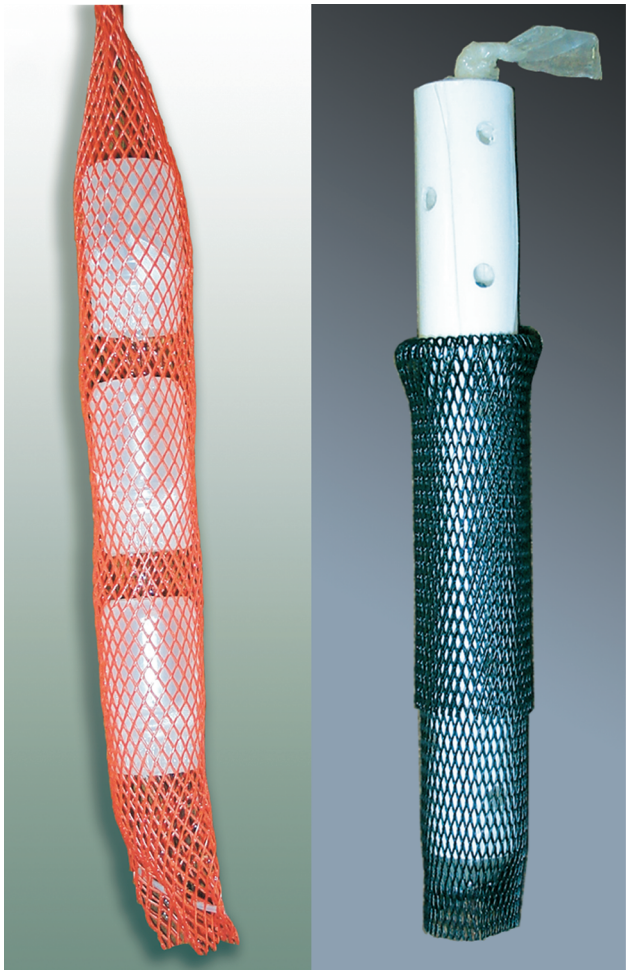
FIELD TESTS OF DIFFUSION SAMPLERS FOR INORGANIC CONSTITUENTS IN WELLS AND AT A GROUND-WATER DISCHARGE ZONE

Water-Resources Investigations Report 02-4031



Prepared in cooperation with the
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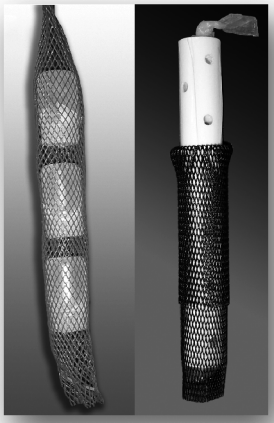

COVER PHOTOGRAPHS : Dialysis Samplers.
Photographs by Don A. Vroblesky

Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone

By Don A. Vroblesky, Matthew D. Petkewich, *and* Ted R. Campbell

U.S. Geological Survey

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For additional information write to:

District Chief
U.S. Geological Survey
Suite 129
720 Gracern Road
Columbia, SC 29210-7651

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CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS, AND ABBREVIATIONS

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
gallon (gal)	3.785	liter

Sea level: In this report, “sea level” refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order levels 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).

EDTA	ethylenediaminetetra acetic acid
LDPE	low-density polyethylene
µg/L	micrograms per liter
µ	micron
mg/L	milligrams per liter
mL	milliliter
mL/min	milliliter per minute
NAS Fort Worth JRB	Naval Air Station Fort Worth Joint Reserve Base
NIROP	Naval Industrial Reserve Ordnance Plant
VOC	Volatile organic compound
P	Wilcoxon signed rank test P value

Field Tests of Diffusion Samplers for Inorganic Constituents in Wells and at a Ground-Water-Discharge Zone

By Don A. Vroblesky, Matthew D. Petkewich, *and* Ted R. Campbell

ABSTRACT

Field tests were performed on two types of diffusion samplers to collect representative samples of inorganic constituents from ground water in wells and at an arsenic-contaminated ground-water-discharge zone beneath a stream. Nylon-screen samplers and dialysis samplers were tested for the collection of arsenic, calcium, chloride, iron, manganese, sulfate, and dissolved oxygen. The investigations were conducted at the Naval Industrial Reserve Ordnance Plant (NIROP), Fridley, Minnesota, and at the Naval Air Station Fort Worth Joint Reserve Base (NAS Fort Worth JRB), Texas.

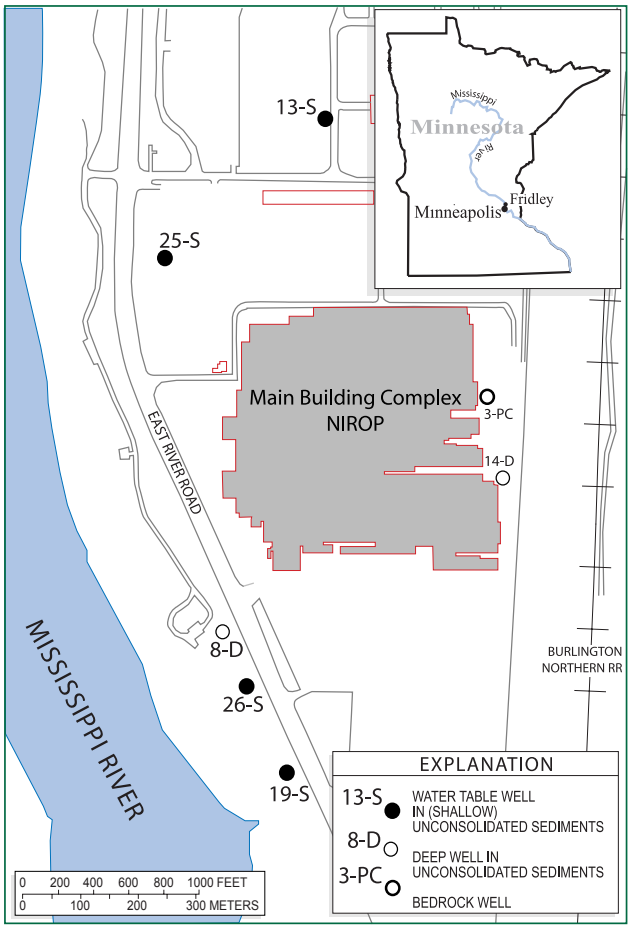
Data indicate that, in general, nylon-screen and dialysis diffusion samplers are capable of obtaining concentrations of inorganic solutes in ground water that correspond to concentrations obtained by low-flow sampling. Diffusion samplers offer a potentially time-saving approach to well sampling. Particular care must be taken, however, when sampling for iron and other metals, because of the potential for iron precipitation by oxygenation and when dealing with chemically stratified sampling intervals. Simple nylon-screen jar samplers buried beneath creekbed sediment appear to be effective tools for locating discharge zones of arsenic-contaminated ground water.

INTRODUCTION

Diffusion samplers have been used in environmental studies for several years. Low-density polyethylene (LDPE) diffusion samplers have been used to collect samples of volatile organic compounds (VOCs) in ground water at wells (Vroblesky and Hyde, 1997; Parsons Engineering Science, Inc., 1999; 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, 1999b; 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), filter paper (Davis and Atkins, 2001), and dialysis membranes (Mayer, 1976; Bottomley and Bayly, 1984; Ronen and others, 1986; Webster and others, 1998; Diog and Liber, 2000; Theodore A. Ehlke, U.S. Geological Survey, written commun., 2001), among others. Multiport 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 the LDPE samplers have proven to be inexpensive and simple to use in wells, they are limited by their inability to provide a representative sample of ionic solutes. The success of nylon-screen samplers in sediment studies suggests that these simple samplers may be useful for collecting water samples for inorganic constituents in wells. Results using dialysis bags deployed in wells suggest 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; Theodore A. Ehlke, U.S. Geological Survey, written commun., 2001).

The purpose of this report is to provide results of field tests investigating the potential to use diffusion samplers to collect representative samples of inorganic constituents from ground water in wells and at an arsenic-contaminated ground-water-discharge zone beneath a stream. The investigations were performed at NIROP, Fridley, Minn. (fig. 1) and at NAS Fort Worth JRB, Texas (fig. 2). Two types of samplers were tested. One type was a nylon-screen sampler, which consisted of a 30-mL jar filled with deionized water, with its opening covered by a nylon screen. The second type was a dialysis sampler that consisted of a tube of dialysis membrane filled with deionized water. The nylon-screen samplers were deployed in wells at NIROP Fridley and NAS Fort Worth JRB and beneath the ground-water/surface-water interface of a stream at NAS Fort Worth JRB. The dialysis samplers were deployed only in wells at NAS Fort Worth JRB.



Basemap from Tetra Tech NUS, Inc., written commun., 2000

Figure 1. Location of wells at the Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999 and May 2000.

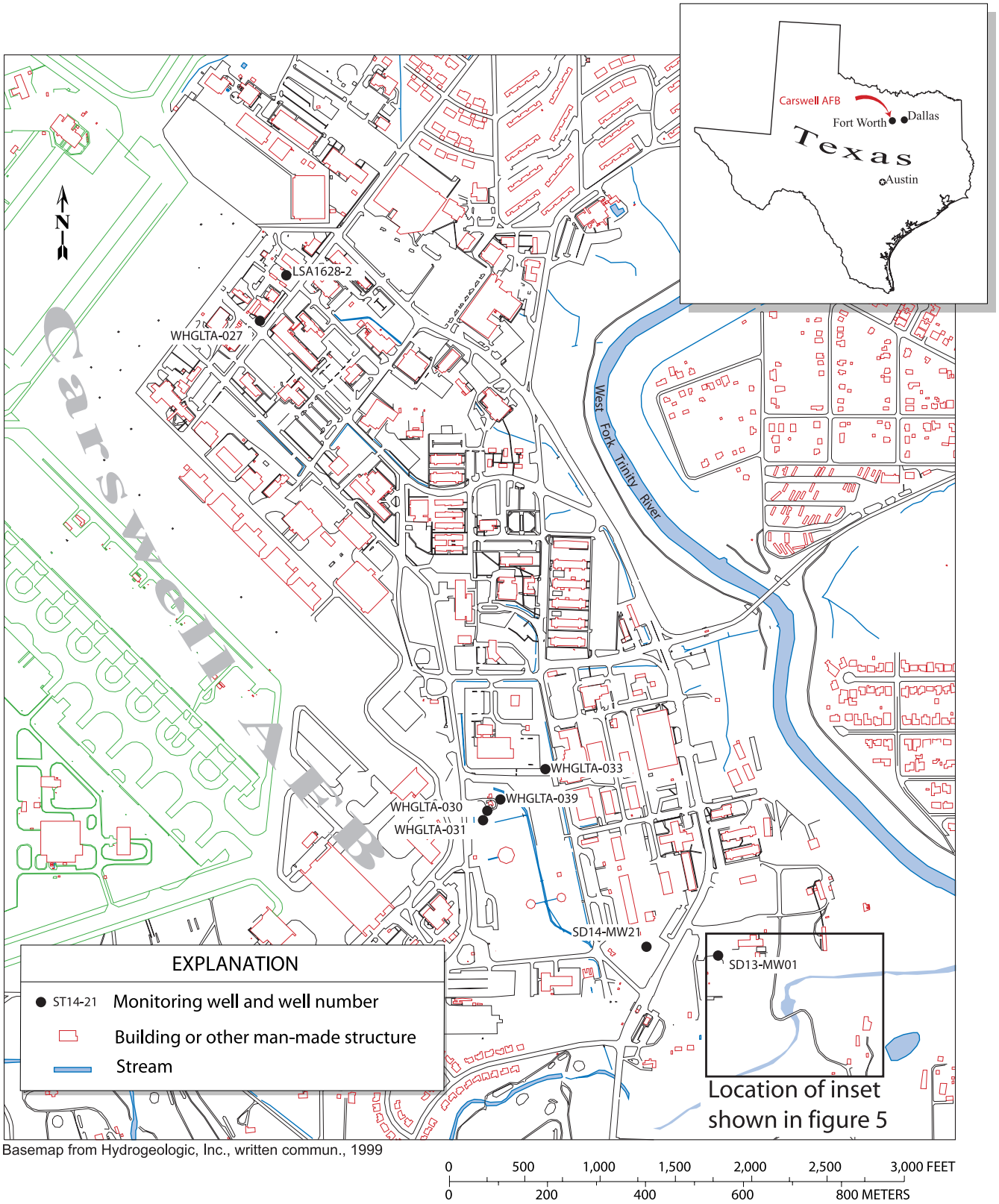
METHODS

Two types of water-filled diffusion samplers were used for this investigation. Nylon-screen samplers were deployed in seven wells at NIROP Fridley, and at eight wells at NAS Fort Worth JRB. Dialysis samplers were installed in two wells at NAS Fort Worth JRB.

