



**US Army Corps
of Engineers**

Cold Regions Research &
Engineering Laboratory

ADA 275507

The Effects of Groundwater Samplers on Water Quality

A Literature Review

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October 1993

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Abstract

This report reviews both field and laboratory studies that test or compare the ability of various types of samplers to deliver representative groundwater samples. Several types of grab samplers, positive displacement devices, and suction-lift devices are evaluated. It was found that most of these devices can, under certain circumstances, alter the chemistry of a groundwater sample. Gas-lift pumps, older types of submersible centrifugal pumps, and suction-lift devices are not recommended when sampling for sensitive constituents such as volatile organics and inorganics and inorganics that are subject to oxidation/precipitation reactions. Generally, of the devices reviewed in this report, bladder pumps gave the best recovery of these sensitive constituents. However, better performance could be achieved for several devices if better operational guidelines were developed by additional testing. Clearly, further research is warranted. Issues that need to be addressed in future studies include pumping rate, use of flow control mechanisms, and dedication of samplers.

Cover: Emptying a sample from a bailer (without a bottom-emptying device) causes aeration of the sample. In addition to those mentioned in this report, other problems have been encountered when sampling in the cold. (Photo by Louise V. Parker.)

For conversion of SI metric units to U.S./British customary units of measurement consult *Standard Practice for Use of the International System of Units (SI)*, ASTM Standard E380-89a, published by the American Society for Testing and Materials, 1916 Race Street, Philadelphia, Pennsylvania 19103.

PREFACE

This report was prepared by Louise V. Parker, Research Physical Scientist, Applied Research Branch, Experimental Engineering Division. Funding for this work was provided by the U.S. Army Environmental Center (formerly USATHAMA), Aberdeen Proving Ground, Maryland, Martin H. Stutz, Project Monitor.

The author thanks Dr. Jacob Gibbs and Thomas Imbrigiotta, New Jersey District, Water Resources Division, U.S. Geological Survey; John Sanda, Geotechnical and Civil Engineering Branch, Office of the Chief of Engineering, U.S. Army Corps of Engineers; and Jack Keeton, Geotechnical Branch of the Geotechnical and Technical Engineering Division, U.S. Army Engineer Division, Missouri River, for their technical reviews.

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INTRODUCTION

Improvements in analytical methods have resulted in extending detection limits for most contaminants in water samples to ppb-levels and lower. As detection limits drop, proper sample collection becomes increasingly more important. In reviewing the literature regarding the possible effects that materials used in samplers could have on the integrity of groundwater samples, it became increasingly evident that how a sample is taken or the type of sampling device can have a large impact on sample integrity. In fact, Houghton and Berger (1984) found that the effects of samplers on groundwater quality were greater than any material effects caused by well casings (PVC, steel, and acrylonitrile-butadiene-styrene). According to Barcelona et al. (1985), sampling mechanisms for collecting groundwater samples are among the most error-prone elements of monitoring programs.

In 1985, Nielsen and Yeates categorized the types of samplers that were available and summarized some of the advantages and disadvantages associated with each type of sampler. This material was updated and revised by Herzog et al. in 1991. These reviews address some of the following important considerations (as outlined by Nacht 1983): borehole and sampler diameter, sampling depth, ease of cleaning, initial and operational cost, maintenance requirements, power supply, portability, ease of use, sampler volume, durability, and ability to purge the well. There is also limited discussion on the suitability of the various types of samplers for monitoring different types of contaminants. In 1988, Pohlmann and Hess outlined the suitability of the various types of samplers for monitoring various

groundwater constituents. However, they did not document or give any justification for their recommendations. Thus, the purpose of this literature review is to focus specifically on the ability of the principal types of sampling devices to obtain a representative sample. Devices that are still being developed and are not yet commercially available were not included in this review.

