Evaluation of Passive Diffusion Bag and Dialysis Samplers in Selected Wells at Hickam Air Force Base, July 2001

Water-Resources Investigations Report 02-4159

Prepared in cooperation with the
AIR FORCE CENTER FOR ENVIRONMENTAL EXCELLENCE

U.S. Department of the Interior
U.S. Geological Survey

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By Don A. Vroblesky and Tasha Pravecek

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Columbia, South Carolina
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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
inch (in.)	25.4	millimeter (mm)
foot (ft)	0.3048	meter
mile (mi)	1.609	kilometer
gallon (gal)	3.785	liter

Sea Level: In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929—A geodetic datum derived from a general adjustment of the first-order level nets of the United States and Canada, formerly called Sea Level Datum of 1929.

Chemical concentration: In this report, chemical concentration in water is expressed in metric units as milligrams per liter (mg/L) or micrograms per liter (µg/L).

Temperature can be converted from degrees Celsius (^{o}C) to degrees Fahrenheit (^{o}F) as follows:
$^{o}C = (^{o}F - 32) \times 5/9$

AFB	Air Force Base
EDTA	ethylene diaminetetra acetic acid
LDPE	low-density polyethylene
µ	micron
mL/min	milliliter per minute
PDB	passive diffusion bag
RPD	ralative percent difference
USGS	U.S. Geological Survey
VOC	volatile organic compound

Evaluation of Passive Diffusion Bag and Dialysis Samplers in Selected Wells at Hickam Air Force Base, Hawaii, July 2001

By Don A. Vroblesky[1] *and* Tasha Pravecek[2]

ABSTRACT

Field comparisons of chemical concentrations obtained from dialysis samplers, passive diffusion bag samplers, and low-flow samplers showed generally close agreement in most of the 13 wells tested during July 2001 at Hickam Air Force Base, Hawaii. The data for chloride, sulfate, iron, alkalinity, arsenic, and methane appear to show that the dialysis samplers are capable of accurately collecting a passive sample for these constituents. In general, the comparisons of volatile organic compound concentrations showed a relatively close correspondence between the two different types of diffusion samples and between the diffusion samples and the low-flow samples collected in most wells. Divergence appears to have resulted primarily from the pumping method, either producing a mixed sample or water not characteristic of aquifer water moving through the borehole under ambient conditions. The fact that alkalinity was not detected in the passive diffusion bag samplers, even when deployed in alkaline water, implies that the passive diffusion bag samplers can be used to collect volatile organic compounds from highly alkaline waters without volatilization loss from effervescence, which can occur when a sample is acidified for preservation. Both dialysis and passive diffusion bag samplers are relatively inexpensive and can be deployed rapidly and easily. Passive diffusion bag samplers are intended for sampling volatile organic compounds only, but dialysis samplers can be used to sample both volatile organic compounds and inorganic solutes. Regenerated cellulose dialysis samplers, however, are subject to biodegradation and probably should be deployed no sooner than 2 weeks prior to recovery.

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INTRODUCTION

Diffusion samplers have been used in environmental studies for several years. Low-density polyethylene (LDPE) diffusion samplers have been shown to be a cost-effective alternative to conventional methods to provide samples of volatile organic compounds (VOCs) in ground water at wells (Vroblesky and Hyde, 1997; Parsons Engineering Science, Inc., 1999; Church, 2000; Hare, 2000; McClellan AFB Environmental Management Directorate, 2000; Vroblesky and others, 2000; Vroblesky and Peters, 2000; Vroblesky and Petkewich, 2000) and at zones where VOC-contaminated ground water discharges to surface water (Vroblesky and others, 1991, 1996, 1999; Vroblesky and Robertson, 1996; Lyford and others, 1999a,b; Savoie and others, 1999, 2000; Vroblesky, 2000). In addition, a wide variety of diffusion samplers have been used to determine porewater concentrations of inorganic solutes. Samplers for inorganic constitutents include variations of the samplers introduced by Hesslein (1976) and Mayer (1976). Membranes have included nylon screens (Paludan and Morris, 1999; Vroblesky and others, 2002), filter paper (Davis and Atkins, 2001), and dialysis membranes (Mayer, 1976; Bottomly and Bayley, 1984; Ronen and others, 1986; Webster and others, 1998; Diog and Liber; 2000, Vroblesky and others, 2002), among others. Mulitport configurations of dialysis cells have been used to define heterogeneity in the screened intervals of wells (Ronen and others, 1986, Kaplan and others, 1991).

Although use of the LDPE passive diffusion bag (PDB) samplers has provided cost savings (McClellan AFB Environmental Management Directorate, 2000), their application has been limited to sites where VOCs were the target contaminants. If a simple, inexpensive diffusion sampler were available that was capable of sampling both VOCs and inorganic solutes, then the scope of wells suitable for application of diffusion sampling would be substantially increased. Tests of dialysis bags deployed in wells implies that these types of samplers have the potential to provide a representative sample of both VOCs and ionic solutes from ground water (Kaplan and others, 1991; Vroblesky and others, 2002; Thomas Imbrigiotta, U.S. Geological Survey, written commun., 2002).

The purpose of this report is to compare groundwater concentrations of both VOCs and inorganic solutes obtained from side-by-side tests of an updated dialysis sampler configuration (Vroblesky and others, 2002) and PDB samplers to concentrations obtained by using low-flow samplers in wells. The tests were conducted during July 2001 in 13 wells at Hickam Air Force Base (AFB), Hawaii, in cooperation with the Air Force Center for Environmental Excellence, San Antonio, Texas.

Site Description

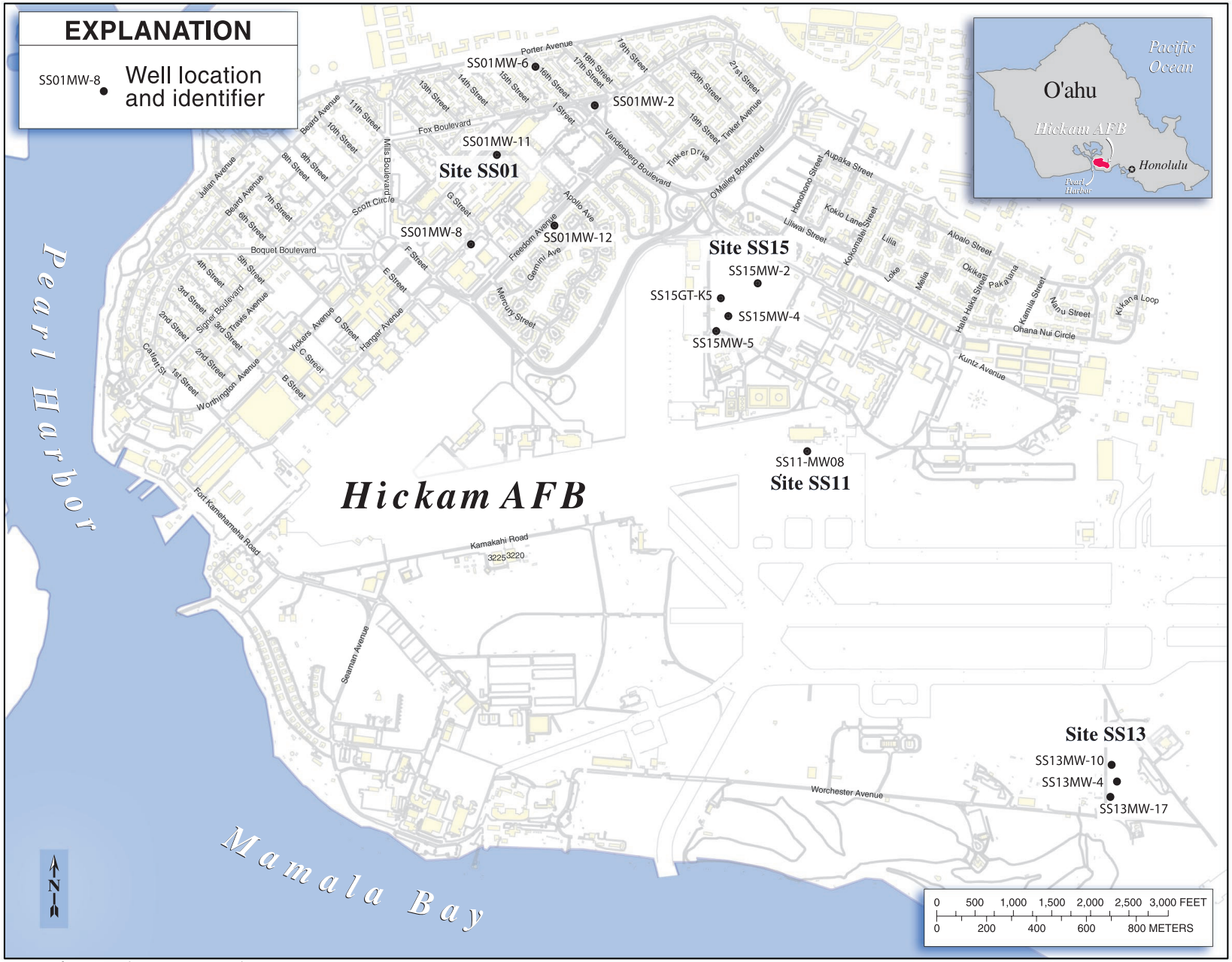
Ground water at Hickam AFB is recharged by precipitation and lateral flow from upgradient areas. Discharge is predominantly to surface-water bodies. Depth to the water table at the tested wells ranges from about 7.3 to 12.7 ft below top of casing. Drillers' logs indicate that the water-table aquifer consists primarily of weathered and fractured tuff and sandy coralline gravel (Mark Peterson, 15 Civil Engineering Squadron, U.S. Air Force, written commun., 2002). Four areas containing contaminated ground water at Hickam AFB were examined during this investigation: site SS01, which contains a gas station and a residential area; site SS11, which is a ramp area near the runway; site SS13, which includes a tank farm; and site SS15, which is a golf course near the flight line (fig. 1). The contaminants at sites SS01, SS11, and SS15 are primarily hydrocarbons related to petroleum. Light non-aqueous-phase liquid is present in some parts of these sites. Site SS13 historically has had high mercury and copper values, but these solutes were either not detected during this investigation, or the concentrations were flagged as having laboratory uncertainties.

Acknowledgments

This investigation would not have been possible without the assistance of William Grannis and Mark Peterson of the 15 Civil Engineering Squadron, U.S. Air Force, Hickam AFB, Hawaii. We also would like to thank Shana Bagley and Manish Joshi of Earth Tech, San Antonio, Texas. Ms. Bagley provided valuable field assistance and Mr. Joshi provided a substantial amount of organizational and logistical assistance.

METHODS

Diffusion samplers and PDB samplers were deployed in 13 wells at Hickam AFB, Hawaii, as a test to compare diffusion-sampling methods to a conventional sampling method. The conventional method used for comparison was low-flow sampling. Well and sampling data are listed in table 1.



Basemap from 15 Civil Engineering Squadron, U.S. Air Force

Figure 1. Locations of observation wells at Hickam Air Force Base, Hawaii, July 2001.

Table 1. Well and sampling data, Hickam Air Force Base, Hawaii, July 2001

[ft BLS, below land surface; ft BTOC, feet below top of casing;---, data not collected; all samplers were deployed for 14 days]

Well	Well diam-eter (inches)	Screen length (feet)	Screened interval (ft BLS)	Flow meter test?	Depth to water at time of deploy-ment (ft BTOC)	Sounded depth to well bottom (ft BTOC)	Satu-rated interval (feet)	Distance from well bottom to sampler center (feet)	Depth of sampler center (ft BTOC)	Sampler deploy-ment date	Sampler recovery date	Low-flow sampling date
SITE SS01												
SS01 MW-2	4	15	9.5-24.5	no	14.56	24.34	9.78	8.3	16.04	07/10/01	7/24/01	---
								5.3	19.04	07/10/01	7/24/01	07/26/01
								2.3	22.04	07/10/01	7/24/01	---
SS01 MW-6	4	15	9.5-24.5	yes	9.45	24.83	15.38	8.3	16.53	07/12/01	7/26/01	---
								5.3	19.53	07/12/01	7/26/01	07/27/01
								2.3	22.53	07/12/01	7/26/01	---
SS01 MW-8	4	15.5	4-19.5 feet BTOC	no	9.09	18.5	9.41	8.3	10.2	07/10/01	7/24/01	07/26/01
								5.3	13.2	07/10/01	7/24/01	---
								2.3	16.2	07/10/01	7/24/01	---
SS01 MW-11	4	15	9.5-24.5	yes	14.4	24.61	10.21	8.3	16.31	07/12/01	7/26/01	---
								5.3	19.31	07/12/01	7/26/01	07/27/01
								2.3	22.31	07/12/01	7/26/01	---
SS01 MW-12	4	15	9.5-24.5	yes	12.73	24.68	11.95	11.3	13.38	07/12/01	7/26/01	---
								8.3	16.38	07/12/01	7/26/01	07/27/01
								5.3	19.38	07/12/01	7/26/01	---
								2.3	22.38	07/12/01	7/26/01	---
SITE SS11 (ramp area)												
SS11 MW-8	4	10	4-14	no	7.61	14.49	6.88	4.8	9.69	07/11/01	7/25/01	07/26/01
								1.8	12.69	07/11/01	7/25/01	---
SITE SS13 (tank farm)												
SS13 MW-4	4	14.5	5-19.5	yes	8.13	19.83	11.7	10.3	9.53	07/12/01	7/26/01	---
								7.3	12.53	07/12/01	7/26/01	07/27/01
								4.3	15.53	07/12/01	7/26/01	---
								1.3	18.53	07/12/01	7/26/01	---
SS13 MW-10	4	10.6	5-15.6		7.29	15.09	7.8	5.3	9.79	07/11/01	7/25/01	07/26/01
								2.3	12.79	07/11/01	7/25/01	---
SS13 MW-17	4	10	5-15	no	6.78	15.1	8.32	7.3	7.8	07/11/01	7/25/01	---
								4.3	10.8	07/11/01	7/25/01	07/26/01
								1.3	13.8	07/11/01	7/25/01	---
SITE SS15 (golf course)												
SS15 MW-2	4	10	7.5-17.5	no	9.96	17.94	7.98	5.6	12.34	07/10/01	7/24/01	07/25/01
								2	15.94	07/10/01	7/24/01	---
SS15 MW-4	4	10	5-15	no	6.55	14.02	7.47	5.9	8.12	07/10/01	7/24/01	07/25/01
								2	12.02	07/10/01	7/24/01	---
SS15 MW-5	4	15	1.5-14.5		5.07	15	9.93	8.3	6.7	07/11/01	7/25/01	---
								5.3	9.7	07/11/01	7/25/01	07/26/01
								2.3	12.7	07/11/01	7/25/01	---
SS15 GT-K5	4	17	3-20 TOC	yes	7.61	22.4	14.79	12.3	10.1	07/12/01	7/26/01	---
								9.3	13.1	07/12/01	7/26/01	07/27/01
								6.3	16.1	07/12/01	7/26/01	---
								3.3	19.1	07/12/01	7/26/01	---

Diffusion Sampler Construction and Deployment

The PDB samplers consisted of sealed polyethylene bags containing anaerobic deionized water. The general method of deployment and recovery for PDB samplers is discussed in Vroblesky (2001). The PDB samplers used in this investigation were purchased commercially (Eon Products, Inc.). The samplers were about 1 ft long and were filled in the field by means of a removable plug at the sampler bottom.

