylene	1,1-dichloroethylene	1,1,1-trichloroethane	Trichloroethylene	Tetrachloroethylene	Order
1	PSB	PSB	PSB	PSB	GEAR	1.03
2	GEAR	GEAR	GEAR	GEAR	PSB	1.55
3	OB	HR	HR	OB	OB	3.34
4	SYR	SYR	SYR	SYR	HR	3.42
5	HR	OB	OB	HR	SYR	3.51
6	BLAD	BLAD	BLAD	BLAD	BLAD	5.75
7	PER	PER	PER	PER	PER	7.00
Range (μg/L)	70–48	49–32	920–630	56–4[illegible]	260–170	

[a] BLAD = bladder pump; OB = open bailer; HR = helical-rotor submersible pump; PSB = p[illegible] bailer; GEAR = gear submersible pump; SYR = syringe sampler; PER = peristaltic pump

[b] Sampling devices within a bracket do not differ significantly at the 95% confidence level in their [illegible] mean POC concentrations.

The poor performance of the bladder pump was surprising because this pump was [illegible] most effective samplers at Cape Cod and it was highly rated in previous studies [illegible] northern New Jersey well had a static water level of approximately 2 m (6 ft) below la[illegible] and was sampled at a depth of 4 m (12 ft). The bladder pump was 2 m (6 ft) long so th[illegible] of the sampler was at or near the top of the water column in the well. Any drawdo[illegible] sample collection would have caused the pumping level to decline below the top of th[illegible] pump. A loose connection between the bladder pump and the discharge line may hav[illegible] air to leak into the system, or the pump body may have been unable to fill completely w[illegible] resulting in a gas head space for POCs to partition into. Either possibility could lead to [illegible] of a mixture of air and water, thereby promoting aeration and stripping of the volatile[illegible] sampled water. It is believed that the poor bladder pump performance at this site w[illegible] simply by the operational problem that the height of the wate[illegible] column in the well was [illegible] to keep a pump of this size submerged.

Southern New Jersey Site

Statistical analysis of the southern New Jersey results was done on 12 to 23 replicate conc[illegible] for each of the 7 samplers for each of 11 compounds. The difference in numbers of repl[illegible] caused by analytical difficulties and by an effect of sampling order/pumping rate simil[illegible] experienced at the northern New Jersey site that resulted in the loss of a round of da[illegible] samplers. This problem will be discussed in the "Effect of Pumping Rate" subsection.

Analysis of variance of the southern New Jersey data indicated that the standardi[illegible] concentrations of the samplers differ significantly (at $p \leq 0.05$) for only 6 of the 11 [illegible] organic compounds identified at this site. The Tukey's test results for the six affected c[illegible] are given in Table 5. The groupings show much overlap between samplers at this site. N[illegible] or group of samplers was consistently more or less effective than the others. Indeed, the [illegible] pump, which had previously been the least effective sampler at the first two sites, wa[illegible] effective pump for three of the six compounds at this site.

The overall order and grouping of samplers at this site (last 2 columns in Table 5)

TABLE 5—*Tukey's test results, individual purgeable organic compounds and overall orders and groupings of samplers for the southern New Jersey site.*

	Individual Compounds[a,b]						Overall	
Order	Vinyl chloride	1,1-dichloro-ethane	Chloro-form	Tri-chloro-ethylene	Benzene	Ethyl-benzene	Order	Sampler
1	PSB	PSB	PER	PSB	PER	PER	2.95	PER
2	GEAR	OB	HR	OB	BLAD	HR	3.11	BLAD
3	BLAD	GEAR	BLAD	BLAD	HR	BLAD	3.49	PSB
4	OB	BLAD	OB	GEAR	GEAR	PSB	3.98	OB
5	PER	SYR	GEAR	PER	PSB	GEAR	4.05	GEAR
6	HR	PER	SYR	SYR	OB	OB	5.14	HR
7	SYR	HR	PSB	HR	SYR	SYR	6.45	SYR
Range (μg/L)	83-69	17-11	17-12	39-28	69-58	29-22		

[a] BLAD = bladder pump; OB = open bailer; HR = helical-rotor submersible pump; PSB = point-source bailer; GEAR = gear submersible pump; SYR = syringe sampler; PER = peristaltic pump.

[b] Sampling devices within a bracket do not differ significantly at the 95% confidence level in their standardized mean POC concentrations.

all samplers except the syringe are included in the top group. Even the syringe overlaps with most other samplers.