Nielsen and Yeates (1985) categorized the principal types of sampling devices as either grab, positive displacement, or suction-lift. Since then, a new type of pump, the inertial-lift pump (Waterra), has also become commercially available. With grab samplers, some type of container is lowered into the water column, allowed to fill, and then withdrawn from the well. Common types of grab samplers include open and point source bailers, Kemmerer samplers, and syringe samplers. Positive displacement devices use positive pressure to drive water from the well to the surface. Some of the more common types of positive displacement devices include submersible piston pumps, gas-lift pumps, gas-driven bladder pumps, gas-driven submersible piston pumps, and electric submersible pumps (gear-drive, helical rotor, and submersible centrifugal) (Pohlmann and Hess 1988, Gillham et al. 1983, Nielsen and Yeates 1985). Suction-lift sampling devices operate by applying negative pressure, or vacuum, at the surface. Some of the more commonly used suction-lift devices include a hand-vacuum pump connected to a vacuum flask, or a piston, centrifugal, or peristaltic pump (Gillham et al. 1983). The inertial-lift pump consists of a plastic tube with a one-way foot valve at the bottom. Water is brought to the surface by momentum that is created by rapidly moving the tube up and down in the well.

Changes in temperature and pressure of a sample can have a tremendous effect on the chemistry of the water. Specifically, temperature can affect the solubility and volatility of constituents in groundwater. The temperature of a sample may change because the ambient air is warmer (or colder) than the groundwater temperature. Samples may also be heated as a result of warmer air being entrained in the sample, as a result of heat generated by a pump, or if the sample passes through tubing that has been heated by solar radiation. Degassing can result either from an increase in temperature or a decrease in pressure. Groundwater samples taken from deeper wells will be under considerable pressure and normally will undergo degassing when brought to the surface.

Also, if air or other gases are introduced into the well, either directly by pumping air or other gases into the well, or inadvertently by agitation, they can cause volatilization, oxidation, precipitation, adsorption, and ion exchange reactions to occur. Among the chemical parameters altered as a result of aeration and degassing are pH, Eh, dissolved oxygen, inorganic carbon, alkalinity, Total Organic Compounds (TOC), Volatile Organic Carbon (VOC) (total VOCs and specific volatiles), ammonium, nitrate/nitrite, sulfide, cyanide, molybdenum, mercury, selenium, dissolved iron, dissolved manganese, dissolved cadmium, dissolved lead, dissolved vanadium, dissolved arsenic, and dissolved phosphate (Stolzenburg and Nichols 1985).

Sampling devices for groundwater monitoring can be used in a number of wells or dedicated to a particular well. Dedication of a sampler to a particular well reduces the potential of cross-contamination from other wells but does not eliminate the potential of contamination resulting from desorption of sorbed contaminants should the concentration of the contaminants in the aquifer improve. However, an even more important consideration is the long-term interaction that will occur between the well water and any dedicated device that is left in the well. These devices must be able to withstand the effects of the environment. This is especially important for pump parts that are made of metals that are subject to corrosion.

Although the initial focus of this literature review was to look for papers that documented the effects materials used in samplers had on sample integrity, only a few reports that documented sorption and leaching of organics by the flexible

tubings used in samplers were found (Junk et al. 1974, Christensen et al. 1976, Fayz et al. 1977, Boettner et al. 1981, Curran and Tomson 1983, Ho 1983, Barcelona et al. 1985, Reynolds and Gillham 1985, Devlin 1987, Pearsall and Eckhardt 1987, and Gillham and O'Hannesin 1990). These effects will be discussed in more detail later.

This report will review both laboratory and field studies. Laboratory studies assess the ability of a sampling device to obtain a representative sample by comparing the sample concentrations of the contaminants with known concentrations. However, these studies usually do not closely simulate the more rigorous conditions often found in the field. Field studies allow one to compare the performance of various types of samplers under real conditions (such as in a deep well) where changes due to cavitation, degassing, and/or change in redox potential can have a dramatic effect on analyte concentrations. The disadvantage with these types of studies is that the actual concentrations of analytes in situ are not known. Thus, the sampler that yields the highest concentrations is usually chosen as the "control" with which the others are compared, unless there is some reason not to do so, e.g., the leaching of constituent metals from a stainless steel sampler. However, it is possible that none of the devices tested were efficient in recovering a particular contaminant(s).

Many of these studies appear to contradict each other, even though they appear to be similar. This is because there can be many subtle or even unknown differences between apparently similar studies. Often, little specific information is given on the sampler model, manufacturer, or materials used in manufacturing the sampler. Site conditions such as sampling depth, lift height, solution chemistry (including the presence of high levels of dissolved solids or gases), and pumping flow rate may vary. Any of these differences can significantly affect a sampler's performance.