Each dialysis sampler was constructed onsite and consisted of a perforated acetate or plastic pipe inside a sleeve of high-grade regenerated cellulose tubular dialysis membrane (Membrane Filtration Products, Inc., Seguin, Texas) with an outer protective LDPE mesh (Vroblesky and others, 2002).

The membranes used for the dialysis samplers had a nominal molecular-weight cutoff of 8,000 daltons, or about 18 angstroms pore size, and a flat width of about 3 in. (76 mm) (cost was about $180 for a 32.8-ft roll). The dialysis membrane was supplied pretreated to remove sulfur compounds and residual metals. The pretreated membrane was packaged in a solution of methanol and ethylene diaminetetra acetic acid (EDTA), which was removed by rinsing with deionized water prior to use. An alternative approach not used in this investigation would be to use less expensive dry membranes (about $110-180 for a 98.4-ft roll) that must be cleaned through a series of steps that involve soaking and rinsing with deionized water, heated sodium bicarbonate solution, EDTA, and sodium azide solution to remove residual glycerol, sulfide, cadmium, chromium, copper, iron, nickel, zinc, and lead. The inner plastic sleeve and outer protective LDPE mesh were washed with deionized water prior to use.

To construct a dialysis sampler, holes were drilled in a plastic pipe (about 1 to 1.5 ft long, 0.005 in. thick, 1.45 in. outside diameter), and the pipe then was sanded to remove burrs that could tear the membrane. The cellulose acetate dialysis tube was cut to a length of about 2 to 2.5 ft and was thoroughly washed with deionized water. One end of the tube was tied in a knot. The precleaned perforated plastic pipe then was slid into the dialysis tube for structural support (fig. 2). The sampler was filled with deionized water at the time of sampler deployment, and the other end of the membrane was tied. The second knot was tied as closely as possible to the inner plastic pipe because, as water diffuses out of the bag, the bag volume decreases. Placing the knot as closely as possible to the inner plastic pipe reduces the amount of bag-volume lost during equilibration. The assembly was slid into a length of precleaned low-density polyethylene mesh for abrasion protection.

The structural support provided by the inner perforated acetate or plastic pipe is important to allow the sampler to retain water by preventing its collapse during diffusion. Dialysis allows equilibrium concentrations to be achieved by two basic processes. The first involves the transfer of water from an area of low solute concentration to an area of high solute concentration. Thus, a diffusion sampler filled with deionized water will tend to collapse as water exits the bag when deployed in nondilute aqueous solutions. The second mechanism of dialysis transfer involves the movement of solutes from an area of high solute concentration to an area of low solute concentration. Solute transfer is the dominant mechanism by which water within the diffusion sampler achieves chemical equilibrium with water outside the diffusion sampler once the bag can no longer collapse because of the inner perforated pipe. Such a pipe is not needed for PDB samplers because polyethylene does not transmit water.

The PDB samplers and dialysis samplers were filled with anaerobic deionized water at the time of sampler deployment. Anaerobic water was prepared by bubbling nitrogen through approximately 5 gallons of deionized water until the dissolved oxygen concentration was reduced to less than 0.5 mg/L (as measured by CheMets colorimetric methodology, Calverton, Va.). A peristaltic pump was used to transfer the water from the container into the samplers.

Deployment of the samplers in wells consisted of attaching the samplers to a weighted support line and lowering them into the well. A PDB sampler was attached to a dialysis sampler at each targeted sampling depth or horizon. Each well consisted of at least two targeted horizons (table 1), although in two wells (SS13 MW10 and SS15 MW4), inorganic data were collected at only one of the horizons.

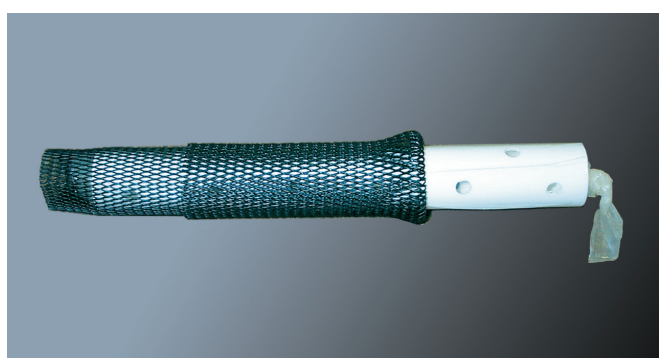


Figure 2. Dialysis bag on perforated pipe with the outer low-density polyethylene mesh pulled partway back.

Equilibration time of dialysis samplers in a laboratory study at 25 ^{o}C was between 20.5 and 92 hours (Vroblesky and others, 2002). This time range is approximately consistent with an independent test of dialysis-sampler equilibration times in which iron and bromide and a variety of chlorinated solvents attained equilibrium within 3 days (Theodore A. Ehlke, U.S. Geological Survey, written commun., 2001). Chloride and manganese attained complete equilibrium and sulfate attained 80 percent equilibrium within 48 hours (Ronen and others, 1986; Magaritz and others, 1989).

When deployed in sediment, the limiting factor in equilibration is predominantly the solute diffusion through the sediments (Webster and others, 1998). Equilibration times of various dialysis samplers for determining porewater inorganic concentrations in previous investigations include 15 to 20 days (Carignan, 1984), 100 hours in unconsolidated clay and silt (Mayer, 1976), and 10 days using a 0.45-µ polysulfone membrane (Bottomley and Bayly, 1984). A variety of studies reported that 2 weeks was adequate for equilibration of these types of samplers in saturated sediment (Carignan and others, 1985; Gaillard and others, 1986; Tessier and others, 1989; Davis and Galloway, 1993; Hare and others, 1994; Bertolin and others, 1995). Based on these data and the previously cited laboratory investigations, a minimum 2-week equilibration time was used in this investigation.

Water-Sample Collection and Diffusion-Sampler Recovery

Low-flow sampling methodology (Barcelona and others, 1994; Shanklin and others, 1995) was used to collect ground-water samples from the wells at Hickam AFB, Hawaii. The wells were purged at a rate of approximately 75-200 mL/min, until the temperature, pH, and specific conductance stabilized and no additional water-level drawdowns were observed. Typically, stabilization required purging over a time period of less than 30 minutes. The low-flow ground-water samples at most wells were collected the day following retrieval of the diffusion samplers from the well. At wells SS01 MW-2 and SS01 MW-8, the low-flow samples were collected 2 days after diffusion-sample recovery.

Inorganic constituents were measured in water from dialysis samples and low-flow samples. Water samples were analyzed by U.S. Environmental Protection Agency method E300.0 for anions and by method SW6010B for metals (U.S. Environmental Protection Agency, 1983, 1992). Inorganic constituents measured during this investigation were alkalinity, arsenic, chloride, iron, lead, methane, sulfate, sulfide, and zinc; however, the suite of inorganic constituents measured at each well varied, depending on the historical sampling data of the well. Water from the dialysis, PDB, and low-flow samplers were analyzed for VOCs by using method 8260B (U.S. Environmental Protection Agency, 1999).

Duplicate diffusion samples were collected from approximately 10 percent of the sampling sites. In general, the diffusion samples compared well with their respective duplicate samples. For most organic constituents, differences between concentrations in diffusion samples and their duplicates were less than 15 percent or less than 2 µg/L. For inorganic constituents, differences between concentrations in diffusion samples and their duplicates at concentrations above 0.5 mg/L were less than 10 percent At a concentration less than 0.5 mg/L, a dialysis iron sample differed from its duplicate by about 0.05 mg/L. Results of duplicate samples analyzed for VOCs by separate laboratories differed by 10 percent or less.

Data Evaluation

Statistical comparisons of the data were conducted in this investigation to provide a general comparison among sample concentrations. Caution should be exercised, however, when using statistics to compare diffusion samples to low-flow samples for a variety of reasons. Comparisons within single-well data usually involve a relatively small data set, thus reducing the confidence level of the comparison. In addition, low-flow sampling and diffusion sampling constitute two different approaches that sometimes produce different types of samples. The low-flow sample typically represents some degree of mixed waters, and the diffusion sample represents only the water that contacted the sampler. Near interfaces of contaminant stratification, even a relatively small amount of mixing can result in low-flow sample concentrations that differ substantially from concentrations obtained by using a diffusion sampler (Vroblesky and Peters, 2000). Therefore, near interfaces of contaminant stratification, statistics can produce an overly harsh evaluation of the comparison, despite the fact that both low-flow and diffusion methods may be producing accurate results.

When the two methods disagree at a particular depth in a chemically stratified well, a more reasonable approach to resolving the difference is to visually compare a plot of concentrations defined by multiple

diffusion samplers to concentrations obtained by low-flow samplers. The evaluation may reveal that the low-flow sample represents a mixing of water over some interval, whereas the diffusion samples represent a more discrete evaluation of the same waters. In this case, both methods correctly represent the ambient concentrations despite a difference in concentrations. On the other hand, if the evaluation shows that the low-flow sampler collects water that does not move through the screened or open interval under nonpumping conditions, then the resulting concentration difference indicates that the two methods are sampling different waters. These conclusions, which require an in-well comparison, are lost when a statistical approach is used in which the population consists of many wells across a particular site and the data from each well are the result from the two methods at a single corresponding depth. Again, this statistical approach has the potential to produce an overly harsh evaluation of the comparison.

If these cautions are taken into account, however, a statistical evaluation sometimes can provide meaningful comparisons. Although it is probable that the statistical evaluation may provide an overly harsh evaluation of the comparison, it is less likely that the evaluation will falsely produce a favorable comparison. If the relative percent difference (RPD) between concentrations obtained by the two methods at a particular depth is small, then it probably is true that the methods agree at that depth in that well.

For this investigation, RPDs were calculated to compare the two different types of diffusion samplers tested, because both types of samplers probably represent approximately the same sampled water. In some cases, the RPD also was used to compare a diffusion sampler at a single depth and the corresponding low-flow sample in a particular well when multiple diffusion-sampler data points were not present in that well. RPDs were calculated using

$$(100)\frac{C_1 - C_2}{0.5(C_1 + C_2)},$$

where C_1 is the larger and C_2 is the smaller of the two compared concentrations.

In wells where multiple diffusion samplers were present, a different evaluation approach was used. Because the pumped sample usually represents some degree of mixing, the average concentration from the diffusion samplers in a particular well was compared to the single concentration from the low-flow sample in that well using a one-side approximate t-test. This approach also has shortcomings in that even when the two sampling methods produce the same concentrations at a particular horizon, the low-flow sampling result may not be the average concentration obtained from the diffusion samplers, resulting in an overly harsh statistical evaluation of the comparison. Again, however, it is much less likely that the approach will imply a good comparison when the two methods are sampling different waters. Therefore, a favorable comparison from the one-sided approximate t-test probably is an accurate indication that the two sampling methods are comparable in the evaluated well.

Statistical comparison of results was conducted at an alpha level of 0.05 (95-percent confidence level), using a modified t-test for normally distributed data. Of the inorganic solutes, the modified t-test was applied to chloride, sulfate, and iron because they had the most samples showing detections without laboratory qualifier flags. Duplicate samples from the same depth were averaged to provide a single value for that depth. The one-sided approximate t-test is described by the following equation:

$$t' = \frac{|x_1 - x_2| - d_0}{\sqrt{\frac{s_1^2}{n_1} + \frac{s_2^2}{n_2}}},$$

where

t' = approximate t statistic;

x_1 = mean of the dialysis sampler concentration;

x_2 = low-flow sample concentration;

d_0 = percent difference to account for analytical error (that is, error factor x low-flow concentration) (the error factor is based on comparison of duplicate samples, and in this investigation it was 0.03 for chloride, 0.08 for iron, and 0.01 for sulfate);

s_1 = standard deviation of the diffusion sampler concentrations;

s_2 = standard deviation of the low-flow sample concentrations (this value is zero because there was only one low-flow sample per well);

n_1 = number of diffusion samplers in the well; and

n_2 = number of the low-flow samples from the well (this value is one).