The performance of the peristaltic pump at this site is very different from its previous performances at the other sites. The effect of temperature on the operation of the peristaltic pump may offer one possible explanation. Both the northern and southern New Jersey wells are shallow and unconfined and sampled at similar depths. The only difference is that the northern New Jersey well was sampled in August, when the ambient air temperature was 29°C (85°F), whereas the southern New Jersey well was sampled in December when the ambient air temperature was close to 0°C (32°F). Solar heating of the discharge line and the receiving flask at the surface probably combined with the high air temperature to produce favorable conditions for degassing of purgeables from the water samples during the northern New Jersey sampling. At the southern New Jersey sampling site the weather was cloudy and the air temperature was lower than that of the sampled ground water. Therefore, conditions were optimal for the POC's to stay in solution and be recovered in the samples. This may partially explain why all the samplers overlap so much in the Tukey's test results at the southern New Jersey site.

Overall Order and Grouping

To summarize the results for all three sites, an overall order was calculated using the standardized mean concentrations for each of the 7 samplers for each of the 15 compounds that exhibited significant differences between sampling devices (4 compounds at the Cape Cod site, 5 compounds at the northern New Jersey site, and 6 compounds at the southern New Jersey site). The standardized means of each sampler were averaged over all 15 compounds and converted to a 1 to 7 scale for ease of understanding and presentation. An analysis of variance and Tukey's test were not used in this overall comparison because the known differences in results between sites would result in a significant sampler by site interaction term in any analysis of variance model. The results are given in the left half of Table 6.

The gear submersible pump, point-source bailer, open bailer, helical-rotor submersible pump, and bladder pump are all closely grouped; their scores differing by only 0.64 on a scale from 1

TABLE 6—*Overall orders of sampling devices based on standardized mean concentration coefficient-of-variation data from all three well sites.*

Standardized Mean Concentration Data		Coefficient-of-Variation Da	
Overall Scores	Sampler	Overall Percentages	Sampler
3.01	gear submersible pump	17.6	gear submersible pump
3.02	point-source bailer	17.7	bladder pump
3.15	open bailer	20.4	helical-rotor submersibl
3.51	helical-rotor submersible pump	20.6	peristaltic pump
3.65	bladder pump	20.8	syringe sampler
5.12	syringe sampler	22.3	open bailer
5.15	peristaltic pump	22.3	point-source bailer

to 7. This implies that overall there are only minor diffe ences in the ability of the devices to recover the purgeable organic compounds sampled at the three test sites because of previously discussed operational problems, the overall scores of the point and the bladder pump are lower than they could have been. Thus, the actual differe the highest and lowest scores for these five samplers may be even less.

The peristaltic pump and the syringe sampler are the only two samplers that consist lower POC concentrations than the others. Previous studies [*1–3*] have also found reduc of purgeable organic compounds with the peristaltic pump in laboratory tests. Pr losses are due to the POCs degassing into the vacuum created by the suction-lift m which the pump operates. The reduced recoveries of the syringe sampler were appa by failure of the seal between the Teflon piston and the syringe barrel. Suspend matter in the well may have caused this seal to wear and then leak, exposing the samp pressures when the sampler was being filled or to increased pressures when the sampl emptied. Degassing or stripping of the purgeables from the water samples appar during these sampling operations.

The coefficients of variation of the mean concentration data are a measure of the which the sampling devices are able to recover purgeable organic compounds. To s coefficient of variation data from all three sites, an overall order was calculated iden of the mean concentration data using the actual coefficient of variation percentage each sampler for each compound. These results are presented in the right half of clear groupings are obvious based on these values, with less than 5% separating least precise samplers. There is no indication that a significant difference exists in P precision between the sampling devices. However, the three samplers with the lowe of variation (highest precision) in Table 6 are all positive-displacement pumps, whe with the highest coefficients of variation (lowest precision) are all grab sampling d depending on the general class of sampler used, there may be a slight effect on th POC sampling. Barcelona and others [*3*] noted that grab samplers were subject to grea in POC recoveries due to their heavy dependence on the experience of the sampling the care with which they are used.

Effect of Pumping Rate

Two different effects caused by pumping rate were observed in this study. First different well flushing rates prior to sampling was purposely tested at the northern