Diffusion-Sampler Construction and Deployment

Each nylon-screen sampler consisted of a 30-mL polyethylene wide-mouth bottle with a nylon-screen cloth (Small Parts Inc., Miami Lakes, Fla.) secured over the opening (fig. 3). Each dialysis sampler consisted of a perforated acetate or plastic pipe inside a sleeve of high-grade regenerated cellulose tubular dialysis membrane (Membrane Filtration Products, Inc., Seguin, Tex.) (fig. 4).

To prepare a nylon-screen sampler, a 2 by 2 in. section of nylon screen was secured by holding it in place over the jar opening and screwing the open-top cap onto the jar and screen. Screen-opening sizes used in the field were 125 and 250 µ. Each sampler consisted of three to four such jars held in a sleeve of 2-in-diameter flexible LDPE mesh, giving a total of approximately 80 to 110 mL of available water. The jars were separated in the LDPE mesh by a distance of approximately 0.5 to 1 in. (fig. 3B). Each jar was filled with deionized water at the time of sampler deployment. The jars were filled in a bucket of deionized water by screwing the lids onto the jars under water. When the samplers were to be filled with anaerobic water, helium was bubbled through the water in the bucket until the dissolved-oxygen concentration was reduced to less than 0.5 mg/L (as measured by CheMetrics titration).



Basemap from Hydrogeologic, Inc., written commun., 1999

Figure 2. Location of wells used for diffusion-sampler deployment and location of inset, Naval Air Station Fort Worth Joint Reserve Base, Texas, July 2000 to March 2001.

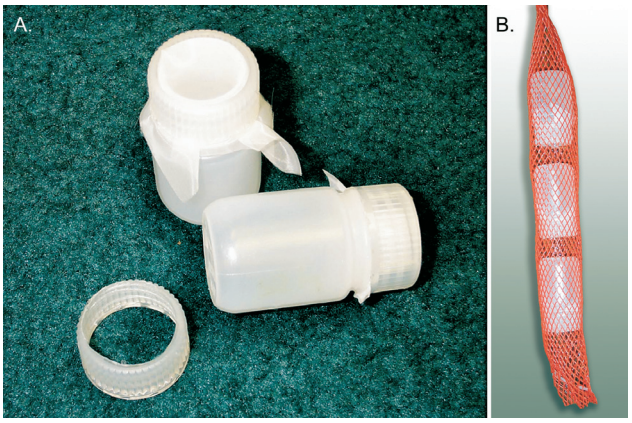


Figure 3. Nylon screen secured on (A) open-top jar, and (B) three jars in low-density polyethylene mesh.

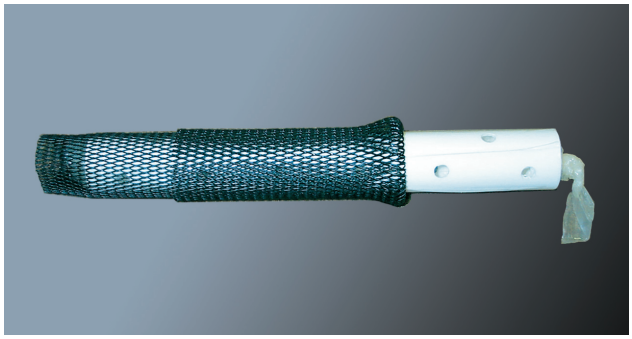


Figure 4. Dialysis bag on perforated pipe with outer low-density polyethylene mesh partly removed.

Dialysis samplers were prepared from pretreated tubular dialysis membrane having a nominal molecular-weight cutoff of 8,000 daltons (approximately cost was $180 for a 32.8-ft roll). Pretreatment was designed to remove sulfur compounds and residual metals. The pretreated membrane is packaged in a solution of methanol and ethylenediaminetetra acetic acid (EDTA), which is 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 (approximately $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.

Dialysis samplers used in this investigation differ slightly from samplers described in previous publications, which typically involve a relatively small container with a dialysis membrane over the opening (Mayer, 1976; Bottomley and Bayly, 1984; Ronen and others, 1986; Webster and others, 1998; Diog and Liber, 2000). Dialysis samplers used in this investigation are similar to those of Ehlke (Theodore A. Ehlke, U.S. Geological Survey, written commun., 2001) in that they were designed to supply a much larger amount of water (about 350 mL) to increase analytical flexibility. To construct a dialysis sampler, the cellulose acetate dialysis tube was cut to a length of approximately 2 ft. The dialysis membrane was thoroughly washed with deionized water. One end of the tube was tied in a knot. The samples differ from those of Ehlke in that, for these samplers, a pipe of perforated acetate or plastic was slid into the dialysis tube for structural support (fig. 4). The sampler was filled with approximately 350 mL of deionized water at the time of sampler deployment, and the other end of the membrane was tied. The assembly was slid into a length of LDPE mesh for abrasion protection. In wells where dialysis samplers were tested, both the dialysis samplers and the nylon-screen samplers were deployed simultaneously.

Structural support provided by the inner perforated acetate or plastic pipe is important to allow the sampler to retain water by preventing 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.

Deployment of the samplers in wells consisted of attaching to a support line. At NAS Fort Worth JRB, the support line was a length of ¼-in-diameter stiff polyethylene tubing. The samplers were attached to the tubing by using zip ties at positions representing the target horizons, with the jar openings facing downward. Sampling tubing, extending to the top of the well, was attached with the downhole opening adjacent to the centers of

selected diffusion samplers. In this way, a peristaltic pump sequentially attached to the upper end of each sampling tube could be used to collect water from horizons directly adjacent to each diffusion sampler. The samplers were deployed by pushing the tubing into the well until the support tubing contacted the well bottom. The tubing was cut to the length of the well, and the well was sealed. An alternative approach would be to attach the samplers to a weighted line rather than to stiff LDPE tubing. At NIROP Fridley, the samplers were deployed along with positive-displacement pumps by attaching them onto the discharge tubing near the pump. The samplers were allowed to equilibrate undisturbed for 24 to 27 days at NAS Fort Worth JRB and for 27 to 29 days at NIROP Fridley (table 1).

The nylon-screen samplers were deployed with the opening of the jar facing downward. The purpose of this orientation was to minimize mixing of water in the samplers with shallower well water during sampler recovery. The screen retained the water in the sampler by means of a vacuum. Although this approach is sound for the waters tested in this investigation, it is not preferable for waters having a large ionic strength, such as saltwater. Webster and others (1998) found that vials oriented with the membrane facing downward failed to equilibrate with saltwater after 60 hours because density differences eliminated the tendency for saline convection to develop within the samplers. Vials oriented with the membrane facing upward or to the side equilibrated faster (85 percent equilibration in 15 hours) than samplers oriented downward; however, samplers oriented with the membrane facing upward equilibrated more slowly than samplers oriented with the membrane facing sideways.

For deployment at a ground-water/surface-water interface in an attempt to map the discharge area of an arsenic plume, anaerobic water (to minimize oxidation of redox-sensitive solutes) was used to fill 25-mL nylon-screened jars, as above. In this case, however, individual sample jars were attached to wire surveyor flags and buried, opening downward, approximately 8 in. into the creekbed sediment. The samplers were buried along the edge of the shoreline where ground-water contamination was suspected to discharge (fig. 5). Samplers were deployed in pairs on July 19, 2000. One sampler from each pair was recovered on July 21 and the other was recovered on August 16, 2000.

Table 1. Well-construction details and diffusion-sampler deployment and recovery dates, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, and Naval Air Station Fort Worth Joint Reserve Base, Texas

[BLS, below land surface; BTOC, below top of casing; NA, data not available]

Well number	Well diameter (inches)	Screen length (feet)	Top of well screen (feet BLS)	Bottom of well screen (feet BLS)	Depth to water (feet BTOC)	Diffusion-sampler deployment	Diffusion-sampler recovery	Days of equilibration
Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota								
3-PC	4	27	130.0	156.7	22.8	10/5/99	11/2/99	28
					22.8	4/17/00	5/16/00	29
8-D	2	10	115.0	125.0	30.2	4/18/00	5/15/00	27
13-S	2	10	21.4	31.4	18.4	10/5/99	11/2/99	28
14-D	2	10	80.0	90.0	25.0	10/4/99	11/2/99	29
19-S	2	10	32.5	42.5	34.2	4/18/00	5/15/00	27
25-S	2	10	20.0	30.0	18.5	10/4/99	11/2/99	29
26-S	2	NA	NA	40	30	4/18/00	5/16/00	28
Naval Air Station Fort Worth Joint Reserve Base, Texas								
LSA1628-2	4	10	10	20	10.6	2/17/01	3/13/01	24
SD13-MW01	2	7.2	7.12	14.32	10.8	2/16/01	3/12/01	24
ST14-MW21	2	9	8	17	10.1	2/15/01	3/14/01	27
WHGLTA-027	2	10	8.5	18.5	11.4	2/15/01	3/12/01	25
WHGLTA-030	2	10	5	15	0.6	2/16/01	3/14/01	26
WHGLTA-031	2	5	6	11	3.6	2/16/01	3/13/01	25
WHGLTA-033	2	15	13	28	10.2	2/16/01	3/13/01	25
WHGLTA-039	2	10	15.5	25.5	15.6	2/16/01	3/14/01	26