Because there was only one low-flow sample collected from each well, the above equation reduces to the following equation (Earth Tech, Inc., 2001):

$$t' = \frac{|x_1 - x_2| - d_0}{\sqrt{\frac{s_1^2}{n_1}}} .$$

A close match between concentrations in diffusion samples (dialysis and/or PDB samplers) and low-flow samples in a well was determined by applying the following criteria to the analytical results. A match was considered to be good if the computed t-statistic was greater than the critical t in the modified t-test at the 95 percent confidence level. When RPDs were used, a close match was considered to be an RPD of less than 20 percent. For low-level concentrations (less than about 5 mg/L for sulfate and less than 10 µg/L for VOCs), analytical results were considered to be a close match when the concentration differences were less than 2 mg/L for sulfate and less than 3 µg/L for VOCs. The last criterion is applied to low-level data, because RPDs are more sensitive to differences in concentrations at low levels and, therefore, may not fully reflect similarities in methods. Of the inorganic constituents, RPD is applied only to sulfate, because only sulfate concentrations range from very low (2 mg/L) to very high (1,303 mg/L) at Hickam AFB.

RESULTS AND DISCUSSION

The diffusion-sampler tests show that the dialysis samplers are capable of providing concentrations of inorganic solutes that closely match concentrations from low-flow sampling in most tested wells in the study area. A comparison of VOC concentrations in dialysis samples and PDB samples also showed a close match. The general agreement between the VOC concentrations in PDB samples and concentrations in low-flow samples implies that both PDB and dialysis samples provide representative VOC concentrations in most of the tested wells.

Inorganic Solutes

In general, relatively favorable comparisons were found between concentrations in dialysis samples and low-flow samples for the inorganic solutes examined for this investigation (table 2). Meaningful comparisons could not be made for some of the tested inorganic solutes because of limited data points. Of the inorganic solutes, chloride, sulfate, and iron had the most samples showing detections without laboratory qualifier flags and, therefore, are discussed in further detail in the following paragraphs.

Chloride concentrations in the dialysis samples closely matched concentrations in most of the low-flow samples (fig. 3A). A modified t-test comparison showed that the dialysis-sample chloride concentrations were not statistically different from the low-flow chloride concentrations in 8 of the 13 tested wells (table 3). In 2 of the remaining 5 wells (wells SS13 MW-10 and SS15 MW-4) insufficient data were available to run a t-test. However, the low RPDs (6 and 3 percent, respectively) between concentrations from the low-flow sample and dialysis sample deployed at the same depth indicated a close match. In one of the remaining wells (well SS10 MW-12), the data could not be analyzed using the t-test because they were not normally or natural log-normally distributed, and insufficient data were available to run a nonparametric test.

In most of the wells, the dialysis sampler data showed that chloride had a vertical concentration gradient or stratification (fig. 4D, E, G, H, I, J, K). In these wells, it is likely that mixing during low-flow pumping produces some degree of concentration deviation from the adjacent dialysis sampler.

The chloride concentrations in two wells (SS01 MW-2, and SS11 MW-8) showed a statistical difference between the dialysis and low-flow samples (table 3, fig. 4A and F). In these wells, and in a well in which the chloride concentrations were not statistically analyzed (well SS01 MW-12; fig. 4E), the chloride concentrations in the low-flow samples were higher than in the dialysis samples. The close match in chloride concentrations between sampling methods in other wells suggests that the differences in these wells may be attributed to well-specific factors rather than a diffusion-sampler deficiency. The fact that wells SS01 MW-12 and SS11 MW-8 also exhibited substantial differences in organic-compound concentrations between sampling methods (as will be discussed later in this report), suggests the possibility that the low-flow pumping induced movement of water into the well that did not flow to the well under nonpumping conditions.

Sulfate concentrations showed a close match between results from dialysis samples and low-flow samples (fig. 3B). Eight out of the ten wells statistically examined showed no statistical difference between the dialysis and low-flow sample sulfate concentrations

Table 2. Concentrations of inorganic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001

[Depth of well is feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS, unfiltered low-flow sample; FiLFS, filtered low-flow sample; mg/L, milligrams per liter; µg/L, micrograms per liter; d, duplicate sample; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; ---, data not collected; <, less than]

Well	Depth	Alkalinity, mg/L			Arsenic, mg/L			Chloride, mg/L		Iron, mg/L			Lead, mg/L			Methane, µg/L			Sulfate, mg/L		Sulfide, mg/L			Zinc, mg/L		
		DS	PDBS	UnLFS	DS	UnLFS	FiLFS	DS	UnLFS	DS	UnLFS	FiLFS	DS	UnLFS	FiLFS	DS	PDBS	UnLFS	DS	UnLFS	DS	PDBS	UnLFS	DS	UnLFS	FiLFS
SS01 MW-2	16.04	---	---	---	---	---	---	463	---	0.525	---	---	0.0179	---	---	---	---	---	32.16	---	1	---	---	---	---	---
	19.04	---	---	---	---	---	---	478	503.5	0.345	0.317	0.192F	0.0145	0.0015F	0.0012F	---	---	---	37.75	31.29	1.5	0.6	0.2	---	---	---
	22.04	---	---	---	---	---	---	460	---	0.287	---	---	0.0091	---	---	---	---	---	42.8	---	2.5	1	---	---	---	---
SS01 MW-6	16.53	---	---	---	---	---	---	146.7	---	1.02	---	---	0.0044F	---	---	---	---	---	1.95	---	---	---	---	0.004F	---	---
	19.53	---	---	---	---	---	---	145.8	145.4	1.04	1.16	1	0.004F	---	0.0008F	---	---	---	2.08	1.1	---	---	---	0.003F	---	---
	22.53	---	---	---	---	---	---	144	---	1.01	---	---	0.0036F	---	---	---	---	---	1.97	---	---	---	---	---	---	---
SS01 MW-8	10.2	---	---	---	---	---	---	73.7	69.5	0.73	0.811	0.708	0.0018F	<0.0003	0.0005F	4,100	5,400	5,000	1.65	2.88	---	0.4	---	---	---	---
	13.2	---	---	---	---	---	---	74.1	---	0.732	---	---	0.0018F	---	---	4,000	5,800	---	0.69F	---	---	0.3	<0.1	---	---	---
	13.2d	---	---	---	---	---	---	71.9	---	0.763	---	---	0.002F	---	---	---	---	---	0.68F	---	---	---	---	---	---	---
	16.2	---	---	---	---	---	---	70.5	---	0.735	---	---	0.0017F	---	---	---	---	---	0.89F	---	---	0.3	---	---	---	---
SS01 MW-11	16.31	---	---	---	---	---	---	287.3	---	0.109F	---	---	0.0027F	---	---	---	---	---	20.93	---	---	---	---	0.045	---	---
	19.31	500	<10	375	---	---	---	303.6	344	0.094F	0.132F	0.053F	0.0037F	<0.003	<0.003	---	---	---	21.59	25.35	---	---	---	0.015	0.008F	<0.002
	22.31	---	---	---	---	---	---	358.8	---	0.119F	---	---	0.005	---	---	---	---	---	51.09	---	---	---	---	0.012	---	---
SS01 MW-12	13.38	---	---	---	---	---	---	282	---	0.234	---	---	0.0047F	---	---	---	---	---	6.38	---	---	---	---	0.004F	---	---
	16.38	---	---	---	---	---	---	356.6	391	0.325	0.132F	0.087F	0.0036F	<0.0003	<0.0003	3,900	---	3,800	3.33	4.2	---	---	---	0.007F	<0.002	<0.002
	16.38d	---	---	---	---	---	---	---	---	0.272	---	---	0.0034F	---	---	---	---	---	---	---	---	---	---	0.006F	---	---
	19.38	---	---	---	---	---	---	354	---	0.246	---	---	0.0018F	---	---	---	---	---	4.32	---	---	---	---	0.003F	---	---
		---	---	---	---	---	---	357.2	---	---	---	---	---	---	---	---	---	---	4.39	---	---	---	---	---	---	---
	22.38	---	---	---	---	---	---	355.6	---	0.242	---	---	0.0032F	---	---	---	---	---	3.74	---	---	---	---	0.006F	---	---
SS11 MW-8	9.69	---	---	---	---	---	---	1,201	1,490	0.801	0.84	0.592	0.004F	0.0006F	0.0009F	---	---	---	2.13	3.36	0.15	0.1	0.1	0.013	0.004F	<0.002
	12.69	---	---	---	---	---	---	1,226	---	0.939	---	---	0.0042F	---	---	---	---	---	2	---	<0.1	---	---	0.004F	---	---

Table 2. Concentrations of inorganic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001 (Continued)

[Depth of well is feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS, unfiltered low-flow sample; FiLFS, filtered low-flow sample; mg/L, milligrams per liter; µg/L, micrograms per liter; d, duplicate sample; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; ---, data not collected; <, less than]

Well	Depth	Alkalinity, mg/L			Arsenic, mg/L			Chloride, mg/L		Iron, mg/L			Lead, mg/L			Methane, µg/L			Sulfate, mg/L		Sulfide, mg/L			Zinc, mg/L		
		DS	PDBS	UnLFS	DS	UnLFS	FiLFS	DS	UnLFS	DS	UnLFS	FiLFS	DS	UnLFS	FiLFS	DS	PDBS	UnLFS	DS	UnLFS	DS	PDBS	UnLFS	DS	UnLFS	FiLFS
SS13 MW-4	9.53	---	---	---	---	---	---	3,790	---	0.031F	---	---	---	---	---	---	---	---	536.7	---	---	---	---	---	---	---
	9.53d	---	---	---	---	---	---	3,845	---	---	---	---	---	---	---	---	---	---	532.3	---	---	---	---	---	---	---
	12.53	---	---	---	---	---	---	4,775	4,244	0.046F	0.01F	0.004F	---	---	---	---	---	---	690	621	---	---	---	---	---	---
	12.53d	---	---	---	---	---	---	---	---	0.05F	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
	15.53	---	---	---	---	---	---	4,657	---	0.033F	---	---	---	---	---	---	---	---	764	---	---	---	---	---	---	---
	18.53	---	---	---	---	---	---	5,125	---	0.066F	---	---	---	---	---	---	---	---	834	---	---	---	---	---	---	---
SS13 MW-10	9.79	---	---	---	---	---	---	7,524	7,979	0.69F	0.051F	0.011F	---	---	---	---	---	---	1303	1138	15	---	15	---	---	---
	12.79	---	---	---	---	---	---	---	---	0.172F	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
SS13 MW-17	7.8	---	---	---	---	---	---	6,183	---	0.08F	---	---	---	---	---	---	---	---	1096	---	>20	6	---	---	---	---
	10.8	---	---	---	---	---	---	8,976	6,419	0.064F	0.06F	0.013F	---	---	---	---	---	---	1112	1109	25	5	15	---	---	---
	13.8	---	---	---	---	---	---	6,584	---	0.102F	---	---	---	---	---	---	---	---	1121	---	25	7.5	---	---	---	---
SS15 MW-2	12.34	---	---	---	0.0714	0.106	0.107	569	6,54.2	2.88	3.38	3.03	---	---	---	---	---	---	87.3	97	---	---	---	0.009F	0.005F	0.004F
	15.94	---	---	---	0.055	---	---	596	---	2.58	---	---	---	---	---	---	---	---	176.7	---	---	---	---	0.002F	---	---
SS15 MW-4	8.12	---	---	---	0.0363	0.034	0.0334	82.1	79.4	1.14	1.25	0.925	---	---	---	---	---	---	0.5F	0.58F	---	---	---	0.005F	0.009F	0.003F
	8.12d	---	---	---	---	---	---	82.1	---	---	---	---	---	---	---	---	---	---	0.54F	---	---	---	---	---	---	---
	12.02	---	---	---	0.0369	---	---	---	---	1.24	---	---	---	---	---	---	---	---	---	---	---	---	---	0.007F	---	---
SS15 MW-5	6.7	---	---	---	---	---	---	278.8	---	0.821	---	---	0.0022F	---	---	---	---	---	135.3	---	---	---	---	0.007F	---	---
	9.7	---	---	---	---	---	---	332.3	338	0.86	1.69	1.32	0.0047F	<0.003	<0.003	---	---	---	184.7	193.8	---	---	---	0.005F	0.003F	0.006F
	9.7d	---	---	---	---	---	---	330.5	---	0.93	---	---	0.0053	---	---	---	---	---	185.1	---	---	---	---	---	---	---
	12.7	---	---	---	---	---	---	338.2	---	0.951	---	---	0.005	---	---	---	---	---	201	---	---	---	---	0.014	---	---
SS15 GT-K5	10.1	340	<10	---	---	---	---	298.1	---	1.01	---	---	---	---	---	---	---	---	60.13	---	---	---	---	0.008F	---	---
	13.1	350	<10	350	---	---	---	365.2	419	0.603	0.292	0.195F	---	---	---	---	---	---	98.9	121.9	---	---	---	0.01	<0.002	0.003F
	16.1	340	<10	---	---	---	---	438.1	---	0.151F	---	---	---	---	---	---	---	---	130	---	---	---	---	0.009F	---	---
	19.1	---	---	---	---	---	---	471.4	---	0.192F	---	---	---	---	---	---	---	---	145.1	---	---	---	---	0.004F	---	---