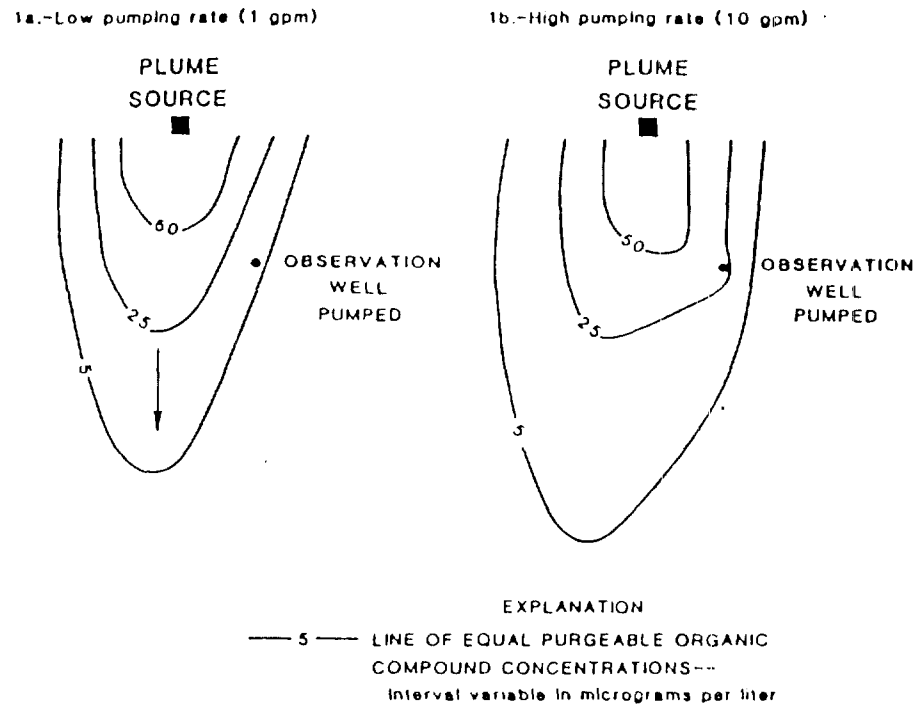

FIG. 1—*Effect of pumping rate on lines of equal purgeable organic compound concentrations in a hypothetical plume*

site. Secondly, the effect of a greatly reduced flushing rate was observed unintentionally in sampling for POCs at the southern New Jersey site.

At the northern New Jersey site, the well was flushed at pumping rates of 3.8 L/min (1 gpm) the first day and 38 L/min (10 gpm) on the second day. When field water-quality measurements stabilized each day, the sampling was carried out using the seven sampling devices in a randomly determined order. The mean concentrations of the five POCs determined to be significantly affected by sampling device were 21 to 41% higher on the second day than on the first day for the sampler with the highest overall recoveries. The difference between the mean concentrations for the most effective and least effective samplers ranged from 28 to 40% for these five POCs. Thus, the pumping rate at which a well is flushed prior to sampling for POCs can be of the same importance as the type of sampling device used.

The probable explanation of the difference in mean POC concentrations at the two pumping rates is illustrated by the hypothetical plumes shown in Fig. 1. In Fig. 1*a*, a low pump rate [3.8 L/min (1 gpm)] is used to flush a well and has a certain minimal effect on the shape of the contaminant concentration contours. In Fig. 1*b*, a higher pump rate [38 L/min (10 gpm)] is used to flush the same well and, due to its larger cone of depression and increased hydraulic stress on the system, distorts the contaminant concentration contours and draws in a different (higher) concentration than the lower pump rate. It is probable that such a scenario occurred at the northern New Jersey well. However, depending on the well location with respect to the plume and the site

hydrogeology, it is also possible for POC concentrations to decrease with increased pu such a case, the higher pumping rate would increase the rad us of the cone of depression in less-contaminated ground water from a larger area of the aquifer.

At the southern New Jersey site, the well was flushed the first day at a uniform [approximately 3.8 L/min (1 gpm)] until stable field measurements indicated water of un water quality was being produced. Sampling then took place with the seven sampling d a randomly determined order. As an example, the mean concentrations of trichloroethylene for each of the samplers is plotted in Fig. 2 in the order in which they were used. In th order, the first four samplers (B, G, A, and C) were pumping devices and the last thr and E) were grab samplers. The mean concentration of trichloroethylene remained stabilized level for all four pumping devices and for the first grab sampler. However, concentrations for the final two grab samplers decreased by an average of 39%. This water quality was confirmed by corresponding decreases in the field water-quality meas (specific conductance, chloride, and UV absorbance). Thus, within one hour of the ces pumping, the trichloroethylene concentration contours apparently changed from a situati to that illustrated in Fig. 1*b* to that in Fig. 1*a*. The rapid decrease in POC concentrat have been aided by the fact that the plume is not areally extensive.

Summary and Conclusions

Significant differences among the mean concentrations recovered with seven sampl found for selected POCs at each of the three test sites. The relative order of sampler effe varied between sites and among compounds detected at any single site.

The gear submersible pump, point-source bailer, open bailer, helical-rotor submersib and bladder pump were all closely grouped, suggesting a lack of any real differences am in their ability to recover the POCs sampled under the conditions present at the three s peristaltic pump and the syringe sampler were the only samplers that consistently recove POC concentrations than the others. Presumably the peristaltic pump losses were c degassing of the POCs into the vacuum created by the suction-lift mechanism by which operates. Reduced POC concentrations obtained with the syringe sampler were apparent by leakage of the gastight seal between the Teflon piston and the syringe barrel, whic the samples to both very low and very high pressures during the sampling process.