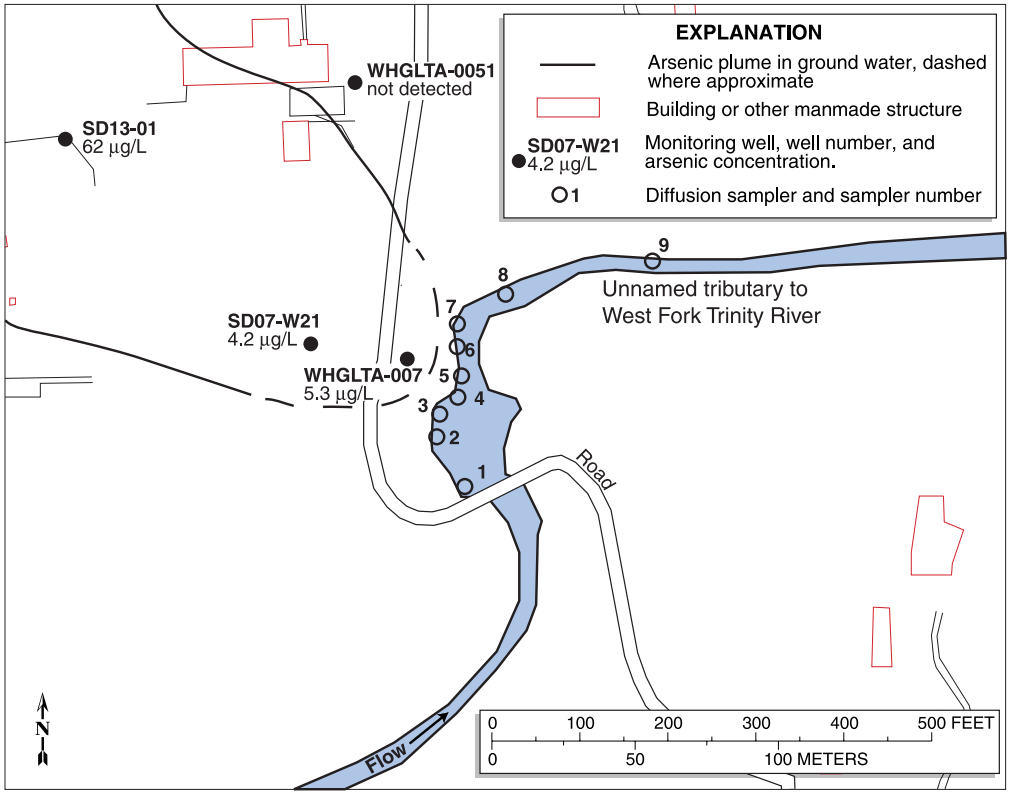


Figure 5. Arsenic plume in ground water, July 1999, and locations of nylon-screen diffusion samplers in the bed sediment of an unnamed tributary to the West Fork Trinity River, Naval Air Station Fort Worth Joint Reserve Base, Texas, July 2000.

Recovery consisted of pulling the samplers out of the wells or creekbed sediments, removing the caps, and pouring the contents into sample bottles. The sample bottles then were shipped to a commercial laboratory for analysis by U.S. Environmental Protection Agency methods SW6010B for metals and E300.0 for anions (U.S. Environmental Protection Agency, 1983, 1992). Dissolved oxygen was measured onsite by using CheMetrics ampules.

Diffusion-Sampler Equilibration Times and Accuracy

Prior to deploying the diffusion samplers in the field, the samplers were tested to determine approximate equilibration times and accuracy of quantitation. Four of each diffusion-sampler type (nylon screen and dialysis) were filled with deionized water and added to a bucket containing 4 gallons of anaerobic deionized water amended to contain approximately 240 µg/L of arsenic, 265 mg/L of chloride, 75 µg/L of chromium, 3,700 µg/L of iron, 300 µg/L of lead, 350 µg/L of manganese, 580 µg/L of selenium, and 120 µg/L of sulfate. An attempt was made to maintain anaerobic conditions in the test water by continuously bubbling nitrogen through the solution, but the rate of nitrogen bubbling apparently was too low because the dissolved-oxygen concentration remained in the 1 to 2 mg/L range, as measured by CheMetrics methodology, for the duration of the experiment.

Recovery of the samples consisted of removing one of each sampler type from the bucket at specific time points and shipping the enclosed water to a commercial laboratory for analysis. At each sample-collection time, a sample of the test-bucket water also was collected and sent to the commercial laboratory for analysis. By the first sampling point, 20.5 hours following deployment, the concentrations of all tested solutes in the nylon-screen samplers were as high as

the concentrations in the test-bucket water. By the second sampling point, 92 hours following deployment, the concentrations of all tested solutes in the dialysis samplers were as high as the concentrations in the test-bucket water. Thus, it appears that the nylon-screen samplers equilibrated in 20.5 hours or less, and the dialysis samplers equilibrated between 20.5 and 92 hours.

These equilibration times are consistent with independent tests of dialysis-sampler equilibration times in which iron and bromide attained equilibrium within 3 days (Theodore A. Ehlke, U.S. Geological Survey, written commun., 2001), and chloride and manganese attained complete equilibrium and sulfate attained 80 percent equilibrium within 48 hours (Ronen and others, 1986; Magaritz and others, 1989). An independent laboratory test of nylon-screen samplers with a screen opening of 45 µ showed an equilibration time of approximately 95 hours (Paludan and Morris, 1999). The shorter equilibration found during this investigation probably is due to the use in this study of a much larger screen-size opening (125 µ).

When deployed in sediment, the limiting factor in equilibration is predominantly the solute diffusion through the sediments (Webster and others, 1998). Equilibration times determined for various dialysis samplers for determining subaqueous porewater concentrations of inorganics 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).

In this investigation, the total iron concentrations in the diffusion samplers tended to be higher than in the test-bucket water. The probable explanation is that some of the iron that initially was in solution in the anaerobic test-bucket water precipitated out of solution as the water gained oxygen over the course of the experiment. Part of the iron that diffused into the samplers probably also precipitated out of solution as the test water gained oxygen. The precipitated iron from the test-bucket water would not have been included in the water analysis because the iron would have fallen to the bottom of the bucket. However, the precipitated iron in the samplers probably was retained in the samplers and included in the analytical digestion. Thus, the water analysis from the diffusion samplers included both dissolved and precipitated iron. As will be shown, this type of reaction also can affect iron results under field conditions.

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 both NIROP Fridley and NAS Fort Worth JRB. The wells were purged at a rate of about 300 to 550 mL/min at NIROP Fridley and about 100 to 300 mL/min at NAS Fort Worth JRB, until the temperature, pH, and specific conductance stabilized and no additional water-level drawdowns were observed. Typically, this required purging less than a gallon of water over a time period of approximately 15 minutes. At NIROP Fridley, low-flow ground-water samples were collected immediately prior to retrieving the diffusion samplers from the well.

At NAS Fort Worth JRB, a somewhat different approach was used to collect ground-water and diffusion samples. For comparison purposes in selected wells, the first sample collected from the well was an immediate-flow sample. This consisted of calculating the amount of residual water in the downhole tubing at each sampling horizon and using a peristaltic pump to pump water through the tube. The immediate-flow samples were collected from the tube immediately following discharge of the residual tubing water. To some extent, this sample consisted of water in the well bore in the direct vicinity of the tubing opening and the adjacent diffusion sampler. However, a substantial amount of uncertainty is associated with this interpretation, because even small amounts of pumping can disturb contaminant stratification in the well causing concentrations to change during pumping.

Following collection of the immediate samples from each horizon in a particular well, the diffusion samplers were removed, and the enclosed water was transferred to sampling vials. The tubing then was returned to the well, and each target horizon was sampled with a peristaltic pump by the low-flow methodology described above.

Samples were analyzed for anions by method E300.0 and for metals by method SW6010B (U.S. Environmental Protection Agency, 1983, 1992). Because of the limited sample volumes available from the nylon-screen samplers, the analyses were performed using a minimum of 5 mL for anions and 25 mL for metals. This sometimes required mixing water from more than one nylon-screen jar in a particular sampler. The analytical methods typically use a minimum of 15 mL for anions and 50 mL for metals; however lower concentrations can be used if the resulting increase in detection limits is within acceptable bounds. An additional 25 mL of water was used for field analysis of iron(II) by CheMetrics methodology. Dissolved oxygen was measured by snapping a CheMetrics ampule (American Society for Testing and Materials, 1994) in the 25-mL jars. Because the dissolved-oxygen measurement was not done in a moving stream of water, there is the potential for this approach to slightly overestimate actual dissolved-oxygen concentrations if the jar water became aerated during handling.

Recovery of nylon-screen samplers from the creekbed sediments consisted of pulling the samplers out of the ground by using the wire surveyor flags, removing the caps, and pouring the contents into sample bottles. The samples were analyzed for arsenic by method SW6010B (U.S. Environmental Protection Agency, 1983).

Statistical comparisons were conducted using the nonparametric Wilcoxon signed rank test, which does not require assuming normality or equal variance. The test produces a P value that is the probability of being wrong in concluding that there is a true difference in the concentrations obtained by using each of the two compared methods. Traditionally, a significant difference between the two methods is assumed if the P value is less than 0.05. In this investigation, only nonzero detections were used in the statistical analysis.

RESULTS AND DISCUSSION

As will be shown, the data indicate that, in general, nylon-screen and dialysis diffusion samplers are capable of obtaining concentrations of inorganic solutes in ground water from wells that closely correspond to concentrations obtained by low-flow sampling. Particular care must be taken when sampling for iron and other metals, because of the potential for iron precipitation by oxygenation, and when dealing with chemically stratified sampling intervals. Simple nylon-screen jar samplers buried beneath creekbed sediment appear to be effective tools for locating discharge zones of arsenic-contaminated ground water.

Field Tests of Diffusion Samplers for Inorganic Constituents in Wells

The dissolved-oxygen concentrations obtained from four nylon-screen samplers at NIROP Fridley appeared to be an accurate representation of aquifer dissolved-oxygen concentrations obtained by low-flow sampling (fig. 6, table 2). Although the samplers were filled with aerobic water, by the recovery date in November 1999, all of the samplers contained less than 1 mg/L of dissolved oxygen. The dissolved-oxygen concentrations in nylon-screen samplers from NIROP Fridley were as low or lower than the dissolved-oxygen concentrations obtained from low-flow sampling, suggesting that the nylon-screen samples provided dissolved-oxygen concentrations comparable to results from the low-flow samples. In general, the dissolved-oxygen measurements from nylon-screen samplers filled with aerobic water tended to be slightly higher than the concentrations obtained by low-flow

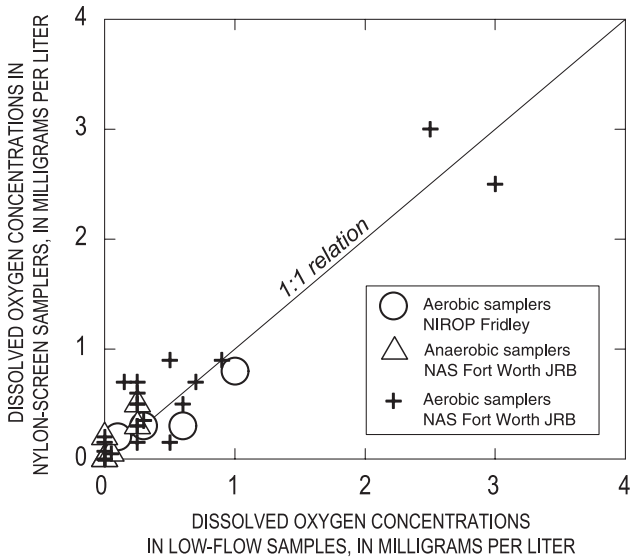


Figure 6. Comparison of ground-water dissolved-oxygen concentrations in nylon-screen samples to concentrations in low-flow samples at the Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999, and Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

Table 2. Comparison of dissolved-oxygen and chloride concentrations in nylon-screen samples and low-flow samples, Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, November 1999 and May 2000

[Concentrations are in milligrams per liter; µ, micron; ---, data not collected; 130/120, concentration in sample and in replicate sample]

Well number	Dissolved oxygen November 1999		Chloride, May 2000		
	Nylon-screen sample	Low-flow sample	Nylon-screen sample (125-µ screen)	Nylon-screen sample (250-µ screen)	Low-flow sample
3-PC	0.8	1	---	---	---
8-D	---	---	48	48	48
13-S	0.2	0.1	---	---	---
14-D	0.3	0.6	---	---	---
19-S	---	---	---	35	41
25-S	0.3	0.3	---	---	---
26-S	---	---	120	130/120	120

sampling; however, all concentrations obtained from the nylon-screen samplers at NAS Fort Worth JRB were within 0.6 mg/L of the results obtained from low-flow sampling (table 3 and fig. 6). The Wilcoxon signed rank test *P* statistic (0.151) implied no significant difference between the results from the two methodologies (table 4).