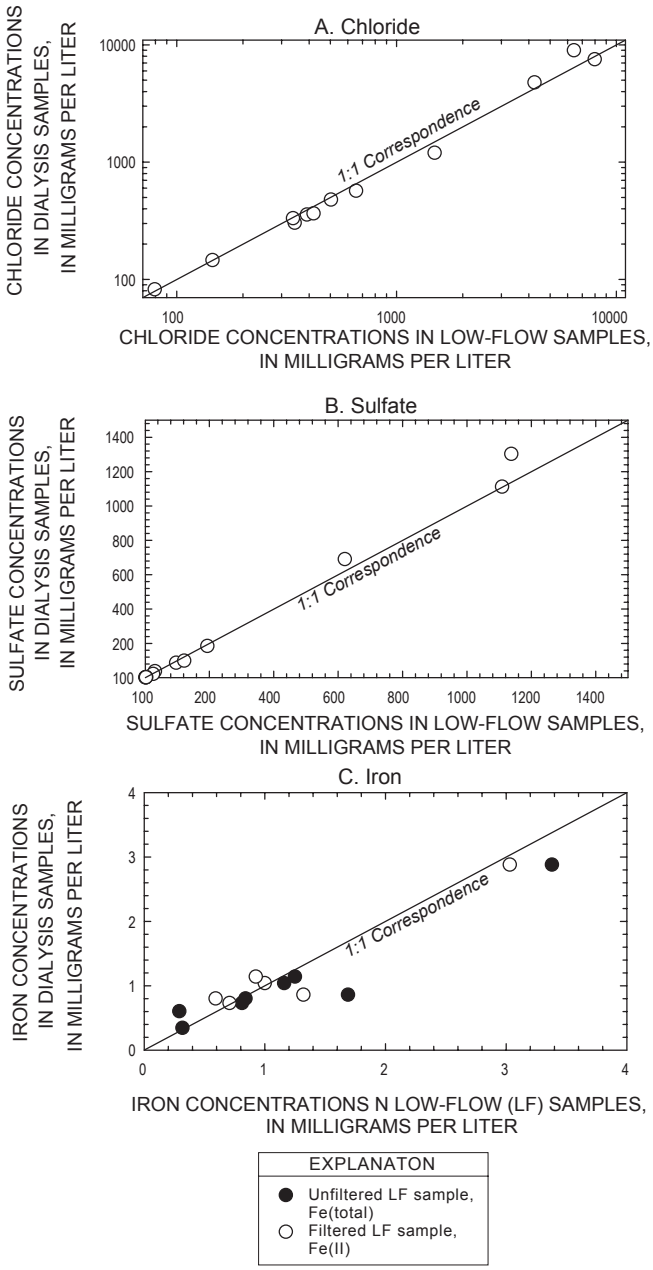


Figure 3. Comparison of chloride, sulfate, and iron concentrations in low-flow samples to concentrations in dialysis samples at the same depth, Hickam Air Force Base, Hawaii, July 2001.

(table 3). In the two remaining wells (SS01 MW-6 and SS11 MW-8 (figs. 5B, and E), however, the concentrations differences were less than 1.3 mg/L and the average concentrations detected were only about 2 mg/L. These small differences in concentrations between dialysis and low-flow sampling methods produce poor t-test matches and RPDs of 45 percent and higher; however, the high RPDs appear to be more a relic of low-range concentrations in a spatially variable aquifer (the sulfate concentrations found in this investigation range from 1.95 to 1,112 mg/L) than a difference in sampling methods. Vertical sulfate distributions show that the concentration differences between the low-flow sample and the adjacent dialysis sample in most wells are due to the sampling method. The low-flow samples represent a mixing of concentrations in a stratified system, whereas the dialysis samples represent localized concentrations (fig. 5).

Iron concentrations also showed close agreement in several of the dialysis and low-flow samples (fig. 3C). Statistical comparison of the iron concentrations without laboratory qualifiers (F values) from dialysis samples to those from unfiltered and filtered low-flow samples showed no statistical difference in five of seven samples when compared to unfiltered low-flow samples and in five of six samples when compared to filtered low-flow samples (table 3). Iron concentrations in unfiltered low-flow samples tended to be slightly higher (10-30 percent) than in filtered low-flow samples (table 2). The comparison between filtered and unfiltered concentrations implies that either particulate iron is being transported through the aquifer or that well disturbances from the removal of the diffusion samplers, or from the emplacement of low-flow tubing and pumping the well, mobilized sediment within the well bore. Because the dialysis samplers have a relatively small pore size (approximately 18 angstroms), iron concentrations from the dialysis sample more closely approximate concentrations from the filtered than from the unfiltered samples (fig. 3C).

The remaining inorganic constituents were analyzed in water samples from only a few wells (alkalinity, arsenic, methane, and sulfide) or the concentrations were too low to provide a meaningful comparison between methods. The data, however, still provide insight into some aspects of sampler capability.

Alkalinity measurements in dialysis samples either closely matched the low-flow sample result (well SS15 GT-K5) or overestimated it (well SS01 MW-11) (table 2). An overestimation typically is not considered a mismatch because it is not unusual for low-flow sampling to dilute concentrations by mixing. Thus, the alkalinity concentrations measured in the dialysis sampler probably approximate alkalinity concentrations in the undisturbed water column in the well. It is important, however, to note that the PDB samplers contained no detectable alkalinity, even when deployed in waters containing greater than 300 mg/L of alkalinity. This is

Table 3. Statistical comparison of chloride, sulfate, and iron concentrations in dialysis and low-flow samples, Hickam Air Force Base, Hawaii, July 2001

[$t_{critical}$, critical value of t-test t statistic; mg/L, milligrams per liter, t', calculated t statistic from modified t-test; ---, not calculated because of qualified or insufficient data. Chloride data from well SS01 MW-12 were not statistically evaluated, because the data were not normally or natural log-normally distributed and there were not enough data points for a nonparametric comparison of groups]

Well	Number of dialysis-sampler depths	Degrees of freedom	$t_{critical}$	Chloride				Sulfate				Iron					
				Concentration in dialysis samples		Comparison of dialysis to low-flow sample concentrations		Concentration in dialysis samples		Comparison of dialysis to low-flow sample concentrations		Concentration in dialysis samples		Comparison of dialysis (ferrous iron) to unfiltered low-flow sample (total iron) concentrations		Comparison of dialysis to filtered low-flow sample (ferrous iron) concentrations	
				Mean (mg/L)	Standard deviation (mg/L)	t'	Are the two methods statistically different?	Mean (mg/L)	Standard deviation (mg/L)	t'	Are the two methods statistically different?	Mean (mg/L)	Standard deviation (mg/L)	t'	Are the two methods statistically different?	t'	Are the two methods statistically different?
SS01 MW-2	3	2	2.92	467	9.64	3.84	yes	35.6	5.3	1.94	no	0.4	0.12	0.604	no	---	---
SS01 MW-6	3	2	2.92	146	1.38	-5.37	no	2	0.07	22	yes	1	0.02	4.97	yes	-6.425	no
SS01 MW-8	3	2	2.92	72	1.68	0.084	no	---	---	---	---	0.7	0.01	1.66	no	-5.21	no
SS01 MW-11	3	2	2.92	317	34.5	0.791	no	31.2	17	0.563	no	---	---	---	---	---	---
SS01 MW-12	4	3	2.35	337	37	---	---	4.45	1.4	0.309	no	0.3	0.04	---	---	---	---
SS11 MW-8	2	1	6.314	1,214	17.7	18.5	yes	2.07	0.09	19.4	yes	0.8	0.10	-0.539	no	3.34	no
SS13 MW-4	4	3	2.35	4,594	554	0.802	no	705	128	1.22	no	---	---	---	---	---	---
SS13 MW-10	1	0	---	7,524	---	---	---	1,303	---	---	---	---	---	---	---	---	---
SS13 MW-17	3	2	2.92	7,248	1,510	0.729	no	1110	12	-1.43	no	---	---	---	---	---	---
SS15 MW-2	2	1	6.314	583	19.1	3.86	no	132	63	0.761	no	2.7	0.21	2.53	no	0.384	no
SS15 MW-4	1	0	---	82	---	---	---	---	---	---	---	1.2	0.07	-0.8	no	3.82	no
SS15 MW-5	3	2	2.92	316	32.5	0.573	no	174	34	1.08	no	0.9	0.07	22	yes	10.7	yes
SS15 GT-K5	4	3	2.353	393	77.4	0.342	no	109	37	0.647	no	---	---	---	---	---	---

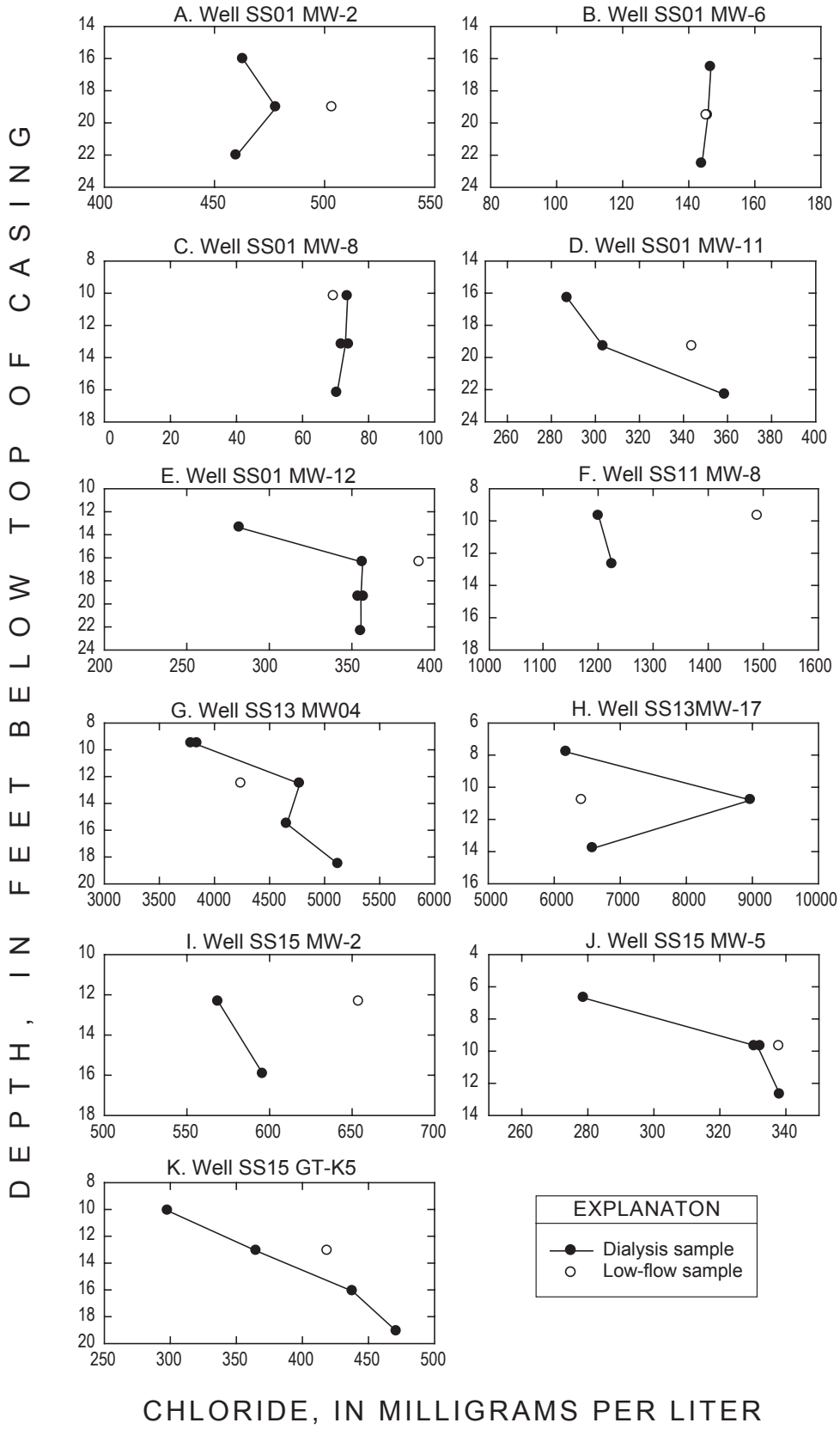


Figure 4. Vertical distribution of chloride in dialysis and low-flow samples from wells at Hickam Air Force Base, Hawaii, July 2001.