GRAB SAMPLERS

Bailers

There are several types of bailers: conventional open (either top- or bottom-loading), and dual check valve (point source). These devices are among the simplest to clean and operate. However, aeration can occur either when a bailer is lowered into the water column or when the

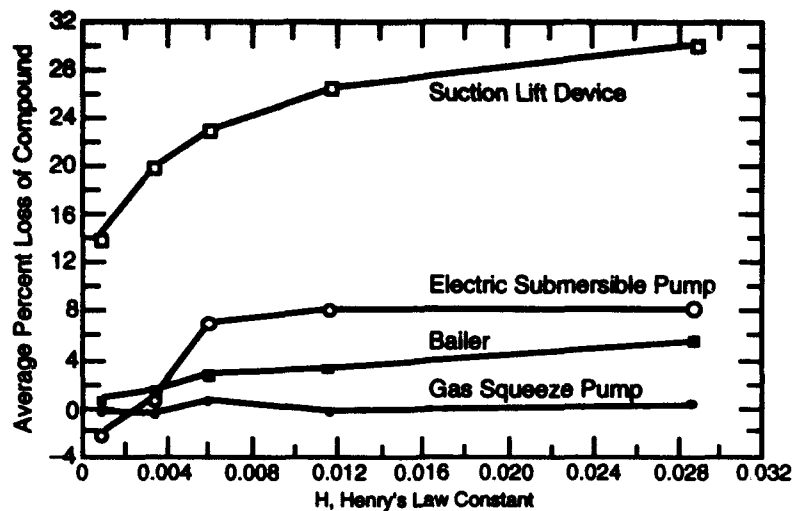


Figure 1. Comparison of the effect of sampler type on loss of volatile organics (Unwin and Maltby 1988).
[Sampling depth = 7 m (23 ft)]

sample is transferred into its storage container. Also, samples taken from deeper wells will be subject to reduction in pressure as the bailer is brought to the surface. Because grab samplers can cause a surging action as they descend the well, they may also increase turbidity of samples or cause mixing with any stagnant water in the well. Use of point source bailers can eliminate problems with mixing of the sample with the water column as the sample is removed. One other problem associated with bailers is that the check valves may not operate properly under some conditions, such as when there are high levels of suspended solids or freezing temperatures (Herzog et al. 1991).

Open bailers

Most of the laboratory studies have shown that the recoveries of most analytes with an open bailer are reasonably good. Barcelona et al. (1984) found that the accuracy and precision of VOCs taken with an open bailer were not significantly different from those of the controls. However, they noted that, since their samples were taken directly from the reservoir, these samples were not subjected to the same disturbance that would be involved in retrieving a bailer from the depths of a well. Thus, they anticipated that losses would be greater in the field. They did find that concentrations of methane and oxygen were significantly lower in samples taken with this type of sampler than they were in control samples.

For samples taken with a conventional, bottom-loading (Teflon) bailer, Unwin and Malt-

by (1988) found that loss increased as the Henry's constant increased (Fig. 1). However, loss was slight (5%) even for the most volatile organic they tested (tetrachloroethylene). Gossett and Hegg (1987) found that recovery of VOCs was less than the controls in samples taken with an open bailer and that recovery decreased dramatically when they raised the lift height from 2.0 to 6.0 meters. Recovery of three VOCs ranged from 94.2% to 97.3% at 2.0 m and from 90.5% to 92.2% at 6.0 m. Presumably, loss of VOCs would be even greater with larger lift heights. For inorganics, it appears that transfer from the bailer can dramatically affect results. Stolzenburg and Nichols (1985) found iron levels taken with an open bailer using in-line filtration were equivalent to control values. However, they also found that when samples were recovered in a more traditional manner (i.e., in-line filtration was not used), lead precipitated as a result of aeration during transfer from the bailer. They maintained that this could be minimized by modifying the bailer slightly.*

In a field study, Imbrigiotta et al. (1988) found that recovery of VOCs in samples taken with an open bailer was not statistically signifi-

*Modifications include either: 1) attaching a fitting to the top of the bailer, attaching tubing to this fitting, and then inverting the bailer gently while directing the tubing to the bottom of the receiving vessel, or 2) attaching the tube directly to a filter, thus avoiding any air contact.

cantly different from the recoveries they found with other types of samplers. However, these samples were taken from relatively shallow wells. When Pearsall and Eckhardt (1987) compared samples taken with a conventional (Teflon) bailer with those taken using a helical rotor pump, they observed small (~7%) losses of DCE and TCE in the samples taken with the bailer at one site (with lower concentrations: 23–29 ppb) but not at another site (76–96 ppb). They thought there might be an effect with concentration. The remaining field studies indicated that several other types of samplers were better at recovering sensitive parameters, such as VOCs.