Comparison of nylon-screen diffusion-sampler chloride concentrations in ground water from NIROP Fridley showed a close match to concentrations obtained by low-flow sampling (table 2, fig. 7A). No significant difference was observed in concentrations obtained by using 125- or 250-µ screen openings (fig. 7A). Comparison of diffusion-sampler chloride concentrations to low-flow concentrations also showed a close match at NAS Fort Worth JRB (table 3, fig. 7B). The concentrations from nylon-screen samplers at NAS Fort Worth JRB showed a Wilcoxon signed rank test *P* value of 0.202, indicating that there was no significant difference between the results from the two sampling methodologies (table 4).

Four dialysis samplers also were tested for chloride concentrations, and each showed a close match (2 to 3 mg/L difference over a range of 15 to 25 mg/L) to concentrations obtained by low-flow sampling (table 4, fig. 7B). These data suggest that both types of diffusion samplers are capable of providing representative ground-water concentrations of chloride. Because chloride is not subject to redox reactions, diffusion samplers for chloride concentrations can be filled with aerobic water.

Calcium concentrations in nylon-screen samplers showed a close match to concentrations in low-flow samples from most wells at NAS Fort Worth JRB (fig. 8). The Wilcoxon signed rank test *P* value (0.11) showed that there was no significant difference in calcium concentrations obtained by the two methods (table 4).

Despite the close statistical match between sampling methods, not all samples showed a close match between methods for calcium (fig. 8). The poorest matches were found in the two shallowest nylon-screen samplers from well WHGLTA-039 (table 3, fig. 9A). The immediate-flow sample calcium concentration in the shallowest horizon of well WHGLTA-039 more closely matched the low-flow sample concentration than the nylon-screen-sample concentration, suggesting that the nylon-screen sampler underestimated the calcium concentration in the well bore at that depth; however, any amount of pumping in a chemically stratified interval has the potential to cause mixing. The deepest nylon-screen sampler calcium concentration differed from the corresponding low-flow calcium concentration by only 5 percent. The close match at the deepest sampler between nylon-screen sample and low-flow sample calcium concentrations and in other wells between nylon-screen-samples, low-flow samples, and immediate-flow samples indicates that the diffusion samplers are capable of providing an accurate measurement of calcium concentrations. Therefore, the much larger percentage differences (21 to 26 percent) in the shallower samplers at well WHGLTA-039 may be attributable to well-specific factors and not related to sampler efficiency.

Table 3. Comparison of inorganic constituents in dialysis samples, nylon-screen samples, immediate-flow samples, and low-flow samples, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001

[BLS, feet below land surface; mg/L, milligrams per liter; µg/L, micrograms per liter; ---, data not collected; 44/43, concentration in sample and in replicate sample; <, less than]

Well number	Date (feet BLS)	Depth	Aquifer dis-solved oxygen (mg/L)	Arsenic (µg/L)						Calcium (mg/L)					
				Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample	Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample
				Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler			Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler		
LSA1628-2	3/13/2001	12.8	0.25	19	---	---	---	16	25	44/43	---	---	---	44	38
LSA1628-2	3/13/2001	14	0.3	---	---	<10	15	---	---	---	---	32	35	---	---
LSA1628-2	3/13/2001	15.5	0.25	17	---	14/17	---	---	22	45	---	35	---	---	38
LSA1628-2	3/13/2001	17.5	0.25	---	---	<10	12	---	24/27	---	---	28	30	---	38/37
SD13-01	3/12/2001	11.1	0.05	---	---	---	---	---	---	---	---	---	120	130	120
SD13-01	3/12/2001	13.6	<0.05	---	---	---	---	---	---	---	---	---	130	---	120
ST14-21	3/14/2001	12.8	0.5	---	---	<10	---	<10	<10	---	---	140	---	140	150
ST14-21	3/14/2001	14.8	0.5	---	---	<10	---	---	<10/<10	---	---	140	---	---	140/150
ST14-21	3/14/2001	16.6	0.3	---	---	<10	---	---	<10	---	---	140	---	---	140
WHGLTA-027	3/12/2001	13	<0.05	---	---	37	---	41	42	---	---	130	---	130	130
WHGLTA-027	3/12/2001	14.5	<0.05	---	---	39	---	---	40	---	---	130	---	---	130
WHGLTA-027	3/12/2001	16.2	<0.05	---	---	44	---	---	38	---	---	130	---	---	120
WHGLTA-030	3/14/2001	6.5	0.05	---	---	---	---	---	---	---	---	110	110	120	110
WHGLTA-030	3/14/2001	8.5	0.75	---	---	---	---	---	---	---	---	---	120	---	---
WHGLTA-030	3/14/2001	11	<0.05	---	---	---	---	---	---	---	---	---	120	110	110
WHGLTA-030	3/14/2001	12.5	0.15	---	---	---	---	---	---	---	---	---	110	---	---
WHGLTA-031	3/13/2001	8	0.25	---	---	---	---	---	---	---	---	120	---	130	140
WHGLTA-031	3/13/2001	9.3	0.15	---	---	---	---	---	---	---	---	130	---	---	130
WHGLTA-033	3/13/2001	22	0.7	---	---	---	---	---	---	---	---	160	---	150	160
WHGLTA-033	3/13/2001	24.5	0.9	---	---	---	---	---	---	---	---	170	---	---	150
WHGLTA-033	3/13/2001	26	0.5	---	---	---	---	---	---	150	---	140	---	---	150
WHGLTA-039	3/14/2001	19.5	3	---	---	---	---	---	---	---	---	140	---	180	190
WHGLTA-039	3/14/2001	21	2.5	---	---	---	---	---	---	---	---	150	---	---	190
WHGLTA-039	3/14/2001	25.3	---	---	---	---	---	---	---	---	---	180	---	---	190

Table 3. Comparison of inorganic constituents in dialysis samples, nylon-screen samples, immediate-flow samples, and low-flow samples, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001 (Continued)

[BLS, feet below land surface; mg/L, milligrams per liter; µg/L, micrograms per liter; ---, data not collected; 44/43, concentration in sample and in replicate sample; <, less than]

Well number	Date	Depth	Aquifer dis-solved oxygen (mg/l)	Chloride (mg/L)						Total iron (mg/L)					
				Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample	Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample
				Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler			Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler		
LSA1628-2	3/13/2001	12.8	0.25	16/15	---	---	---	15	13	---	---	---	---	---	---
LSA1628-2	3/13/2001	14	0.3	---	---	12	13	---	---	---	---	---	---	---	---
LSA1628-2	3/13/2001	15.5	0.25	16	---	13/15	---	---	14	---	---	---	---	---	---
LSA1628-2	3/13/2001	17.5	0.25	---	---	11	12	---	14/14	---	---	---	---	---	---
SD13-01	3/12/2001	11.1	0.05	---	---	---	23	22	22	---	---	---	---	---	---
SD13-01	3/12/2001	13.6	<0.05	---	---	---	23	---	22	---	---	---	---	---	---
ST14-21	3/14/2001	12.8	0.5	---	---	3.5	---	3.2	3.9	---	---	0.41	---	0.11	1.4
ST14-21	3/14/2001	14.8	0.5	---	---	3.4	---	---	4.3/4.3	---	---	0.56	---	---	1.2/1.2
ST14-21	3/14/2001	16.6	0.3	---	---	3.4	---	---	4.8	---	---	0.94	---	---	1.1
WHGLTA-027	3/12/2001	13	<0.05	---	---	100	---	99	98	---	---	---	---	---	---
WHGLTA-027	3/12/2001	14.5	<0.05	---	---	95	---	---	100	---	---	---	---	---	---
WHGLTA-027	3/12/2001	16.2	<0.05	---	---	95	---	---	100	---	---	---	---	---	---
WHGLTA-030	3/14/2001	6.5	0.05	---	---	15	16	15	15	---	---	---	---	---	---
WHGLTA-030	3/14/2001	8.5	0.75	---	---	---	15	---	---	---	---	---	---	---	---
WHGLTA-030	3/14/2001	11	<0.05	---	---	---	16	---	15	---	---	---	---	---	---
WHGLTA-030	3/14/2001	12.5	0.15	---	---	---	15	---	---	---	---	---	---	---	---
WHGLTA-031	3/13/2001	8	0.25	---	---	8.3	---	8.8	8.4	---	---	3.3	---	2.4	5.3
WHGLTA-031	3/13/2001	9.3	0.15	---	---	8.9	---	---	8.9	---	---	20	---	---	6
WHGLTA-033	3/13/2001	22	0.7	---	---	26	---	26	27	---	---	---	---	---	---
WHGLTA-033	3/13/2001	24.5	0.9	---	---	26	---	---	33	---	---	---	---	---	---
WHGLTA-033	3/13/2001	26	0.5	25	---	26	---	---	26	---	---	---	---	---	---
WHGLTA-039	3/14/2001	19.5	3	---	---	6.4	---	6.6	6.4	---	---	---	---	---	---
WHGLTA-039	3/14/2001	21	2.5	---	---	6.2	---	---	6.1	---	---	---	---	---	---
WHGLTA-039	3/14/2001	25.3	---	---	---	6.5	---	---	6.2	---	---	---	---	---	---

Table 3. Comparison of inorganic constituents in dialysis samples, nylon-screen samples, immediate-flow samples, and low-flow samples, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001 (Continued)

[BLS, feet below land surface; mg/L, milligrams per liter; µg/L, micrograms per liter; ---, data not collected; 44/43, concentration in sample and in replicate sample; <, less than]