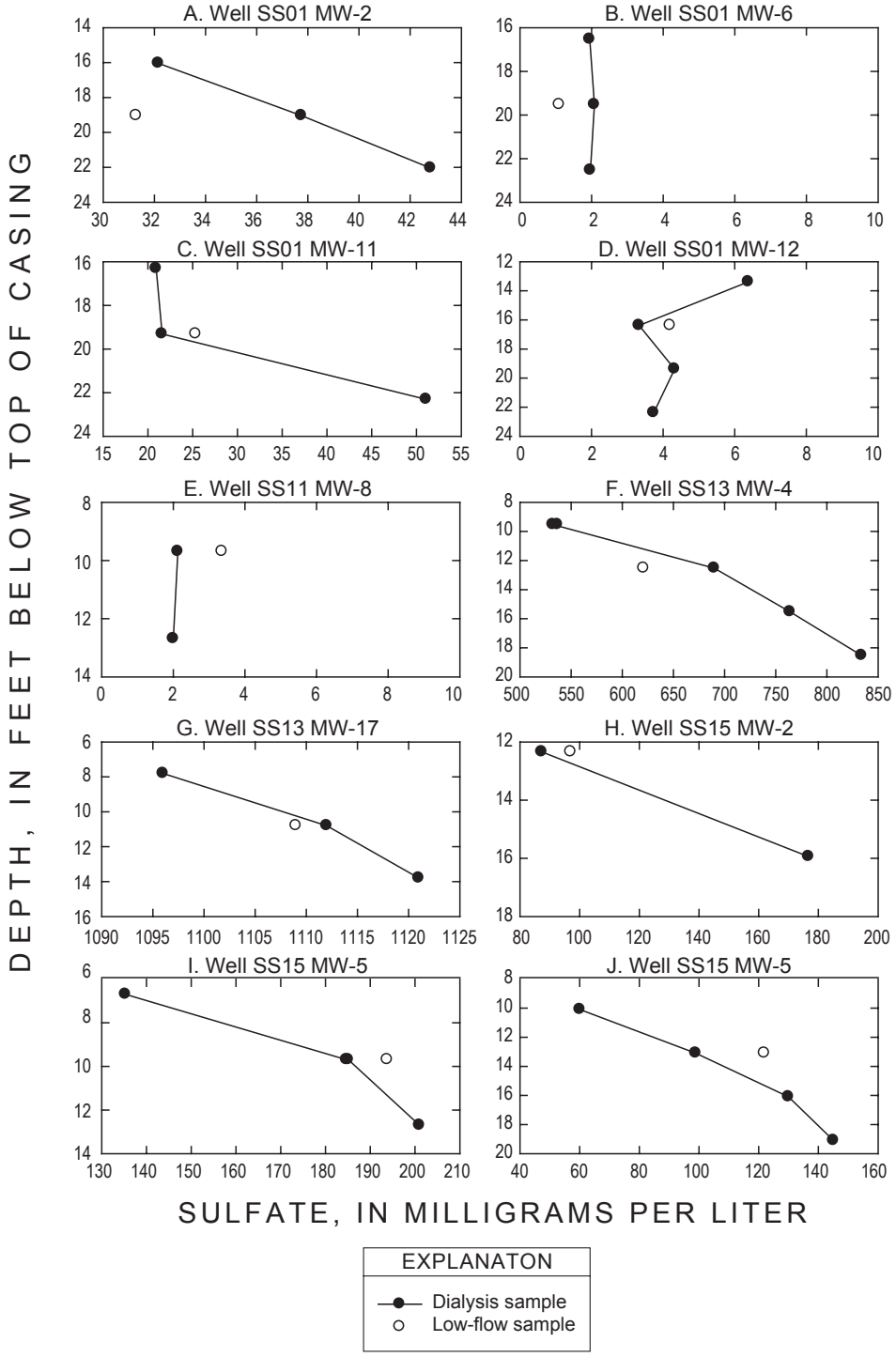


Figure 5. Vertical distribution of sulfate in dialysis and low-flow samples from wells at Hickam Air Force Base, Hawaii, July 2001.

important, because one difficulty in obtaining VOC samples from limestone aquifers is that addition of an acid preservative to high-alkalinity water can cause effervescence due to the neutralization reaction. The effervescence then can volatilize VOCs in the sample, rendering the sample unreliable. A typical response to this situation is to collect another sample and ship it to the laboratory unpreserved, which decreases the holding time from 14 to 7 days (U.S. Environmental Protection Agency, 1992). The fact that the LDPE membrane of PDB samplers differentiates against alkalinity and has been shown to effectively transmit VOC concentrations means that VOC samples can be collected from alkaline waters and preserved with acid in a nonalkaline matrix without VOC loss by effervescence. Additional investigation is ongoing to determine whether this applies to other sites.

A comparison of arsenic concentrations between sampling methodologies was conducted in only two wells because of arsenic's limited distribution. The number of data points was too limited for an adequate evaluation of the dialysis sampler's ability to accurately sample arsenic in ground water. The similarity between arsenic concentrations in dialysis samples and both the unfiltered and filtered low-flow samples in well SS15 MW-4, however, implies that the dialysis samplers are capable of accurately collecting arsenic samples (table 2).

A larger vertical variation of arsenic concentration was observed in well SS15 MW-2 (26 RPD change in arsenic concentrations over a 3.6-ft vertical interval) than at well SS15 MW-4 (no significant variation) (table 2). Arsenic concentrations in dialysis samples from well SS15 MW-2 underestimated low-flow sample concentrations by about 40 RPD. The cause of the difference is unknown because of the limited data set.

Lead and zinc concentrations also were examined in dialysis and low-flow samples (table 2). In both cases, the concentrations were predominantly below the reporting limit. Therefore, the detected concentrations were too low to adequately evaluate dialysis sampler ability to accurately sample these constituents in ground water.

Similarly, only limited data are available for methane and sulfide comparisons (table 2). At two wells, the methane concentrations showed a relatively close match (about 3 to 20 RPD) between same-depth dialysis and low-flow samples, implying that the dialysis samples adequately represented ground-water methane concentrations in those wells. In one sample, the PDB methane concentration differed from the same-depth low-flow sample concentration by only 8 RPD, implying that the PDB samplers also are capable of providing accurate methane samples. Although sulfide concentrations in the dialysis samples varied from concentrations in low-flow samples by a broad range, the sulfide concentrations in the dialysis samples were all equal to or greater than the concentrations in the low-flow samples. In general, when sampling gases, it is easier to lose than to gain concentrations; therefore, the data imply that dialysis samples adequately represented sulfide concentrations.

Mercury (not shown in table 2) was analyzed but was not found (detection limit 1 µg/L) at site SS13 in ground water from well SS13 MW-10 in dialysis samplers from two sampling horizons and in a filtered and unfiltered low-flow sample. Copper (not shown in table 2) also was measured in all three wells at site SS13 but was not found (detection limit 1 µg/L) in low-flow and dialysis samples. A possible exception was well SS13 MW-10, where copper was detected at 6 µg/L in the dialysis sample from 12.79 ft below the top of casing but was not detected in a shallower low-flow sample from 9.79 ft below top of casing. The copper result was "F value," which means that the analyte was positively identified, but the associated numerical value was below the reporting limit.

Volatile Organic Compounds

VOC concentrations were compared between dialysis samples, PDB samples, and low-flow samples (table 4). In general, the comparisons in concentrations between the two different types of diffusion samples showed a relatively close correspondence. At concentrations less than 6 µg/L, the average concentration difference between dialysis and PDB samples for individual VOCs was 0.8 µg/L (range of 0.1 to 2.4 µg/L). Concentrations are used in this comparison because RPD calculations are overly sensitive at low concentrations. At concentrations greater than 6 µg/L, the average RPD for individual VOCs was 16.7 percent (range of 0.3 to 45.1 percent) between dialysis and PDB samplers from corresponding depths. The relatively close match in concentrations from the two different types of diffusion membranes at most locations indicates that the concentrations accurately represent concentrations of the tested constituents in water contacting the samplers.

Table 4. Concentrations of organic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001

[Depth of well is in feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS unfiltered low-flow sample; RPD, relative percent difference; µg/L, micrograms per liter; *, difference in µg/L; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; J, the analyte was positively identified, the quantitation is an estimate, because it is outside the calibration limits or other Air Force Center for Environmental Excellence acceptance criteria were not met; ---, data not collected or not applicable; >, greater than; <, less than]

Well	Depth	Benzene, µg/L				Toluene, µg/L				Ethylbenzene, µg/L			
		DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L
SS01 MW-2	16.04	---	24.31	---	---	---	0.32F	---	---	---	1.31	---	---
	19.04	5.7	7.71	26	0.21*	<0.11	<0.11	0.26F	---	0.35F	0.46F	0.84	---
	22.04	---	3.32	---	---	---	<0.11	---	---	---	0.27F	---	---
SS01 MW-6	16.53	---	<0.08	---	---	---	0.19F	---	---	---	0.29F	---	---
	19.53	<0.01	<0.08	<0.08	---	---	0.17F	---	---	<0.14	0.25F	<0.08	---
	22.53	---	0.39F	---	---	---	0.58F	---	---	---	0.81	---	---
SS01 MW-8	10.2	---	3.28	4.73	---	---	0.15F	0.28F		---	1.46	3.77	---
	10.2	---	2.91	---	---	---	<0.14	---	---	---	1.21	---	---
	13.2	4.68	5.05	---	0.37*	0.18F	0.18F	---	---	2.47	3.03	---	0.56*
	13.2	---	4.82	---	0.14*	---	0.17F	---	---	---	2.82	---	0.35*
	16.2	---	5.05	---	---	---	0.17F	---	---	---	3.1	---	---
	16.2	---	4.97	---	---	---	0.17F	---	---	---	3.09	---	---
SS01 MW-11	16.31	---	0.47	---	---	---	<0.14	---	---	---	0.54F	---	---
	19.31	0.37F	0.47	2.83	---	0.22F	0.2F	<0.1	---	<0.14	0.34F	1.52	---
	22.31	---	0.89	---	---	---	0.78F	---	---	---	<0.14	---	---
SS01 MW-12	13.38		350.5	---	---	---	240.4	---	---	---	332.2	---	---
	16.38	833.7	758.9	973.6	9	441.4	495.6	172.4	12	566.6	528.4	1094	7
	16.38	827.6	801.6	---	3	406.4	528.9	---	26	525.4	613.2	---	15
	19.38	---	904.1	---	---	---	610.1	---	---	---	631.2	---	---
	22.38	---	855.9	---	---	---	537	---	---	---	541.5	---	---
SS11 MW-8	9.69	627.8	806.3	109.8	25	0.38F	0.44F	<1.4	---	169.1	267.6	<1.4	45
	12.69	---	889.7	---	---	---	0.45F	---	---	---	272.5	---	---
SS13 MW-4	9.53	---	0.11F	---	---	---	<0.14	---	---	---	<0.14	---	---
	12.53	<0.1	<0.1	0.08F	---	0.21F	<0.14	<0.1	---	<0.14	<0.14	<0.08	---
	15.53	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
	18.53	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
SS13 MW-10	9.79	<0.1	<0.1	<0.08	---	<0.14	<0.14	<0.1	---	<0.14	<0.14	<0.08	---
	12.79	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
SS13 MW-17	7.8	---	0.23F	---	---	---	<0.14	---	---	---	0.15F	---	---
	10.8	<0.1	<0.1	<0.08	---	0.18F	<0.14	<0.1	---	<0.14	<0.14	<0.08	---
	13.8	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
SS15 MW-2	12.34	<0.14	<0.14	---	---	<0.11	<0.11	<0.14	---	<0.12	<0.12	<0.14	---
SS15 MW-4	8.12	<0.14	<0.14	<0.1	---	<0.11	<0.11	<0.14	---	<0.12	<0.12	<0.12	---
SS15 MW-5	6.7	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
	9.7	<0.1	<0.1	<0.08	---	<0.14	<0.14	<0.14	---	<0.14	<0.14	<0.08	---
	12.7	---	<0.1	---	---	---	<0.14	---	---	---	---	---	---
SS15 GT-K5	10.1	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
	13.1	<0.1	<0.1	0.46	---	<0.14	<0.14	<0.14	---	<0.14	<0.14	0.14F	---
	13.1	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
	16.1	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---
	19.1	---	<0.1	---	---	---	<0.14	---	---	---	<0.14	---	---

Table 4. Concentrations of organic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001 (Continued)

[Depth of well is in feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS unfiltered low-flow sample; RPD, relative percent difference; µg/L, micrograms per liter; *, difference in µg/L; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; J, the analyte was positively identified, the quantitation is an estimate, because it is outside the calibration limits or other Air Force Center for Environmental Excellence acceptance criteria were not met; ---, data not collected or not applicable; >, greater than; <, less than]