The overall order of the samplers based on their coefficients of variation indicated difference between the sampling devices in the precision with which they recovere However, the three samplers with the lowest coefficients of variation (highest precision positive-displacement pumping devices, whereas the three samplers with the highest co of variation (lowest precision) were all grab-sampling devices.

Operating conditions, such as mechanical problems, ambient air temperature, and p the sampler in the water column of the well, can have significant impacts on the abil sampling device to recover purgeable organic compounds. In addition, scale effects, su size of the plume being sampled, the distance from the source to the sampling well pumping rate with which the well is flushed, can significantly influence the recovery of a well site. In this study, these factors were as important as the type of sampling devic take the samples.

The results of these field experiments should have a great deal of transfer value to n where sampling for purgeable organic compounds is of interest. Each of the sites was hydr similar in that all were unconfined sand and gravel aquifers of relatively shallow depth m (12 to 50 ft)]. It is not uncommon to find ground-water contamination problems purgeable organic compounds in aquifers such as these due to their high permeability. detected in this study had a wide range of volatilities and included the compounds most c

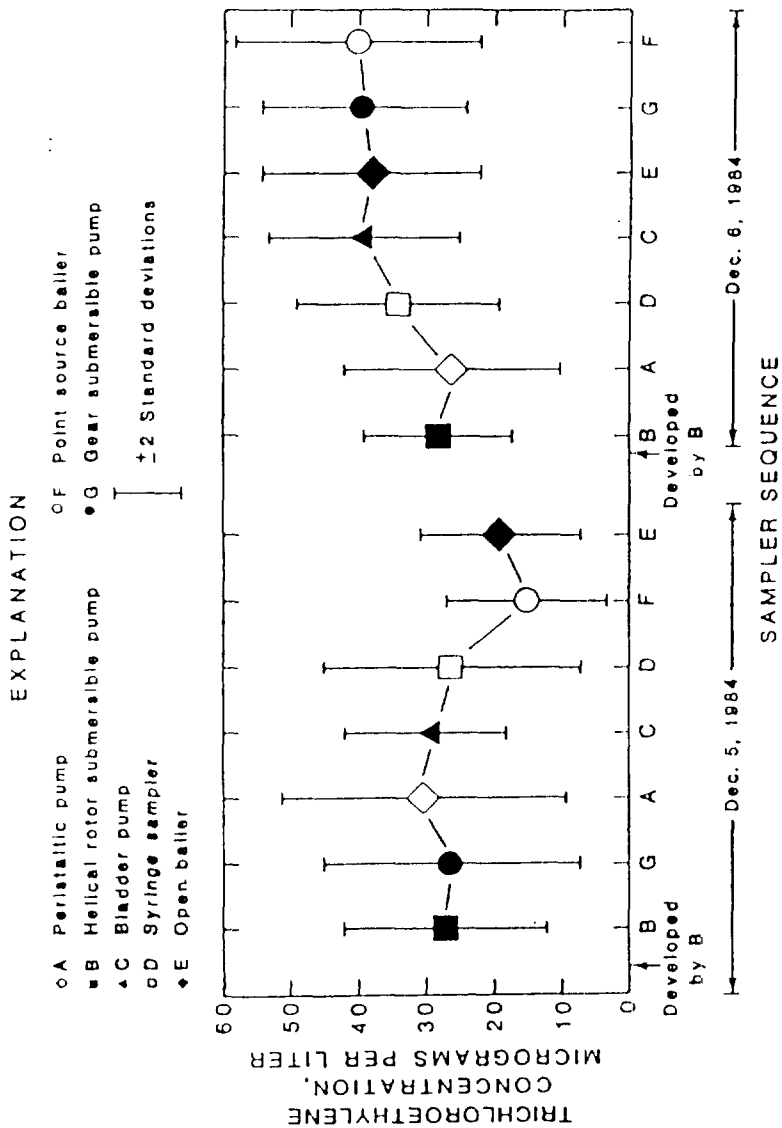

FIG. 2—*Variation of mean trichloroethylene concentrations by sampler at the southern New Jersey test site, 5 and 6 Dec. 1984.*

found in contaminated ground water such as dichloroethylene, trichloroethylene, and t ethylene.

The ideal sampler for purgeable organic compounds would: (1) subject the sample to of turbulence, (2) not expose the sample to negative pressure or vacuum, (3) not heat t and (4) be constructed of nonreactive materials such as stainless steel, Teflon, Vitor The top five sampling devices—the gear submersible pump, point-source bailer, o helical-rotor submersible pump, and bladder pump—all meet these criteria and may be proper care to collect POC samples in suitable situations. If a well is 5 cm (2 in.) with a limited amount of water to flush from the casing, then one of the positive-di pumps can be used to both flush and sample the well for POCs. However, if the well l diameter and a larger volume of water to flush, a nonidea pump that has a higher pu may be used to flush the casing, after which a bailer or a positive-displacement pump to collect the sample for POCs.

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