Well number	Date	Depth	Aquifer dis-solved oxygen (mg/l)	Iron(II) (mg/L)						Manganese (mg/L)					
				Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample	Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample
				Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler			Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler		
LSA1628-2	3/13/2001	12.8	0.25	0.7/0.45	---	0.9	---	1.5	1.5	140/140	---	---	---	150	120
LSA1628-2	3/13/2001	14	0.3	---	---	1.5	1.5	---	2.0	---	---	99	100	---	---
LSA1628-2	3/13/2001	15.5	0.25	0.8	---	1	---	---	1.5	140	---	100/130	---	---	120
LSA1628-2	3/13/2001	17.5	0.25	---	---	1.5	1.5	---	2.0/2.0	---	---	82	89	---	120
SD13-01	3/12/2001	11.1	0.05	---	---	---	16	16	15.0	---	---	---	100	130	120
SD13-01	3/12/2001	13.6	<0.05	---	---	---	15	---	16.0	---	---	---	130	---	100
ST14-21	3/14/2001	12.8	0.5	---	---	<0.1	---	<0.1	0.4	---	---	---	---	---	---
ST14-21	3/14/2001	14.8	0.5	---	---	<0.1	---	---	0.6/0.6	---	---	---	---	---	---
ST14-21	3/14/2001	16.6	0.3	---	---	<0.1	---	---	0.8	---	---	---	---	---	---
WHGLTA-027	3/12/2001	13	<0.05	---	---	11	---	15	15.0	---	---	780	---	790	810
WHGLTA-027	3/12/2001	14.5	<0.05	---	---	15	---	---	15.0	---	---	750	---	---	760
WHGLTA-027	3/12/2001	16.2	<0.05	---	---	12	---	---	14.0	---	---	770	---	---	730
WHGLTA-030	3/14/2001	6.5	0.05	---	---	11.5	11.5	11	11.5	---	---	620	620	630	720
WHGLTA-030	3/14/2001	8.5	0.75	---	---	---	---	---	---	---	---	---	620	---	---
WHGLTA-030	3/14/2001	11	<0.05	---	---	---	11.5	---	11.5	---	---	---	620	---	720
WHGLTA-030	3/14/2001	12.5	0.15	---	---	---	11.5	---	---	---	---	---	610	---	---
WHGLTA-031	3/13/2001	8	0.25	---	---	0.15	---	0.5	4.0	---	---	---	---	---	---
WHGLTA-031	3/13/2001	9.3	0.15	---	---	0.2	---	---	6.5	---	---	---	---	---	---
WHGLTA-033	3/13/2001	22	0.7	---	---	---	---	---	---	---	---	---	---	---	---
WHGLTA-033	3/13/2001	24.5	0.9	---	---	---	---	---	---	---	---	---	---	---	---
WHGLTA-033	3/13/2001	26	0.5	---	---	---	---	---	---	---	---	---	---	---	---
WHGLTA-039	3/14/2001	19.5	3	---	---	<0.1	---	0.1	<0.1	---	---	14	---	20	63
WHGLTA-039	3/14/2001	21	2.5	---	---	<0.1	---	---	<0.1	---	---	15	---	---	36
WHGLTA-039	3/14/2001	25.3	---	---	---	<1	---	---	---	---	---	28	---	---	16

Table 3. Comparison of inorganic constituents in dialysis samples, nylon-screen samples, immediate-flow samples, and low-flow samples, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001 (Continued)

[BLS, feet below land surface; mg/L, milligrams per liter; µg/L, micrograms per liter; ---, data not collected; 44/43, concentration in sample and in replicate sample; <, less than]

Well number	Date	Depth	Aquifer dis-solved oxygen (mg/l)	Sulfate (mg/L)						Dissolved oxygen (mg/L)					
				Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample	Dialysis sample		Nylon-screen sample		Imme-diate-flow sample	Low-flow sample
				Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler			Aerobic sampler	Anaerobic sampler	Aerobic sampler	Anaerobic sampler		
LSA1628-2	3/13/2001	12.8	0.25	<2	---	---	---	<2	<2	---	---	0.6	---	0.35	0.25
LSA1628-2	3/13/2001	14	0.3	---	---	<2	<2	---	---	---	---	0.3/0.28	0.3	---	0.25
LSA1628-2	3/13/2001	15.5	0.25	<2	---	---	---	---	<2	---	---	0.15	---	---	0.25
LSA1628-2	3/13/2001	17.5	0.25	---	---	<2	<2	---	<2/<2	---	---	0.5/0.5	0.5	---	0.25/0.25
SD13-01	3/12/2001	11.1	0.05	---	---	<2	---	<2	<2	---	---	---	<0.05	0.05	<0.05
SD13-01	3/12/2001	13.6	<0.05	---	---	<2	---	---	<2	---	---	---	<0.05	---	<0.05
ST14-21	3/14/2001	12.8	0.5	---	---	36	---	36	36	---	---	0.15	---	0.8	0.5
ST14-21	3/14/2001	14.8	0.5	---	---	36	---	---	35/35	---	---	0.5	---	---	0.6
ST14-21	3/14/2001	16.6	0.3	---	---	36	---	---	33	---	---	0.35	---	---	0.3
WHGLTA-027	3/12/2001	13	<0.05	---	---	56	---	55	55	---	---	<0.05	---	<0.05	<0.05
WHGLTA-027	3/12/2001	14.5	<0.05	---	---	44	---	---	58	---	---	0.07	---	---	<0.05
WHGLTA-027	3/12/2001	16.2	<0.05	---	---	45	---	---	58	---	---	0.15	---	---	<0.05
WHGLTA-030	3/14/2001	6.5	0.05	---	---	11	11	11	11	---	---	0.05	---	0.05	0.05
WHGLTA-030	3/14/2001	8.5	0.75	---	---	---	11	---	---	---	---	---	---	---	---
WHGLTA-030	3/14/2001	11	<0.05	---	---	---	11	---	11	---	---	0.2	---	---	<0.05
WHGLTA-030	3/14/2001	12.5	0.15	---	---	---	11	---	---	---	---	---	---	---	---
WHGLTA-031	3/13/2001	8	0.25	---	---	7.5	---	7.5	7.8	---	---	0.7	---	---	0.25
WHGLTA-031	3/13/2001	9.3	0.15	---	---	7.4	---	---	7.6	---	---	0.7	---	---	0.15
WHGLTA-033	3/13/2001	22	0.7	---	---	24	---	24	23	---	---	0.7	---	0.5	0.7
WHGLTA-033	3/13/2001	24.5	0.9	---	---	27	---	---	23	---	---	0.9	---	---	0.9
WHGLTA-033	3/13/2001	26	0.5	22	---	20	---	---	24	---	---	0.9	---	---	0.5
WHGLTA-039	3/14/2001	19.5	3	---	---	69	---	71	70	---	---	2.5	---	3	3
WHGLTA-039	3/14/2001	21	2.5	---	---	56	---	---	69	---	---	3	---	---	2.5
WHGLTA-039	3/14/2001	25.3	---	---	---	71	---	---	69	---	---	---	---	---	---

Table 4. Statistical comparisons of non-zero nylon-screen sample concentrations to low-flow sample concentrations, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001

[*P*, Wilcoxon signed rank test p value (traditionally a significant difference between the compared data sets is indicated if *P* is less than 0.05); n, number of samples; ---, not applicable]

Property and treatment	Comparison to low-flow sample		Milligrams per liter difference between nylon-mesh sample and low-flow sample				Percent difference between nylon-mesh sample and low-flow sample				Descriptive statistics (milligrams per liter)				
	P	n	Maximum	Minimum	Average	Standard deviation	Maximum	Minimum	Average	Standard deviation	Maximum	Minimum	Average	Standard deviation	n
Calcium															
Nylon screen sample	0.110	23	50	0	9.1	13	26.3	0	7.3	8.7	180	28	121.7	38.4	23
Low-flow sample	---	---	---	---	---	---	---	---	---	---	190	37	124.2	45.8	24
Chloride															
Nylon screen sample	0.202	26	7	0	1.3	1.8	29.2	0	6.4	7.7	100	3.4	22.4	27.7	27
Low-flow sample	---	---	---	---	---	---	---	---	---	---	100	3.9	24.3	29.2	26
Sulfate															
Nylon screen sample	0.635	17	14	0	3.4	4.9	24	0	7.3	8.5	71	7.4	71	21.1	19
Low-flow sample	---	---	---	---	---	---	---	---	---	---	70	7.6	70	23.2	17
Manganese															
Nylon-screen sample filled with aerobic water	0.131	10	100	10	33	27.2	77.8	1.3	25.9	26.1	780	14	308	339	11
Nylon-screen sample filled with anaerobic water	0.118	5	100	20	56.2	40.2	25.8	13.9	18.7	5.5	620	89	361.1	274.3	8
Combined nylon-screen samples	0.035	15	100	10	40.7	32.6	77.8	1.9	23.5	21.5	780	14	309.2	312.7	19
Low-flow sample	---	---	---	---	---	---	---	---	---	---	810	16	337.2	327.1	16
Iron(II)															
Nylon-screen sample filled with aerobic water	0.008	10	6.3	0	1.8	2.2	96.9	0	35.7	34.6	15	0.2	5.5	6	10
Nylon-screen sample filled with anaerobic water	0.625	6	1	0	0.5	0.4	25	0	10.4	11.6	16	1.5	9.8	5.9	7
Combined nylon-screen samples	0.009	16	6.3	0	1.4	1.9	96.9	0	25.3	31.2	16	0.2	7.4	6.3	17
Low-flow sample	---	---	---	---	---	---	---	---	---	---	16	0.4	7.3	6.1	16
Dissolved oxygen															
Nylon-screen sample filled with aerobic water	0.226	15	0.6	0	0.3	0.2	78.6	0	32.3	28.4	3	0.1	0.7	0.8	18
Nylon-screen sample filled with anaerobic water	---	---	0.3	0.1	0.2	0.1	50	16.7	33.3	23.6	0.5	0.3	0.4	0.1	2
Combined nylon-screen samples	0.151	16	0.6	0	0.3	0.2	78.6	0	33.1	27.3	3	0.1	0.7	0.8	19
Low-flow sample	---	---	---	---	---	---	---	---	---	---	3	0.1	0.7	0.8	16

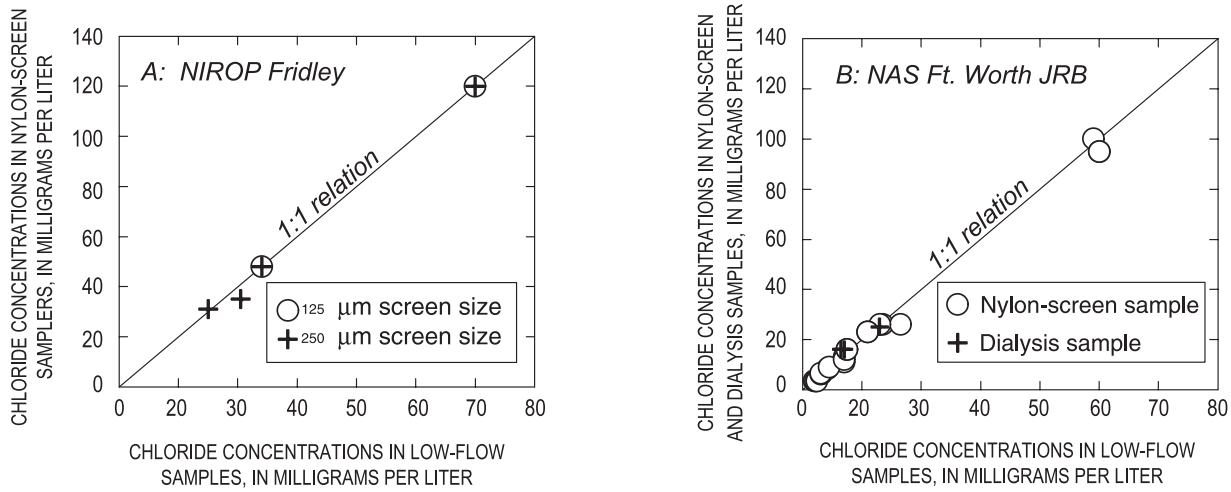


Figure 7. Comparison of ground-water chloride concentrations in diffusion samplers to concentrations in low-flow samplers at the Naval Industrial Reserve Ordnance Plant, Fridley, Minnesota, May 2000, and Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

Supporting evidence that the difference in calcium concentrations between methods is specific to the well rather than to the diffusion-sampler capability is that sulfate concentrations from nylon-screen samplers also did not closely match concentrations from low-flow samples at one horizon in well WHGLTA-039, but approximately matched in all other wells except well WHGLTA-027 (fig. 10). A comparison to lithology at well WHGLTA-039 (fig. 9C) shows that the sulfate concentration from the nylon-screen sample was approximately the same as the concentration from the low-flow sample adjacent to sand horizons and was lower than the concentration in the low-flow sample adjacent to a silty sand (figs. 9B and 9C). Based on permeability considerations, the pumped concentration obtained at a depth of 21 ft is more likely to have been derived from shallower or deeper sand layers than from the adjacent silty sand. Thus, some degree of sample mixing during low-flow sampling is probable in this well and may contribute to the concentration differences between methods.