		o-Xylene, µg/L				*m,p*-Xylene, µg/L				Isopropylbenzene, µg/L			
Well	Depth	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L
SS01 MW-2	16.04	---	<0.07	---	---	---	<0.13	---	---	---	2.7	---	---
	19.04	<0.13	<0.13	<0.07	---	<0.23	<0.23	0.15F	---	1.01	1.21	4.06	0.2*
	22.04	---	<0.13	---	---	---	<0.23	---	---	---	0.85	---	---
SS01 MW-6	16.53	---	0.14F	---	---	---	0.42F	---	---	---	7.53	---	---
	19.53	<0.07	0.13F	<0.11	---	<0.13	0.35F	<0.2	---	6.97	7.56	4.32	0.59*
	22.53	---	0.44F	---	---	---	1.23	---	---	---	6.07	---	---
SS01 MW-8	10.2	---	<0.13	0.09F		---	1.26	3.19	---	---	1.88	6.5	---
	10.2	---	<0.07	---	---	---	1.04	---	---	---	1.57	---	---
	13.2	<0.13	<0.13	---	---	1.63	2.05	---	---	3.43	3.94	---	0.51*
	13.2	---	<0.07	---	---	---	1.92	---	---	---	3.79	---	0.36*
	16.2	---	<0.13	---	---	---	1.91	---	---	---	3.53	---	---
	16.2	---	<0.07	---	---	---	1.9	---	---	---	3.7	---	---
SS01 MW-11	16.31	---	<0.07	---	---	---	<0.13	---	---	---	1.72	---	---
	19.31	<0.07	<0.07	<0.11	---	<0.13	<0.13	<0.2	---	1.07	2.2	7.47	0.23*
	22.31	---	<0.07	---	---	---	<0.13	---	---	---	<0.06	---	---
SS01 MW-12	13.38	---	211.8	---	---	---	635.5	---	---	---	20.74	---	---
	16.38	238.8	261.3J	57.4	---	669.9	722.2	141.3	8	21.48	21.12	40.54	2
	16.38	217.5	331J	---	---	624.5	837.7	---	29	16.03	21.32	---	28
	19.38	---	330.3	---	---	---	840.5	---	---	---	17.96	---	---
	22.38	---	279.2	---	---	---	716	---	---	---	19.7	---	---
SS11 MW-8	9.69	7.06	7.31	4.88J	0.25*	74.4	82.8	3.4F	---	16.13	19.64	<0.6	20
	12.69	---	6.03	---	---	---	97.4	---	---	---	18.43	---	---
SS13 MW-4	9.53	---	0.1F	---	---	---	0.18F	---	---	---	5.93	---	---
	12.53	<0.07	0.08F	<0.11	---	<0.13	0.19F	<0.2	---	2.07	1.61	2.31	0.46*
	15.53	---	<0.07	---	---	---	0.16F	---	---	---	1.07	---	---
	18.53	---	<0.07	---	---	---	0.13F	---	---	---	0.4F	---	---
SS13 MW-10	9.79	<0.07	<0.07	<0.11	---	<0.12	<0.13	<0.2	---	<0.6	<0.6	<0.1	---
	12.79	---	<0.07	---	---	---	<0.13	---	---	---	<0.6	---	---
SS13 MW-17	7.8	---	<0.07	---	---	---	<0.13	---	---	---	<0.6	---	---
	10.8	<0.07	<0.07	<0.11	---	<0.13	<0.13	<0.2	---	<0.6	<0.6	<0.1	---
	13.8	---	<0.07	---	---	---	<0.13	---	---	---	<0.6	---	---
SS15 MW-2	12.34	<0.13	<0.13	<0.07	---	<0.23	<0.23	<0.13	---	0.19F	0.24F	0.34F	---
SS15 MW-4	8.12	<0.13	<0.07	<0.07	---	<0.23	<0.23	<0.13	---	3.75	5.61	<0.06	1.86*
SS15 MW-5	6.7	---	<0.07	---	---	---	<0.13	---	---	---	<0.06	---	---
	9.7	<0.07	<0.07	<0.11	---	<0.13	<0.13	<0.2	---	<0.06	<0.06	<0.1	---
	12.7	---	---	---	---	---	<0.13	---	---	---	<0.06	---	---
SS15 GT-K5	10.1	---	<0.07	---	---	---	<0.13	---	---	---	19.06	---	---
	13.1	<0.07	<0.07	<0.07	---	<0.13	<0.13	0.18F	---	14.38	9.9	0.85	37
	13.1	---	<0.07	---	---	---	<0.13	---	---	---	10.07	---	---
	16.1	---	<0.07	---	---	---	---	---	---	---	1.35	---	---
	19.1	---	<0.07	---	---	---	---	---	---	---	0.11F	---	---

Table 4. Concentrations of organic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001 (Continued)

[Depth of well is in feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS unfiltered low-flow sample; RPD, relative percent difference; µg/L, micrograms per liter; *, difference in µg/L; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; J, the analyte was positively identified, the quantitation is an estimate, because it is outside the calibration limits or other Air Force Center for Environmental Excellence acceptance criteria were not met; ---, data not collected or not applicable; >, greater than; <, less than]

Well	Depth	*n*-Propylbenzene, µg/L				Naphthalene, µg/L				1,2,4-Trimethylbenzene, µg/L			
		DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L
SS01 MW-2	16.04	---	0.7	---	---	---	<0.18	---	---	---	<0.08	---	---
	19.04	0.15F	0.2F	0.22F	---	<0.17	<0.17	0.6	---	<0.11	<0.11	<0.11	---
	22.04	---	0.11F	---	---	---	<0.17	---	---	---	<0.11	---	---
SS01 MW-6	16.53	---	0.58	---	---	---	<0.12	---	---	---	0.18F	---	---
	19.53	0.56	0.59	0.2F	---	<0.18	<0.12	<0.12	---	<0.08	0.16F	<0.1	---
	22.53	---	0.55	---	---	---	0.22F	---	---	---	0.48F	---	---
SS01 MW-8	10.2	---	3.67	16.39	---	---	2.23	7.05	---	---	0.2J	1.06F	---
	10.2	---	3.45	---	---	---	2.01	---	---	---	0.11J	---	---
	13.2	6.78	8.55	---	1.77*	4.18	4.54	---	0.36*	0.38F	0.42J	---	---
	13.2	---	8.69	---	1.91*	---	5.09	---	0.91*	---	0.33J	---	---
	16.2	---	7.87	---	---	---	4.51	---	---	---	0.41F	---	---
	16.2	---	8.7	---	---	---	5.15	---	---	---	0.36F	---	---
SS01 MW-11	16.31	---	0.19F	---	---	---	<0.18	---	---	---	<0.08	---	---
	19.31	0.06F	0.17F	0.49	---	<0.18	<0.18	0.17F	---	<0.08	<0.08	<0.1	---
	22.31	---	---	---	---	---	<0.18	---	---	---	<0.08	---	---
SS01 MW-12	13.38	---	60.46	---	---	---	61.24	---	---	---	294	---	---
	16.38	49.91	55.67	108.7	11	43.4	37.6	51.37	14	237.8	202.8	96.2	16
	16.38	55.05	56.13	---	2	46.56	36.99	---	23	229	284.9	---	22
	19.38	---	45	---	---	---	38.32	---	---	---	239.1	---	---
	22.38	---	46.5	---	---	---	36.48	---	---	---	197.1	---	---
SS11 MW-8	9.69	8.95	13.52	<0.62	41	38.16	43.66	36.9	13	15.33	17.09	<0.8	11
	12.69	---	11.62	---	---	---	37.51	---	---	---	16.85	---	---
SS13 MW-4	9.53	---	0.09F	<0.11	---	---	<0.18	---	---	---	<0.08	---	---
	12.53	<0.11	<0.06	---	---	<0.18	<0.18	<0.12	---	<0.08	<0.08	<0.1	---
	15.53	---	<0.06	---	---	---	<0.18	---	---	---	<0.08	---	---
	18.53	---	<0.06	---	---	---	<0.18	---	---	---	<0.08	---	---
SS13 MW-10	9.79	<0.06	<0.06	<0.11	---	<0.18	<0.18	<0.12	---	<0.08	<0.08	<0.1	---
	12.79	---	<0.06	---	---	---	<0.18	---	---	---	<0.08	---	---
SS13 MW-17	7.8	---	<0.06	---	---	---	0.62	---	---	---	<0.08	---	---
	10.8	<0.06	<0.06	<0.11	---	<0.18	<0.18	<0.12	---	<0.08	<0.08	<0.1	---
	13.8	---	<0.06	---	---	---	<0.18	---	---	---	<0.08	---	---
SS15 MW-2	12.34	<0.08	<0.08	<0.06	---	<0.17	0.3F	<0.18	---	<0.11	<0.11	<0.08	---
SS15 MW-4	8.12	1.38	2.68	<0.06	1.3*	3.11	4.75	1.27	1.64*	<0.11	<0.11	<0.08	---
SS15 MW-5	6.7	---	<0.06	<0.11	---	---	<0.18	---	---	---	<0.08	---	---
	9.7	<0.06	<0.06	---	---	<0.18	<0.18	<0.12	---	<0.08	<0.08	<0.1	---
	12.7	---	<0.06	---	---	---	<0.18	---	---	---	<0.08	---	---
SS15 GT-K5	10.1	---	6.82	---	---	---	2.12	---	---	---	<0.08	---	---
	13.1	4.47	2.05	0.08F	2.42*	1.5	1.31J	0.26F	---	<0.08	<0.08	0.11F	---
	13.1	---	2.17	---	---	---	2.04J	---	---	---	<0.08	---	---
	16.1	---	0.13F	---	---	---	0.55	---	---	---	<0.08	---	---
	19.1	---	<0.06	---	---	---	0.23F	---	---	---	<0.08	---	---

Table 4. Concentrations of organic solutes in dialysis, passive diffusion bag, and low-flow samples, Hickam Air Force Base, Hawaii, July 2001 (Continued)

[[Depth of well is in feet below top of casing; DS, dialysis sample; PDBS, passive diffusion bag sample; UnLFS unfiltered low-flow sample; RPD, relative percent difference; µg/L, micrograms per liter; *, difference in µg/L; F, the analyte was positively identified, but the associated numerical value was below the reporting limit; J, the analyte was positively identified, the quantitation is an estimate, because it is outside the calibration limits or other Air Force Center for Environmental Excellence acceptance criteria were not met; ---, data not collected or not applicable; >, greater than; <, less than]

		1,3,5-Trimethylbenzene, µg/L				*sec*-Butylbenzene, µg/L			*tert*-Butylbenzene, µg/L		
Well	Depth	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS	UnLFS	Difference between dialysis and PDB samples as RPD, in percent, for concentrations >10 µg/L or as µg/L* for concentrations <10 µg/L	DS	PDBS
SS01 MW-2	16.04	---	<0.07	---	---	---	<0.08	---	---	<0.07	---
	19.04	<0.12	<0.12	<0.07	---	<0.11	<0.11	0.13F	<0.11	<0.11	<0.07
	22.04	---	<0.12	---	---	---	<0.11	---	---	<0.11	---
SS01 MW-6	16.53	---	<0.11	---	---	---	0.11F	---	---	0.68F	---
	19.53	<0.07	<0.11	<0.11	---	0.11F	0.11F	0.13F	0.76F	0.69F	0.76F
	22.53	---	0.14F	---	---	---	0.11F	---	---	0.65F	---
SS01 MW-8	10.2	---	0.16J	0.74	---	---	0.18F	1.68	---	<0.11	0.42F
	10.2	---	0.1J	---	---	---	0.12F	---	---	<0.07	---
	13.2	0.32F	0.35J	---	---	0.36F	0.37F	---	0.17F	0.15F	---
	13.2	---	0.26J	---	---	---	0.31F	---	---	0.11F	---
	16.2	---	0.32F	---	---	---	0.3F	---	---	0.12F	---
	16.2	---	0.27F	---	---	---	0.28F	---	---	0.11F	---
SS01 MW-11	16.31	---	<0.07	---	---	---	<0.08	---	---	<0.07	---
	19.31	<0.07	<0.07	<0.11	---	<0.08	<0.08	0.11F	<0.07	<0.07	0.52F
	22.31	---	<0.07	---	---	---	<0.08	---	---	<0.07	---
SS01 MW-12	13.38	---	91.09	---	---	---	2.19	---	---	<0.07	---
	16.38	69.11	68.89	30.53	0	1.23F	1.26F	4.93	<0.07	<0.7	0.13F
	16.38	75.48	70.76	---	6	1.02F	1.71	---	<0.07	<0.18	---
	19.38	---	55.34	---	---	---	1.08F	---	---	<0.18	---
	22.38	---	50.19	---	---	---	1F	---	---	<0.18	---
SS11 MW-8	9.69	8	8.75	24.15	0.75*	0.64F	0.79F	<0.8	0.59	0.57F	2.08J
	12.69	---	8.06	---	---	---	0.62F	---	---	0.4F	---
SS13 MW-4	9.53	---	<0.07	---	---	0.2F	0.2F	---	---	0.88F	---
	12.53	<0.07	<0.07	<0.11	---	0.1F	<0.08	0.47F	0.74F	0.42F	2.51
	15.53	---	<0.07	---	---	---	<0.08	---	---	0.36F	---
	18.53	---	<0.07	---	---	---	<0.08	---	---	0.14F	---
SS13 MW-10	9.79	<0.07	<0.07	<0.11	---	<0.08	<0.08	<0.1	<0.07	<0.07	0.41F
	12.79	---	<0.07	---	---	---	<0.08	---	---	<0.07	---
SS13 MW-17	7.8	---	<0.07	---	---	---	<0.08	---	---	0.1F	---
	10.8	0.1F	<0.07	<0.11	---	<0.08	<0.08	<0.1	0.14F	<0.07	0.46F
	13.8	---	<0.07	---	---	---	<0.08	---	---	<0.07	---
SS15 MW-2	12.34	<0.12	<0.12	<0.07	---	<0.11	<0.11	<0.08	0.14F	0.17F	0.72F
SS15 MW-4	8.12	<0.12	<0.12	<0.07	---	0.19F	0.24F	<0.08	0.28F	0.27F	1.22F
SS15 MW-5	6.7	---	<0.07	---	---	---	<0.08	---	---	0.15F	---
	9.7	<0.07	<0.07	<0.11	---	<0.08	<0.08	<0.1	0.85F	0.81F	2.24
	12.7	---	---	---	---	---	<0.08	---	---	0.78F	---
SS15 GT-K5	10.1	---	<0.07	---	---	---	1.3	---	---	0.58F	---
	13.1	<0.07	<0.07	<0.07	---	1.62	0.85F	0.47F	0.68F	0.38F	0.65F
	13.1	---	<0.07	---	---	---	0.89F	---	---	0.43F	---
	16.1	---	<0.07	---	---	---	0.41F	---	---	0.17F	---
	19.1	---	<0.07	---	---	---	0.13F	---	---	<0.07	---

To determine whether the VOC concentrations in the diffusion samplers correctly reflect aquifer concentrations, the PDB-sample concentrations were compared to low-flow sample concentrations. A statistical evaluation using the modified t-test of means (described earlier in this report) of the PDB-sample and low-flow sample data is reported elsewhere (Earth Tech, Inc., 2001). In general, the statistical evaluation showed that 33 percent of the comparisons of PDB results to low-flow results for individual constituents showed no significant difference between methods at a 95-percent confidence level. Of the remaining comparisons, 42 percent were within 2 µg/L of each other, which is considered a close match.