Houghton and Berger (1984) found evidence of slight degassing, which was accompanied by losses in metals, some of which were fairly substantial (12% loss of iron, 20% loss of mercury) when compared with samples taken with other types of samplers. Their wells ranged in depth from < 100 ft to > 250 ft, and they felt that depressurization was responsible for loss of volatile constituents. Yeskis et al. (1988) found that recovery was poorest and the variability was largest for VOCs taken with an open bailer and a bailer with a bottom-emptying device when compared with samples taken with four different pumps (bladder, air-activated piston pump, and two electric submersible pumps: a helical rotor pump and a submersible centrifugal pump). At five of the six sites they tested, they found that the recovery of TCE and trans-1,2-dichloroethylene in samples taken with the bailers ranged from approximately 25% to 88% of that obtained with a submersible centrifugal (impeller) pump. They did not observe noticeable improvement in the recovery of VOCs by using a bottom-emptying device with an open bailer.

Point source bailers

Several laboratory studies have found recoveries of VOCs using point source bailers to be quite good. While the laboratory study of Barcelona et al. (1984) did not show a significantly reduced recovery of volatile organics using a point source bailer, they did find the precision for recovery of oxygen and methane was poorer by a factor of two to four times that observed for the controls. Tai et al. (1991) tested the ability of a point source bailer (with a bottom-emptying device and Teflon-coated cord) to recover five volatile organics in a laboratory study that used a 100-ft standpipe. They found that, when compared to controls, recovery of the VOCs ranged

from 90.6% to 94.9% for samples taken at 92 ft (28 m) with this type of bailer. In comparison, recovery and precision were better when two USGS prototype samplers (a manual-driven piston sampler and a motor-driven piston sampler) were used.

The recovery of the VOCs was also better in samples that had been pumped using either a helical rotor, peristaltic, or bladder pump. They felt that bubbles introduced into the bailer during insertion of the bottom-emptying device may have caused degassing of the volatiles. However, they also cited operator technique as a contributing factor. Baerg et al. (1992) found that both a stainless steel and Teflon bailer were able to recover more than 95% of five VOCs. Recovery was statistically significantly better with the Teflon bailer than with the stainless steel one, although these differences were only slight.

Several field studies have evaluated performance of point source bailers. While several of these studies found recovery of VOCs to be poorer with this type of bailer, losses of VOCs were generally less than 10%. Muska et al. (1986) found that recovery of TCE was highly variable with a point source bailer. Imbriotta et al. (1988) also found that samples taken with open and point source bailers had the poorest precision of all the samplers they tested, although the difference was only about 5%. They also found that recovery of VOCs with this type of bailer can be excellent in relatively shallow wells when compared with other types of samplers.

However, in a more recent study, Gibs et al. (in prep.) found that recovery of VOCs was statistically significantly poorer for samples taken with a point source bailer when compared with samples taken with a helical rotor pump or a USGS downhole isobaric sampler. The mean overall recovery of VOCs with the point source bailer was 9 to 11% less than that achieved with the other two samplers. They felt that the reason they were able to find a significant difference in the recovery of VOCs with a point source bailer in this study [but not in their previous study (Imbriotta et al. 1988)] was because improved analytical methods resulted in lower variances and thus improved sensitivity.

Gibs et al. (in prep.) also found that recovery of VOCs could be increased by approximately 8% by using a bottom-emptying device, and that precision was also better.

Barcelona et al. (1984) concluded that the performance of bailers was heavily dependent upon

the expertise of sampling personnel and field conditions. Yeskis et al. (1988) also noted that variability occurred not only between operators, but with the same operator.

In addition to concern about the effects of aeration and possible depressurization on removal efficiency with bailers, there has also been concern expressed that the lines used with bailers can be a source of cross contamination if the bailer is not dedicated to the well. While there was not much specific documentation of this, Canova and Muthig (1991) found that a constituent of nylon cord (caprolactam) leached and contaminated many of their samples.

Thus, it appears that bailers (all types) are best suited for sampling semi- to nonvolatile constituents and constituents that are not readily oxidized and thus subject to precipitation reactions. Bailers may be used for sampling volatile or sensitive constituents only if the sample is obtained very carefully and transferred to a sample container using a bottom-emptying device. As mentioned previously, using a point source bailer can eliminate mixing of the sample with the water column as the sample is removed.