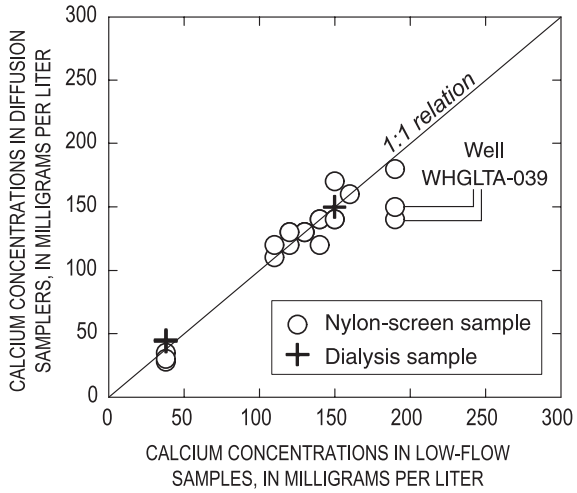


Figure 8. Comparison of ground-water calcium concentrations in nylon-screen samplers and dialysis samplers to concentrations in low-flow samples, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

Sulfate concentrations in most nylon-screen samples and the single dialysis sample showed a close match to concentrations in low-flow samples (fig. 10). The *P* value (0.635) indicated that there was no significant difference in the concentrations obtained from the two sampling methodologies (table 4). Three of the sulfate concentrations, however, were substantially higher in the low-flow samples than in the nylon-screen samples (fig. 10). These outliers were one out of the three samples from well WHGLTA-039 and two out of the three samples from well WHGLTA-027. As previously discussed, the source of the disagreement in concentrations between sampling methods in well WHGLTA-039 is not known, but may be related to sample mixing during pumping.

The sulfate concentrations in the nylon-screen sample, low-flow sample, and an immediate-flow sample closely matched at the shallowest tested horizon (13 ft below land surface) in well WHGLTA-027 (fig. 11), whereas differences between methods were

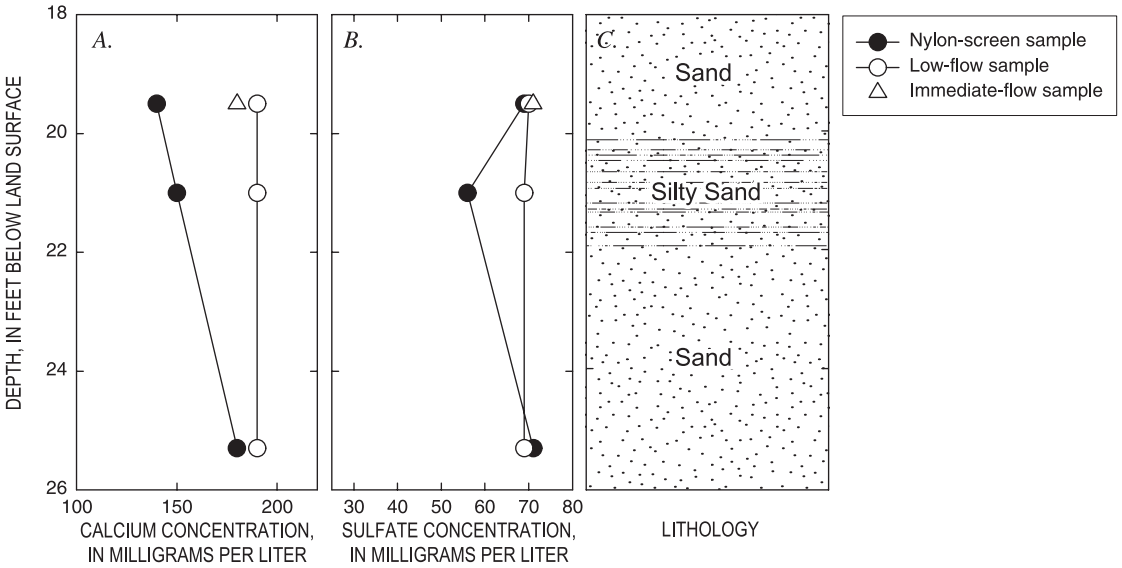


Figure 9. Calcium and sulfate concentrations and lithology in well WHGLTA-039, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

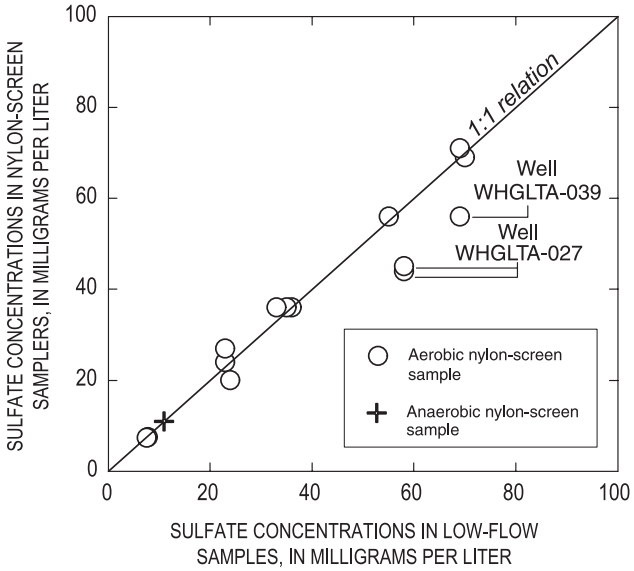


Figure 10. Comparison of ground-water sulfate concentrations obtained from nylon-screen samplers filled with aerobic and anaerobic water to concentrations obtained by low-flow sampling, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

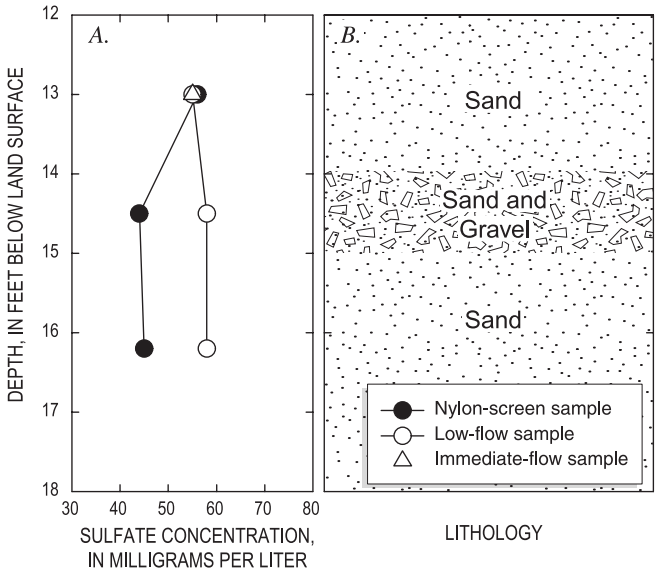


Figure 11. Sulfate concentrations and lithology in well WHGLTA-027, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

observed at other depths. Data from the 13-ft-deep zone suggest that the sulfate concentrations obtained by using a nylon-screen sampler at that depth accurately represents aquifer sulfate concentrations. Therefore, the fact that the sulfate concentrations in the nylon-screen samples at 14.5 ft and 16.2 ft differ by 24 and 22 percent, respectively, from the adjacent low-flow samples suggest that the differences probably are due to factors other than the ability of the sampler to quantify sulfate. The specific nature of these factors is unknown, but the presence of lithologic stratification within the screened interval suggests the possibility of sulfate stratification and of mixing during pumping.

The use of diffusion samplers in wells for sampling solutes that respond quickly to the presence of oxygen, such as iron, can be more challenging than sampling for a conservative tracer, such as chloride. Iron(II) concentrations in nylon-screen samplers filled with anaerobic water showed no significant difference when compared to concentrations obtained by low-flow sampling (*P* value was 0.625; table 4). However, iron(II) concentrations in nylon-screen samplers filled with aerobic water showed a close match to iron(II) concentrations from low-flow sampling in some wells and a very poor match in other wells (fig. 12), resulting in an overall poor statistical comparison for iron(II) (*P* value was 0.009; table 4).

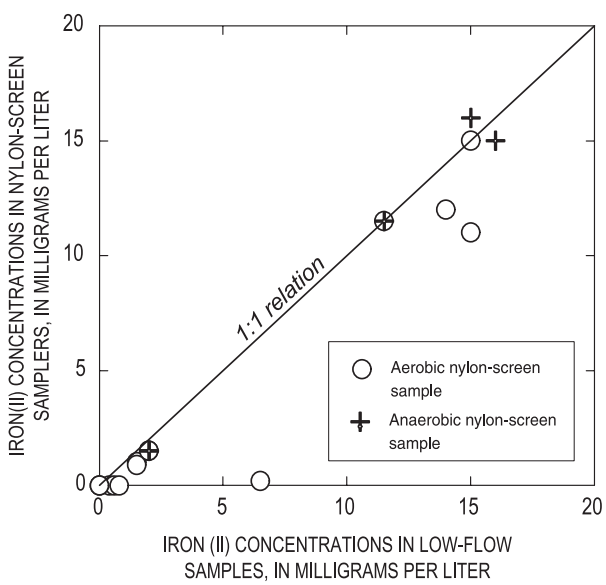


Figure 12. Comparison of ground-water iron(II) concentrations from nylon-screen samplers filled with aerobic and anaerobic water to concentrations obtained by low-flow sampling, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

Part of the explanation for the poor match seen in some wells between iron(II) concentrations in water from aerobic-water-filled nylon-screen samplers and in water from low-flow samples is that iron(II) readily oxidizes and precipitates in the presence of oxygen. Similar effects were observed by Carignan (1984) when deploying dialysis samplers in bed sediment. Thus, dissolved iron was depleted in some of the nylon-screen samplers by interaction with dissolved oxygen. The fact that iron(II) concentrations in a few of the aerobic-water-filled nylon-screen samplers closely matched the iron(II) concentrations in low-flow samples suggests that some of the nylon-screen samplers accurately tracked iron(II) concentrations once the enclosed water became anaerobic.