Evaluation of PDB samplers was not appropriate in some of the tested wells, because samples obtained from these wells contained no detectable VOCs without laboratory qualifiers (wells SS13 MW-10, SS13 MW-17, and SS15 MW-2). In well SS15 MW-5, the only detected VOC without laboratory qualifiers was *tert*-butylbenzene, which was present at only 2.2 µg/L in the low-flow sample.

Other wells, however, contained only low concentrations of VOCs and showed a close match between sampling methodologies. In well SS13 MW-4, the only detected VOC without laboratory qualifiers was isopropylbenzene, which showed no significant concentration difference between sampling methods at the 95-percent confidence level with the modified t-test (Earth Tech, 2001). A VOC sample was collected from only one depth at well SS15 MW-4 and contained quantifiable concentrations at less than 6 µg/L each of *n*-propylbenzene, isopropylbenzene, and naphthalene. For each of these constituents, the diffusion samplers contained higher concentrations than the low-flow samples, implying that the diffusion samples produced the more precise concentrations. VOC samples from well SS15 GT-K5 contained quantifiable concentrations at less than 7 µg/L each of *n*-propylbenzene, naphthalene, and sec-butylbenzene, with the diffusion samples probably providing more precise concentrations because they contained higher concentrations than the low-flow samples. Well SS15 GT-K5 also contained isopropylbenzene concentrations, ranging from less than 1 to 19.1 µg/L (table 4). Application of the modified t-test to the isopropylbenzene data from well SS15 GT-K5 showed no significant difference between sampling methods (Earth Tech, 2001).

In well SS01 MW-11, the only VOCs detected at concentrations without laboratory qualifiers were benzene (less than 1 to 2.8 µg/L), *n*-propylbenzene (0.5 µg/L), ethylbenzene (less than 0.14 to 1.5 µg/L), and isopropylbenzene (less than 0.06 to 7.5 µg/L). For benzene, the concentration difference between methods was only about 2.4 µg/L, indicating that the diffusion samplers provided an accurate concentration for this constituent. For *n*-propylbenzene and ethylbenzene, the concentrations were higher in the low-flow sample than in the diffusion samples, but overall concentrations were too low to draw a conclusion regarding the relative efficiency of the sampling methods. Isopropylbenzene was more concentrated in the low-flow sample than in the diffusion samplers by concentrations of 5.3 to 6.4 µg/L. The relatively close agreement between methods in well SS01 MW-11 probably indicates that the diffusion samples provide representative VOC concentrations in that well. The slightly larger difference in isopropylbenzene concentrations, however, suggests that further testing may be warranted if that constituent is of major interest.

Samples from well SS01 MW-8 contained several VOCs at quantifiable concentrations less than 10 µg/L (table 4). Of these, concentrations between diffusion and low-flow sampling methodology differed by less than 3 µg/L for benzene, ethylbenzene, and *m,p*-xylene, indicating a close match. Isopropylbenzene, and naphthalene concentrations were higher in the same-depth low-flow than diffusion samplers by concentrations ranging from 4.8 to 12.7 µg/L; however, the concentrations differed by less than 3 µg/L when the low-flow sample was compared to the PDB samples from 3 ft deeper. It is not unreasonable to expect that the low-flow sampling could have derived water from 3 ft deeper. Therefore, the diffusion sampling and low-flow sampling methodologies appear to have produced comparable concentrations for these constituents in well SS01 MW-08. In contrast, *n*-propylbenzene was more concentrated by about 7.7 to 13 µg/L than in nearby diffusion samplers. If *n*-propylbenzene is a constituent of major concern in this well, then additional testing is warranted.

Substantial concentration differences between sampling methods were observed at some wells. Benzene, ethylbenzene, and xylene concentrations from well SS11 MW-8 were substantially lower in water from low-flow samples than in water from diffusion samplers (table 4). The benzene concentration ranged from 628 to 890 µg/L in the diffusion samples but was only 110 µg/L in the low-flow sample. Ethylbenzene concentrations in the diffusion samples were greater than 150 µg/L, but the concentration was less than 1.4 µg/L in the low-flow sample.

The source of the difference is not known, however, some amount of disagreement between diffusion-sample and low-flow sample results is not surprising. Low-flow samples typically represent some degree of mixing from pumping whereas the diffusion samples usually constitute an approximate point sample defined by the length of the sampler, and this mixing sometimes can misrepresent local concentrations by incorporating into the sample nonlocal waters having higher or lower contaminant concentrations. Well SS11-MW8 intersected less than 7 ft of saturated thickness and was tested using 1- to 1.5-ft-long diffusion samplers separated vertically by less than 3 ft. Therefore, it seems unlikely that the diffusion samplers missed a thick contributing zone of water in the screened interval. It is possible, however, that the pumping induced movement of relatively uncontaminated water into the well from a zone at the bottom of the well or from a thin zone not adjacent to the diffusion samplers. This interpretation is supported by the observation that the comparison of chloride concentrations between dialysis and low-flow samples also showed an uncharacteristically high difference. Under this circumstance, the low-flow sample would represent water not characteristic of the borehole water under ambient conditions.

It is also possible that the pumped sample somehow was compromised in the field or laboratory, resulting in a loss of some volatile constituents. Historical low-flow sampling data show that during the previous sampling event in December 2000, the benzene concentration was 1,058 µg/L and the ethylbenzene concentration was 404 µg/L (Mark Peterson, 15 Civil Engineering Squadron, U.S. Air Force, written commun., 2002), much more closely resembling the August 2001 diffusion-sampler data than August 2001 low-flow data.

Although the source of the difference in well SS11 MW-8 is not known, the comparatively higher VOC concentrations in the diffusion samples show that more VOC contamination is present than would be indicated by the low-flow sample. These data indicate that the diffusion samples provide a better indication of the contamination in the adjacent aquifer than the low-flow samples in this well. A possible exception is 1,3,5-trimethylbenzene, which was more concentrated in the low-flow sample than the diffusion samplers. Additional investigation is warranted if 1,3,5-trimethylbenzene is a constituent of major concern in this well.

Differences between diffusion sample and low-flow sample concentrations tend to be more pronounced in areas of contaminant stratification because of the potentially larger concentration differences in the mixed water (Vroblesky and Peters, 2000). Vertical stratification of VOCs was present in some of the tested wells at Hickam AFB.

Well SS01 MW-2 is an example of a well where VOCs are vertically stratified. VOCs present in the well were most concentrated near the top of the well screen. The benzene concentration was 24 µg/L at a depth of 16 ft and only 3 µg/L at a depth of 22 ft (table 4). Although the benzene concentration in the low-flow sample differed from the concentration in the dialysis and PDB samples at the same depth by RPDs of 128 and 109 percent, respectively, the concentration differed from the shallower PDB sample concentration (16 ft depth) by only about 7 percent. Thus, a simple explanation is that the low-flow sample in this well was composed primarily of water from the shallowest part of the well, and that the diffusion samples accurately reflect contaminant stratification within the screened interval.

Well SS01 MW-12 is an example of a well at Hickam AFB showing vertical variations in VOC concentration in the screened interval in which many of the VOCs showed differences between the PDB and low-flow results (fig. 6). In this case, the stratification is more complex than at well SS01 MW-2. The PDB samplers indicate that concentrations of benzene, toluene, ethylbenzene, and xylenes in ground water at well SS01 MW-12 are highest slightly below the approximate center of the well screen, at a depth of about 16 to 19 ft (fig. 6A, B, C, D). Other constituents, such as *n*-propylbenzene, naphthalene, 1,2,4-trimethylbenzene, and 1,3,5-trimethylbenzene, show the highest concentrations near the top of the well screen and a general decrease in concentrations with depth (fig. 6E, F, G, H,). Isopropylbenzene shows only slight changes in concentration across the screened interval (fig. 6I). Thus, the data imply that, not only are the contaminants vertically stratified within the plume, but that individual contaminants also have different vertical distributions. Unless the water pumped from this well during low-flow sampling is uniformly entering the well along the length of the screen, it is highly unlikely that the pumped sample will provide a uniform mixing of aquifer water over the screened interval. The drilling log of boring SS01 MW-12 shows volcanic tuff with fractures

at depths of 14, 18, and 19 ft and a porous, wet weathered tuff between 19.05 and 22.5 ft below land surface (Mark Peterson, 15 Civil Engineering Squadron, U.S. Air Force, written commun., 2002). It is probable that water enters the well nonuniformly with primary movement through the wet weathered tuff near the bottom of the screen or through fractures. Thus, it is not surprising that several of the VOC concentrations show disagreement between the PDB and low-flow method in this well.

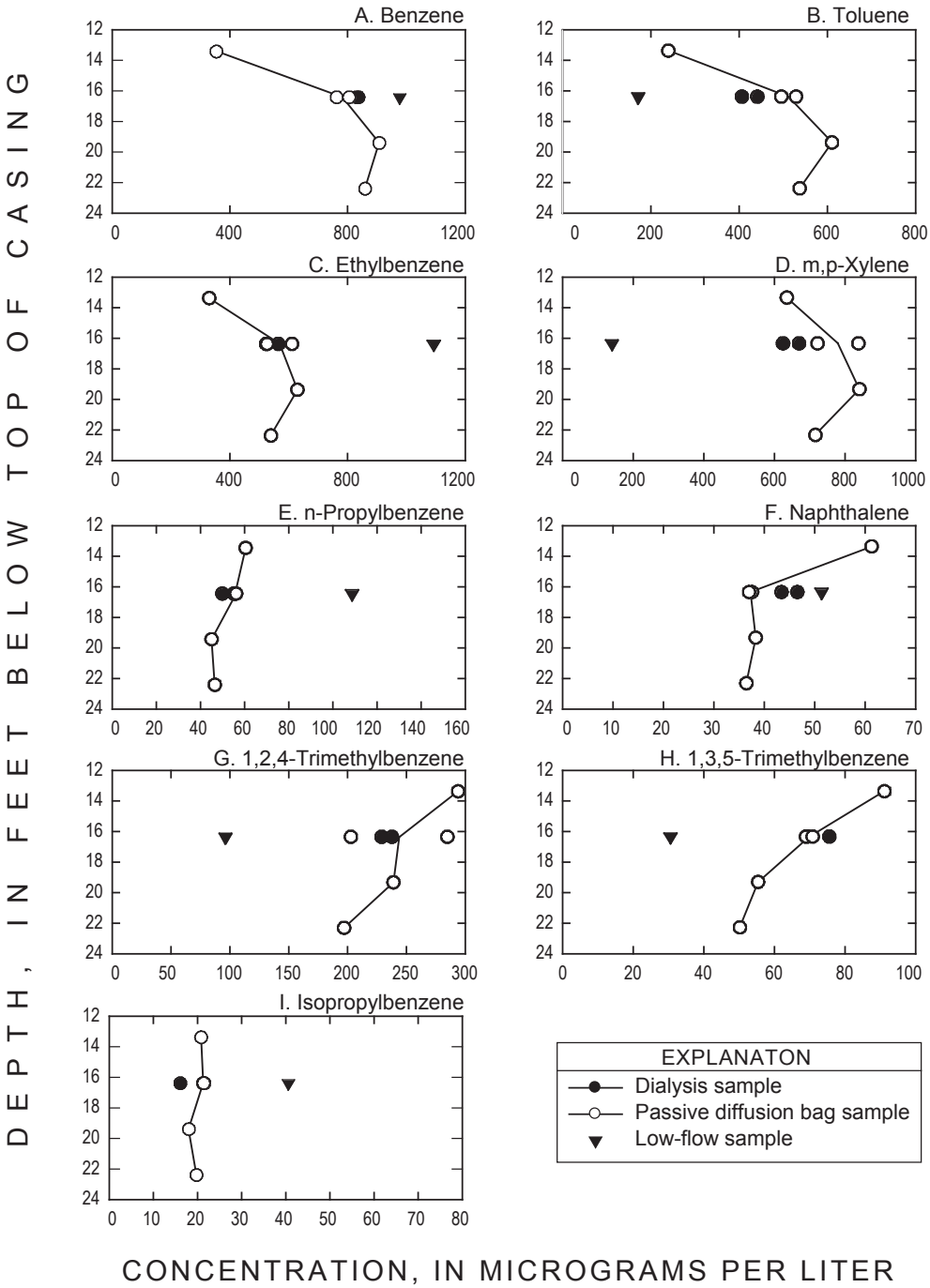


Figure 6. Vertical distributions of volatile organic compounds in dialysis and low-flow samples from well SS01 MW-12, Hickam Air Force Base, Hawaii, July 2001.

Another situation that can produce concentration differences between diffusion and low-flow methods is when the pumping draws VOCs toward the well from areas of higher concentration not directly adjacent to the screen, resulting in higher concentrations in the pumped sample than in the diffusion sample. It is reasonable to expect an area of complex vertical VOC stratification, such as at well SS01 MW-12, to also be characterized by complex lateral VOC distribution. Thus, it is likely that the pumped sample from well SS01 MW-12 represents, not only a complex integration of vertical constituents, but also the lateral movement of concentrations toward the well that may differ from those in the aquifer directly adjacent to the well screen. In such a situation, the concentrations of specific VOCs in the pumped sample may deviate from concentrations in diffusion samples by varying amounts in the same well. Thus, some VOCs, such as benzene and ethylbenzene, are more concentrated in the pumped sample than in the diffusion samples, whereas others, such as toluene and *m,p*-xylene, are more concentrated in the diffusion samples than in the pumped sample (fig. 6). The data from well SS01 MW-12 imply that the diffusion-sample results represent VOC concentrations under ambient conditions. The low-flow sample results represent VOC concentrations resulting from preferential flow and/or mixing in a complexly stratified system and possibly include concentrations representing conditions not in the direct vicinity of the well screen for some constituents.