Syringe samplers

These devices can be used in relatively small diameter wells, allow sampling at discrete depths, can be used at any depth, and can be used in wells with very slow recharge (Gillham 1982). Samples taken with syringe samplers do not come in contact with any atmospheric gases and are subject to only a slight negative pressure, and thus should not cause aeration or degassing (Herzog et al. 1991). However, recovery of volatile organics and dissolved gases was not as good as might be expected in the three studies that evaluated these devices (Barcelona et al. 1984, Muska et al. 1986, and Imbrigiotta et al. 1988).

Barcelona et al. (1984) found significantly lower recovery of dissolved oxygen and methane in samples taken with a syringe sampler. They also found that samples taken with this device had the poorest precision of any tested.

Muska et al. (1986) found that other samplers they tested yielded higher concentrations of trichloroethylene with better precision than syringe samplers.

Imbrigiotta et al. (1988) also found that syringe samplers yielded some of the poorest recoveries of volatile organics among the devices they tested. However, they attributed these losses

to wear by particulate matter that resulted in failure of the Teflon piston seal, which was due to reusing the samplers. Recent guidelines recommend that these devices should not be reused when samples have high levels of suspended solids contents (Herzog et al. 1991). Gillham (1982) found it necessary to modify these devices so that the intake was pointed upwards to avoid problems caused by the entrapment of air.

Kemmerer samplers

Bryden et al. (1986) felt that Kemmerer samplers are simple to operate, very dependable, and allow sampling at a predetermined point in the water column. While they did not recommend using these samplers for sampling organics because of the rubber end caps, only one study (Houghton and Berger 1984) actually evaluated their performance. Houghton and Berger (1984) found their performance in the field with respect to eleven major constituents, three nutrients, and sixteen trace metal constituents was as good as any of the devices they tested. However, they did note a slight (6%) enrichment in the total and dissolved organic carbon in acidic waters, which they attributed to leaching from the neoprene end caps.

Because several studies (Ho 1983, Barcelona et al. 1985, Reynolds and Gillham 1985, and Pearsall and Eckhardt 1987) have shown that various (silicone and latex) rubber tubings are highly sorptive of organics, and other studies (Junk et al. 1974, Barcelona et al. 1985) have shown that leaching of constituents from various rubbers also is a concern, this would indicate that concern regarding their use for sampling organics is valid. Also, because these samplers remain open while descending the water column, interaction can occur between the sampler materials and any contaminated zones the sampler passes through. Thus, it appears that further testing of this device would indicate that these devices are not ideal for sampling groundwater.

SUCTION-LIFT DEVICES

Because all suction-lift pumps apply a vacuum to the groundwater samples, these devices can cause depressurization and degassing of the samples and thus may not be suitable for volatiles and gas-sensitive constituents. These devices are practical only for wells where the water table is less than 20 to 25 ft from the surface (Scalf

et al. 1981, Nielsen and Yeates 1985). Unwin and Maltby (1988) found that losses of volatile organics increased with Henry's constants with these devices (Fig. 1).

Centrifugal pumps

According to Nielsen and Yeates (1985), some additional problems associated with these pumps are that the pump has to be primed and thus introduces a potential for sample contamination; the sample comes in direct contact with the pump body and impeller and these materials are not generally made of inert, non-contaminating materials; and the gasoline used to drive the motor or its combustion products may be a source of contamination. Pearsall and Eckhardt (1987) found that there was greater variation in the VOCs of samples that were taken using a centrifugal pump than in samples taken using a peristaltic pump, a helical rotor pump, and a bailer. Recovery ranged from 90 to 100% when compared with a helical rotor pump. Stolzenburg and Nichols (1985) evaluated the performance of a (surface) centrifugal pump for recovering metals and found very poor recoveries of iron with this type of pump.

Peristaltic pumps

Several studies have shown that there can be serious problems when a peristaltic pump is used. These include significant changes in the solution chemistry due to degassing and loss of oxidizable and volatile inorganic constituents and volatile organic constituents. In a laboratory study, Barcelona et al. (1984) found that losses of trihalomethanes ranged from 4.1 to 16.1% when compared with controls. In their field study, Houghton and Berger (1984) observed a slight increase in pH and decrease in alkalinity (4%), a loss of dissolved solids, and found that DO was 18% lower than with a bladder pump. Other analytes that were affected included a 7 to 17% loss of boron, barium, and strontium, and lower levels of ammonium, mercury, molybdenum, and selenium. They felt the degassing was due to the partial vacuum exerted by the pump for lift, and concluded that these pumps should not be used for volatiles and other constituents subject to degassing.