Potential sources for the differences between iron(II) concentrations in nylon-screen samples and low-flow samples in some of the wells can be seen by examining data from well WHGLTA-031. Water from nylon-screen samplers that had been deployed when filled with aerobic water showed a substantial amount of iron precipitate, whereas the low-flow sample water was clear (fig. 13). This indicates that dissolved iron entered the diffusion sampler in the well and precipitated out of solution after contacting dissolved oxygen.

Data from well WHGLTA-031 further suggests that the water in the well at the time of sampling may have been substantially different than the aquifer water. The iron(II) concentration in an immediate-flow sample (0.5 mg/L) from a depth of 8 ft was more similar to the iron(II) concentration in the adjacent nylon-screen sample (0.15 mg/L) than in the low-flow sample (4 mg/L). This suggests that water in the well was characterized by substantially lower iron(II) concentrations than water that was induced to flow into the well by low-flow sampling. This well is flush mounted, and the surface casings of several flush-mounted wells onsite were observed to contain standing water following rainfall events. A possible scenario, therefore, is that rainfall events immediately prior to the sampling event may have allowed oxygenated water to infiltrate the well, causing iron precipitation in the well. During the week prior to sampling this well, the area received approximately 1.4 in. of rain, with most of it falling on March 8 (0.77 in.) and March 11 (0.57 in.) (Office of the Texas State Climatologist, Texas A&M University, oral commun., 2001). Alternatively, the well water also may become oxygenated if the rate of exchange of water through the well screen is small relative to the rate of oxygenation at the water surface in the well and potential subsequent oxygenated-water convection in the well bore.

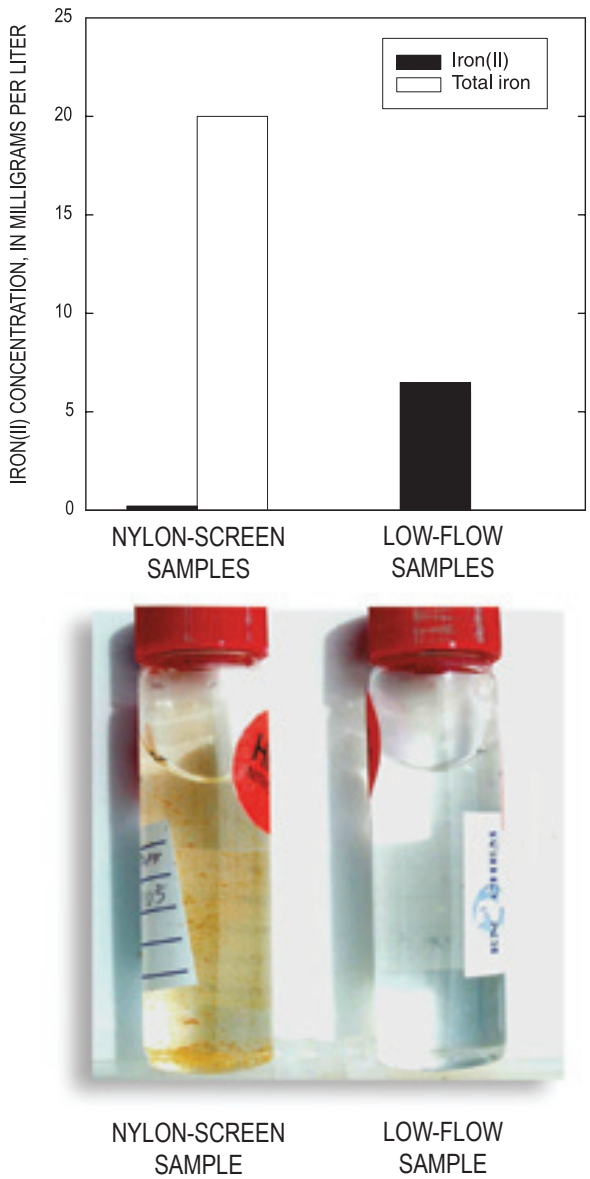


Figure 13. Comparison of ground-water iron(II) to total iron concentrations from a nylon-screen sampler and a low-flow sample at well WHGLTA-031, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

Supporting evidence that the water in well WHGLTA-031 was subjected to an oxidation event is that dissolved-oxygen concentrations in nylon-screen samplers from the well exceeded the corresponding low-flow sample dissolved-oxygen concentrations by a larger amount than was found in any other well. In this case, it appears that the iron(II) concentrations in the ambient well water were not characteristic of the iron(II) concentrations in the aquifer, possibly because of a poor well seal in a flush-mounted casing. The pumped sample, however, also may have inadequately characterized the dissolved-iron concentration because of potential localized rainwater infiltration into the aquifer through the screened zone. These data indicate that diffusion samplers can provide iron concentrations characteristic of the aquifer in many cases, but caution should be exercised when using diffusion samplers, or any sampling methodology, in a flush-mounted well with an inadequate seal.

Oxygenation of dissolved iron also can have a significant effect on the total iron analysis. If iron is allowed to oxidize and precipitate within the diffusion sampler, then the precipitate probably will remain within the diffusion sampler and may contribute to the total iron concentration in water collected from the sampler if the sample is not filtered. When the samples from well WHGLTA-031 were sent to a laboratory for total iron analysis, the nylon-screen sample showed substantially higher iron concentration than the low-flow sample (fig. 13) because the analytical digestion incorporated the precipitated iron.

Manganese is similar to iron in the sense that reduced dissolved forms can rapidly oxidize in the presence of dissolved oxygen; however, dissolved manganese is stable under a broader range of oxygen concentrations than dissolved iron. Like iron, the comparison of manganese concentrations between nylon-screen samples and low-flow or immediate-flow samples closely matched at some tested intervals (for example, well WHGLTA-027) and poorly matched at others (for example, the shallowest horizon at well WHGLTA-039) (table 3). The reason for the variation is not known; however, the close match at some tested horizons suggests that the variation is due to well-specific factors not related to the ability of the nylon-screen samplers to equilibrate to ambient manganese concentrations.

Arsenic concentrations showed a close match between an aerobic nylon-screen sample and a low-flow sample at a depth of 14.5 ft in well WHGLTA-027 (2.5 percent difference) (fig. 14A). Aerobic nylon-screen sample arsenic concentrations slightly underestimated the low-flow and immediate-flow sample arsenic concentrations at a shallower depth (10 percent difference) and slightly overestimated low-flow arsenic concentration at a deeper depth (14 percent difference). The close match at the 14.5-ft depth suggests that the nylon-screen sampler adequately equilibrated with ambient water and provided an arsenic concentration representative of aquifer conditions. Therefore, the

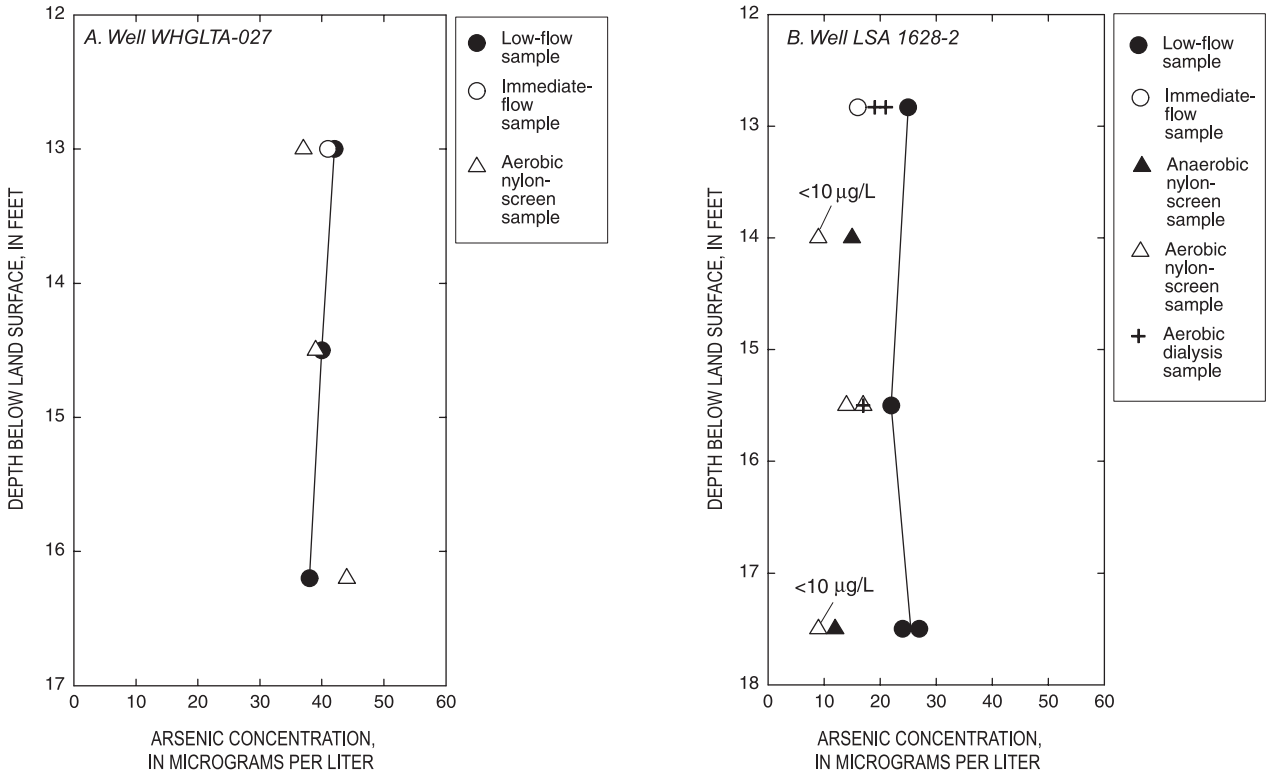


Figure 14. Arsenic concentrations in nylon-screen samples, dialysis samples, and low-flow samples in wells WHGLTA-027 and LSA 1628-2, Naval Air Station Fort Worth Joint Reserve Base, Texas, March 2001.

relatively slight differences in concentrations at shallower and deeper depths probably do not reflect diffusion-sampler inadequacy. These data suggest that the nylon-screen diffusion samplers are capable of providing arsenic concentrations characteristic of aquifer concentrations in this well.

At well LSA 1628-2, all of the diffusion samplers underestimated the arsenic concentrations detected in the low-flow samples (fig. 14B) with differences ranging from 22 percent to greater than 63 percent. This included dialysis samplers filled with aerobic water and nylon-screen samplers filled with aerobic and anaerobic water. Moreover, an immediate-flow sample showed an arsenic concentration similar to the concentrations detected by the diffusion samplers. These data suggest that the arsenic concentrations in the diffusion samplers accurately represented the arsenic concentrations in the well, but did not accurately represent the arsenic concentrations in the aquifer because the ambient well water differed from the aquifer water. A possible scenario to explain the difference between well water and aquifer water is that this flush-mounted well was subjected to an oxidation event by rainwater leaking through the well seal, as postulated above for well WHGLTA-031. Supporting evidence for an oxidation event is that the dissolved iron(II) sampled by all of the diffusion samplers in well LSA 1628-2 was lower than the iron(II) in the corresponding low-flow sample.