In general, the two types of diffusion samplers appeared to produce concentrations that represented ambient conditions for most constituents in most wells. A general summary is shown in table 5.

Table 5. Summary of diffusion sampler ability to produce an accurate representation of the ambient water in tested wells at Hickam Air Force Base, Hawaii, July 2001

[VOCs, volatile organic compounds; PDB, passive diffusion bag; ---, data not available; µg/L, micrograms per liter]

Well	Does the diffusion sampler appear to produce an accurate representation of the ambient water?				
	Chloride (dialysis samplers)	Sulfate (dialysis samplers)	Total iron (dialysis sample)	Dissolved iron (dialysis sample)	VOCs (dialysis and low-flow samples)
SS01 MW-2	Possibly, but does not reflect pumped water.	Yes	Yes	---	Probably yes. The low-flow samples may represent water coming in near the top of the screen.
SS01 MW-6	Yes	Yes	Probably not	Yes	Yes
SS01 MW-8	Yes	---	Yes	Yes	Proably yes; however, a comparatively poor match was obtained for *n*-propylbenzene. Further testing may be warranted if n-propylbenzene is a parameter of major concern in this well.
SS01 MW-11	Yes	Yes	---	---	Yes, however, isopropylbenzene was more concentrated in the low-flow than in the PDB sample (5.3 µg/L), so further testing in this well may be warranted if isopropylbenzene is a parameter of major concern.
SS01 MW-12	Insufficient data for statistical analysis, but it does not appear to reflect pumped water.	Yes	---	---	Uncertain. The well exhibited complex stratification with a close match for some major VOCs and a poor match for others. It is unclear whether the low-flow sample or the diffusion sample is producing the more representative sample.
SS11 MW-8	Possibly, but does not reflect pumped water.	Yes	Yes	Yes	Yes; however differences were found for 1,3,5-trimethylbenzene. Additional investigation is warranted if 1,3,5-trimethylbenzene is a constituent of major concern in this well.
SS13 MW-4	Yes	Yes	---	---	Yes
SS13 MW-10	Yes	---	---	---	---
SS13 MW-17	Yes	Yes	---	---	---
SS15 MW-2	Yes	Yes	Yes	Yes	---
SS15 MW-4	Yes	---	Yes	Yes	Yes
SS15 MW-5	Yes	Yes	Probably not	Probably not	---
SS15 GT-K5	Yes	Yes	---	---	Yes

Advantages and Limitations of Diffusion Samplers at Hickam Air Force Base

There are several advantages of PDB samplers. They can be deployed and recovered simply and rapidly. The low cost associated with water sampling using PDB samplers makes them a cheaper alternative at Hickam AFB than low-flow sampling (Earth Tech, Inc., 2001). The method requires minimum decontamination and produces little or no investigation-derived wastewater. The samplers appear to be durable for long-term deployment of at least 6 months (Church, 2000) with no loss of bag integrity in most contaminated waters. PDB samplers are particularly practical in carbonate environments, such as Hawaii, where alkalinity can be high enough to cause effervescence when an acid preservative is added. The effervescence results in loss of VOCs by volatilization. Collection of VOCs without addition of acid preservative prevents volatilization loss, but significantly shortens the sample holding time. Because PDB-sampler membranes transmitted VOCs but not alkalinity at this study site, the data imply that the PDB samplers collect VOCs in a nonalkaline matrix, allowing the addition of an acid preservative even when sampling from a highly alkaline aquifer. Additional work is ongoing to determine whether this applies to other sites.

There are also several advantages of dialysis samplers. The samplers are relatively inexpensive and are easy to deploy and recover. They have an advantage over PDB samplers in that the dialysis samplers are effective for both inorganic and organic solutes.

Diffusion samplers have the additional advantage over pumped samples in that the diffusion samplers potentially can measure contaminant stratification in the screened interval. The samplers also are not subject to interferences from turbidity because of the small membrane pore size (about 10 angstroms or less for PDB samplers and about 18 angstroms for dialysis samplers).

Both types of diffusion samplers also have limitations. The limitation of the PDB sampler is that it primarily should be used where VOCs are the main or only constituents being monitored, because inorganic and most semivolatile solutes do not rapidly pass through the membrane. The major limitation of the dialysis sampler is that regenerated cellulose is the only dialysis membrane commercially available in convenient-sized tubing for well applications at the time of this writing (2002). Although regenerated cellulose is a comparatively rugged membrane, it is subject to biodegradation under field conditions. Most, but not all, of the dialysis samplers showed discoloring of the originally white membrane after 2 weeks of deployment during this investigation (fig. 7). Although the membranes remained structurally sound during the 2-week deployment, it is unreasonable to expect them to survive long-term deployment (for example, 3 months). Therefore, when using regenerated cellulose dialysis samplers for quarterly sampling, they probably should be deployed no sooner than 2 weeks prior to recovery unless field tests demonstrate a longer lifespan in the target well. The sampler degradation suggests that microbial activity on the membrane may affect the detected concentrations of bioactive solutes in some environments; however, no obvious detrimental effect from membrane interaction with the detected solute concentrations within the dialysis samplers was observed at the sites tested during this investigation.

An additional potential limitation of diffusion samplers is that they reflect concentrations in the screened or open interval that move to the sampler under ambient flow conditions. This is a limitation in situations where the contamination lies above or below the screen or vertical gradients in the well obscure stratification. However, this also can be an advantage in some situations where there is interest in knowing the concentrations in the vicinity of the screened interval, and the pumped sample represents water not in the vicinity of the screen that was transported to the well as a result of pumping.

Figure 7. Discoloration of dialysis sampler membrane after 2 weeks of deployment in a well, Hickam Air Force Base, Hawaii, July 2001.

Finally, caution must be used when using diffusion samplers deployed in anaerobic waters to collect redox-sensitive inorganic constituents. Oxidation of iron and other solutes can precipitate solutes from solution within the samplers, sometimes producing erroneous results (Vroblesky and others, 2002).

SUMMARY AND CONCLUSIONS

This report presents data comparing groundwater concentrations of both VOCs and inorganic solutes obtained from side-by-side tests of an updated dialysis sampler and PDB samplers to concentrations obtained by low-flow sampling in wells. The tests were conducted during July 2001 in 13 wells at Hickam Air Force Base, Hawaii.

The PDB samplers were purchased commercially. Each dialysis sampler was constructed onsite and consisted of a perforated plastic pipe inside a sleeve of high-grade regenerated cellulose tubular dialysis membrane.

In general, relatively favorable comparisons were found between concentrations in dialysis samples and low-flow samples for the predominant inorganic solutes examined for this investigation. Vertical concentration gradients of solutes were observed in dialysis sampler data from most of the wells.

Chloride concentrations in the dialysis samples closely matched concentrations in most of the low-flow samples. The dialysis-sample chloride concentrations were not statistically different from the low-flow chloride concentrations in 8 of the 13 tested wells. In 2 of the remaining 5 wells (wells SS13 MW-10 and SS15 MW-4) insufficient data were available to run a t-test. However, the low RPDs (6 and 3 percent, respectively) between concentrations from the low-flow sample and dialysis sample deployed at the same depth indicated a close match.

In most of the wells, the dialysis sampler data showed that chloride had a vertical concentration gradient or stratification. In these wells, it is likely that mixing during low-flow pumping produces some degree of concentration deviation from the adjacent dialysis sampler.

The chloride concentrations in two wells (SS01 MW-2, and SS11 MW-8) showed a statistical difference between the dialysis and low-flow samples. In these wells, and in a well in which the chloride concentrations were not statistically analyzed (well SS01 MW-12), the chloride concentrations in the low-flow samples were higher than in the dialysis samples. The close match in chloride concentrations between sampling methods in other wells suggests that the differences in these wells may be attributed to well-specific factors rather than a diffusion-sampler deficiency. For example, it is possible that the low-flow pumping induced movement of water into the well that did not flow to the well under nonpumping conditions.

Sulfate concentrations showed a generally close match between results from dialysis samples and low-flow samples. Examination of vertical sulfate distributions show that the concentration differences between the low-flow sample and the adjacent dialysis sample in most wells probably are due to the low-flow samples representing a mixing of concentrations in a stratified system, whereas the dialysis samples represent localized concentrations.

Iron concentrations also showed generally close agreement in most dialysis and low-flow samples. The data imply that iron concentrations in the dialysis samplers are representative of undisturbed well water, and the unfiltered pumped samples represent water and amounts of suspended sediment not normally moving through the well at the tested horizon.

Alkalinity measurements in dialysis samples closely matched the low-flow sample result or overestimated it. An overestimation typically is not considered a mismatch because it is not unusual for low-flow sampling to dilute concentrations by mixing. Thus, the alkalinity concentrations measured in the dialysis sampler probably approximate alkalinity concentrations in the undisturbed water column in the well. It is important to note, however, that the PDB samplers contained no detectable alkalinity at Hickam AFB, even when deployed in waters containing greater than 300 mg/L of alkalinity. The fact that the LDPE membrane of PDB samplers differentiates against alkalinity and have been shown to effectively transmit VOC concentrations implies that VOC samples can be collected from alkaline waters in a nonalkaline matrix without concern for volatilization loss by effervescence upon addition of acid preservative.

Only limited arsenic data were collected, however, the close match between arsenic concentrations in dialysis samples and both the unfiltered and filtered low-flow samples in well SS15 MW-4 implies that the dialysis samplers are capable of accurately collecting arsenic samples. Similarly, although only

limited data are available for methane comparisons, the methane concentrations showed a relatively close match between dialysis and low-flow samples, implying that the dialysis samples adequately represented ground-water methane concentrations. Lead, zinc, mercury, and copper concentrations were too low for an adequate evaluation of the dialysis sampler's ability to accurately sample these constituents. Although sulfide concentrations in the dialysis samples varied from concentrations in low-flow samples by a broad range, the sulfide concentrations in the dialysis samples were all equal to or greater than the concentrations in the low-flow samples.

In general, the comparisons of VOC concentrations between the two different types of diffusion samples showed a relatively close correspondence. At concentrations less than 6 µg/L, the average concentration difference between dialysis and PDB samples for individual VOCs was 0.8 µg/L. At concentrations greater than 6 µg/L, the average RPD for individual VOCs was 16.7 percent between dialysis and PDB samplers from corresponding depths. The relatively close match in concentrations from the two different types of diffusion membranes indicates that the concentrations accurately represent concentrations of the tested constituents in water contacting the samplers.

Evaluation of diffusion samplers for VOCs was not appropriate in some of the tested wells because the wells contained no detectable VOCs without laboratory qualifiers (wells SS13 MW-10, SS13 MW-17, and SS15 MW-2). In other wells (SS13 MW-4 and SS15 GT-K5) containing only low concentrations of VOCs, the data imply that the diffusion samplers produced representative VOC concentrations. Data from well SS01 MW-11 also showed relatively low concentrations (less than 10 µg/L). The relatively close agreement between diffusion sampling and low-flow sampling in well SS01 MW-11 probably indicates that the diffusion samples provide representative VOC concentrations in that well; however, the slightly larger difference in isopropylbenzene concentrations suggest that further testing may be warranted if that constituent is of major interest. Samples from well SS01 MW-8 contained several VOCs at quantifiable concentrations less than 10 µg/L. Concentrations of most of these constituents from low-flow sampling agreed with concentrations from adjacent or nearby (3 ft) diffusion samplers, suggesting that the two methodologies were comparable at well SS01 MW-8. However, *n*-propylbenzene in well SS01 MW-8 was more concentrated by about 7.7 to 13 µg/L than in nearby diffusion samplers. If *n*-propylbenzene is a constituent of major concern in this well, then additional testing is warranted.

Substantial concentration differences between sampling methods were observed at some wells. Benzene, ethylbenzene, and xylene concentrations from well SS11 MW-8 were substantially lower in water from low-flow samples than in water from diffusion samplers. The data imply that the diffusion samples provide a better indication of the contamination in the adjacent aquifer than the low-flow samples in this well. A possible exception is 1,3,5-trimethylbenzene, which was more concentrated in the low-flow sample than in the diffusion samplers. Additional investigation is warranted if 1,3,5-trimethylbenzene is a constituent of major concern in this well.

Well SS01 MW-2 is an example of a well at Hickam AFB where VOCs are vertically stratified. VOCs present in the well were most concentrated near the top of the well screen. The data imply that the low-flow sample in this well was composed primarily of water from the shallowest part of the well and that the diffusion samples accurately reflect contaminant stratification within the screened interval.

Well SS01 MW-12 is an example of a well at Hickam AFB showing vertical variations in VOC concentration in the screened interval in which many of the VOCs showed differences between the PDB and low-flow results. In this case, the stratification is more complex than at well SS01 MW-2. Different VOCs are concentrated at different depths. The data from well SS01 MW-12 imply that the diffusion-sample results represent VOC concentrations under ambient conditions, and that the low-flow sample results represent VOC concentrations resulting from preferential flow and/or mixing in a complexly stratified system and possibly include concentrations representing conditions not in the direct vicinity of the well screen for some constituents.

Both dialysis and PDB samplers are relatively inexpensive and can be deployed rapidly and easily. PDB samplers are intended for sampling VOCs only, but dialysis samplers can sample both VOCs and inorganic solutes. Regenerated cellulose dialysis samplers, however, are subject to biodegradation and probably should be deployed no sooner than 2 weeks prior to recovery.

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