These data indicate that nylon-screen samples and dialysis samples can provide concentrations of inorganic solutes representative of ambient water. However, the concentrations of oxygen-sensitive inorganic solutes in a well may underestimate concentrations in aquifer water in wells subject to rainwater infiltration, possibly through poorly sealed flush-mounted well caps. If iron(II) is allowed to oxidize and precipitate in the diffusion samplers, then unfiltered water from the diffusion sampler can contain iron precipitate that can be incorporated into the total iron analysis during digestion, resulting in total iron concentrations that exceed the concentrations found in ambient water. Filtering the water from the diffusion sampler can allow collection of only dissolved-phase iron, but oxygenation of the well bore sometimes can result in dissolved-phase iron concentrations from diffusion samplers that underestimate iron concentrations in the formation.

Field Test of Diffusion Samplers for Inorganic Constituents at a Ground-Water-Discharge Zone

Arsenic contamination is present in ground water at NAS Fort Worth JRB near an unnamed tributary to the West Fork Trinity River (fig. 5). In 1999, measured arsenic concentrations in the plume ranged from about 75 micrograms per liter (µg/L) in an upgradient area to about 4 µg/L near the tributary (Lynn Morgan, Hydrogeologic, Inc., written commun., 1999). The source of the arsenic is thought to be mobilization from naturally occurring minerals as a result of reducing conditions produced by petroleum hydrocarbon degradation (Lynn Morgan, Hydrogeologic, Inc., written commun., 1999). The orientation of the plume strongly suggests that the arsenic contamination is moving toward or discharging to the unnamed tributary. Nylon-screen samplers were buried beneath creekbed sediment along the unnamed tributary as a test to determine whether the samplers could be used to locate a discharging arsenic plume (fig. 5).

The first set of samples, recovered after 3 days of equilibration, showed low (less than 20 µg/L) or undetectable (less than 10 µg/L) arsenic concentrations between 0 and 93 ft and between 200 and 400 ft along the traverse. However, high arsenic concentrations (greater than 50 µg/L) were found in the 107-ft reach between 93 and 200 ft along the traverse, coinciding with the projected discharge point of the ground-water arsenic plume (table 5, figs. 5 and 15). Thus, it is clear that even leaving the nylon-screen samplers in place for only 3 days was sufficient to locate the discharge zone of arsenic-contaminated ground water. Allowing the diffusion samplers to remain in place for 28 days produced a similar relative distribution of arsenic, but the longer equilibration time produced higher concentrations at many of the sampling locations (table 5, figs. 5 and 15).

The highest detected concentration in the nylon-screen samplers was 240 µg/L at the center of the projected discharge zone of the ground-water arsenic plume. This is a higher concentration than has been previously observed in the plume. It is possible that the screened intervals of the existing monitoring wells do not intersect the most concentrated part of the arsenic plume; however, additional possibilities are that the large mesh size of the nylon screen (125 µ) allowed entry of fine-grained sediment with arsenic precipitate or that an oxidation event in the shallow bed sediment allowed the samplers to accumulate precipitated iron and arsenic, resulting in a total arsenic analysis that overestimated the dissolved phase. The quantitation issue can be resolved in future investigations by filtering the water or using a smaller mesh size for the membrane. This, however, does not affect identification of the arsenic-discharge zone. Thus, the nylon-screen samplers provide a rapid and simple means of locating an arsenic-discharge zone beneath surface water. By analogy, the approach probably is useful for a wide variety of inorganic contaminants.

Table 5. Arsenic concentrations in water from nylon-screen samples buried in creekbed sediments of an unnamed tributary to the West Fork Trinity River, Naval Air Station Fort Worth Joint Reserve Base, Texas, after 3 and 28 days of equilibration, July-August 2000

[<, less than]

Sample number	Distance along transect (feet)	Arsenic in nylon-screen samplers (micrograms per liter)	
		3 days equilibration	28 days equilibration
1	1	<10	<10
2	70	<10	50
3	93	12	<10
4	120	51	51
5	145	62	130
6	170	71	240
7	200	10	40
8	260	<10	31
9	400	16	82

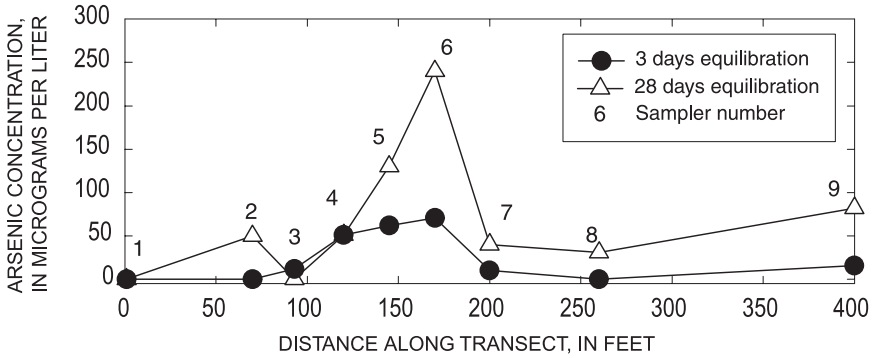


Figure 15. Arsenic concentrations in water from nylon-screen samplers buried in the bottom sediment of an unnamed tributary to the West Fork Trinity River, Naval Air Station Fort Worth Joint Reserve Base, Texas, July-August 2000.

SUMMARY

The U.S. Geological Survey, in cooperation with the Air Force Center for Environmental Excellence and the Southern Division Naval Facilities Engineering Command investigated the use of diffusion samplers to collect representative samples of inorganic constituents from ground water in wells and at a ground-water/surface-water interface. The investigations were conducted at Naval Industrial Reserve Ordnance Plant (NIROP), Fridley, Minnesota, and at Naval Air Station Fort Worth Joint Reserve Base (NAS Fort Worth JRB), Texas.

Two types of samplers were tested. One type was a nylon-screen sampler, which consisted of a 25-mL jar filled with deionized water and with the opening covered by a nylon screen. The second type was a dialysis sampler that consisted of a tube of dialysis membrane filled with deionized water. The nylon-screen samplers were deployed in wells at NIROP Fridley and NAS Fort Worth JRB and beneath the ground-water/surface-water interface of a stream at NAS Fort Worth JRB. The dialysis samplers were deployed only in wells at NAS Fort Worth JRB.

Data indicate that nylon-screen and dialysis diffusion samplers are capable of obtaining concentrations of inorganic solutes in ground water from wells that closely correspond to concentrations obtained by low-flow sampling. Particular care must be taken when sampling for iron and other metals, because of the potential for iron precipitation by oxygenation, and when dealing with chemically stratified sampling intervals. Simple nylon-screen jar samplers buried beneath creekbed sediment appear to be effective tools for locating discharge zones of arsenic-contaminated ground water.

The dissolved-oxygen concentrations in four nylon-screen samplers from NIROP Fridley were as low or lower than the concentrations obtained from low-flow sampling, suggesting that the nylon-screen samples provided results comparable to the low-flow samples. Concentrations obtained from the nylon-screen samplers at NAS Fort Worth JRB were within 0.6 mg/L of the results obtained from low-flow sampling, and the Wilcoxon signed rank test P statistic (0.151) indicated no significant difference between the results from the two methodologies.

Comparison of nylon-screen diffusion-sampler chloride concentrations in ground water from NIROP Fridley and NAS Fort Worth JRB showed a close match to concentrations obtained by low-flow sampling (P value of 0.202 at NAS Fort Worth JRB). Four dialysis samplers also were tested and each showed a close match (2 to 3 mg/L difference) to concentrations obtained by low-flow sampling. These data suggest that both types of diffusion samplers are capable of providing representative ground-water concentrations of chloride. Because chloride is not subject to redox reactions, diffusion samplers for chloride concentrations can be filled with aerobic water.

Calcium concentrations in nylon-screen samplers showed a close match to concentrations in low-flow samples from most wells at NAS Fort Worth JRB. However, in well WHGLTA-039, the nylon-screen calcium concentrations in the two shallowest samplers differed from low-flow concentrations by 21 to 26 percent. The close match of calcium concentrations in other wells and in the shallower samplers at well WHGLTA-039 indicate that the disagreements probably are attributable to factors not related to sampler efficiency.

Sulfate concentrations also showed a relatively close match between methods at most wells but showed some differences between methods at well WHGLTA-039. Sulfate differences at this well may be related to lithologic control, with the nylon-screen samplers accurately reflecting the vertical distribution of chemical stratification, and the pumped sample representing mixing. A similar effect in well WHGLTA-027 may produce some of the differences in sulfate concentrations between the nylon-screen samples and the low-flow samples.

Iron(II) concentrations in nylon-screen samplers filled with aerobic water showed a close match to iron(II) concentrations from low-flow sampling in some wells and a very poor match in other wells, resulting in an overall poor statistical comparison for iron(II). Part of the explanation for the poor match is that the dissolved iron was depleted in some of the nylon-screen samplers by interaction with dissolved oxygen. Data suggest that several of the nylon-screen samplers accurately tracked iron(II) concentrations once the enclosed water became anaerobic. In some cases, however, iron precipitate in the samplers contributed to the total iron measurement, thereby overestimating the total iron concentration while underestimating the iron(II) concentration. In addition, it is probable that rainfall events immediately prior to the sampling event allowed oxygenated water to infiltrate some of the flush-mounted well casings, depleting

the dissolved iron in the well. Similar factors may account for the close match in manganese concentrations between nylon-screen samples and low-flow samples in some wells and the poor match in others.

Arsenic concentrations showed a close match between an aerobic nylon-screen sample and a low-flow sample at a depth of 14.5 ft in well WHGLTA-027 (2.5 percent difference) with slight variations at shallower and deeper depths. Data suggest that the nylon-screen diffusion samplers are capable of providing arsenic concentrations characteristic of aquifer concentrations in this well. At well LSA 1628-2, however, all of the diffusion samplers underestimated the arsenic concentrations detected in the low-flow samples with differences ranging from 22 percent to greater than 63 percent, but approximately matched an immediate-flow sample. These data suggest that the arsenic concentrations in the diffusion samplers accurately represented the arsenic concentrations in the well, but did not accurately represent the arsenic concentrations in the aquifer, because the ambient well water differed from the aquifer water, possibly as a result of rainwater infiltration into the flush-mounted well casing.

These data indicate that nylon-screen samples and dialysis samples can provide concentrations of inorganic solutes representative of ambient water. However, the concentrations of oxygen-sensitive inorganic solutes in a well may underestimate concentrations in aquifer water in wells subject to rainwater infiltration. If iron(II) is allowed to oxidize and precipitate in the diffusion samplers, then unfiltered water from the diffusion sampler can contain iron precipitate that can be incorporated into the total iron analysis during digestion, resulting in an overestimate in total iron concentrations and sometimes an underestimate of the iron(II) concentration.

Nylon-screen samplers buried beneath creekbed sediment along the unnamed tributary in a probable discharge zone of arsenic-contaminated ground water were useful in locating the specific discharge zone. After equilibration of only 3 days, the nylon-screen samplers in a 107-ft reach of the creek showed significantly higher arsenic concentrations than the upstream or downstream samplers. Allowing additional diffusion samplers to remain in place for 28 days produced a similar relative distribution of arsenic, but the longer equilibration time produced higher concentrations at many of the sampling locations. The zone of high arsenic concentrations in the nylon-screen samples was directly downgradient from the arsenic contamination observed in nearby ground water. Thus, the nylon-mesh samplers provide a rapid and simple means of locating an arsenic-discharge zone beneath surface water. By analogy, the approach probably is useful for a wide variety of inorganic contaminants.

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