Several other field studies [Devlin 1987, Imbrigiotta et al. 1988, and Barker and Dickout 1988 (in gas-charged groundwater)] found significantly lower concentrations of VOCs in samples tak-

en with peristaltic pumps compared with samples taken with other types of samplers. Devlin (1987) found concentrations of VOCs were 4 to 70% lower when taken with a peristaltic pump than those taken with a bladder pump. Barker and Dickout (1988) conducted a follow-up laboratory study using gas-charged groundwater and found that recovery of volatiles ranged from 63 to 94% of that found with control samples. They observed that degassing of these types of waters was clearly a problem with this type of pump.

While most pumps can use more rigid and presumably more inert material for the tubing used to transport the sample to the surface, peristaltic pumps must use a flexible (e.g., silicone rubber or PVC) tubing in the head. Often this same type of tubing is used throughout the system. Two studies (Ho 1983, Pearsall and Eckhardt 1987) found that the type of tubing used in these pumps had a significant effect on the recovery of volatile organics, even in shallow wells. They found VOCs were significantly reduced by silicone rubber tubing and that these losses could be reduced or eliminated by using more rigid PTFE lines.

Recovery of TCE was 8 to 14% lower and recovery of 1,2 DCE was 8 to 12% when all silicone rubber tubing was used, as compared with recoveries using PTFE tubing with silicone rubber tubing in the pump head. Ho (1983) looked at four variables: transport line material (silicone rubber vs. PTFE), pumping rate (2.6 vs. 4.0 L/min), sample lift [0.9, 2.4, 4.8 m (3, 8, 16 ft)], and concentration of organics (2 to 18 ppb vs. 11 to 91 ppb). Statistical analyses indicated that transport line was the most important variable with this type of pump. He found that a low pumping rate yielded higher recoveries and recommended that this device should not be used for lift heights > 4.8 m (16 ft). He also found that pumping rate, concentration level, and lift height all affected recovery of volatiles with Henry's constants > 10^{-2} atm m³/mL. Losses were 15 to 20% for the three most volatile compounds at highest lift height [4.8 m (16 ft)].

While Stolzenberg and Nichols (1985) found that in-line filtered iron concentrations taken with this pump exceeded control values (due to the breakup of suspended colloidal iron), they concluded that these devices can yield iron levels equivalent to control values if they are operated gently and equipped with a variable flow con-

troller. Puls and Powell (1992) were able to get stable arsenic levels with this type of pump using low flow rate purging and sampling.

One recent laboratory study (Tai et al. 1991) found good recoveries of VOCs using a peristaltic pump (with Teflon tubing) under low lift conditions. [The standpipe was full of water and the lift was only 5 ft (1.5 m)]. At 92 ft (28 m), recoveries of five chlorinated VOCs ranged from 98.9% to 100.6%, and the relative standard deviations ranged from 0.07 to 0.74%. The reason recoveries were so good may be because of the low lift conditions and because they used a less sorptive tubing material (Teflon), except in the pump head. (They did not give the flow rate used with this sampler.)

Based on the previous studies, this type of pump should not be used for monitoring volatile constituents and constituents subject to oxidation and precipitation reactions, at least until further study produces better operating guidelines.

POSITIVE DISPLACEMENT MECHANISMS

Because of their design, positive displacement devices can be used for sampling deeper wells than suction-lift devices are able to sample (i.e., where the water table is greater than 20 to 25 ft). These devices can be used to sample very deep wells, but samples taken from deep wells would be subject to degassing as a result of changes in pressure.

Gas-lift pumps

Gas-lift pumps include air-lift and nitrogen-lift pumps. The problem with these types of pumps is that the gas contacts the samples directly. Four studies that evaluated their performance (Schuller et al. 1981, Stolzenberg and Nichols 1985, Houghton and Berger 1984, Barcelona et al. 1984) found that these pumps had a profound effect on solution chemistry. Schuller et al. (1981) and Stolzenburg and Nichols (1985) found both the nitrogen-lift and air-lift pumps decreased levels of some metals present in solution. Schuller et al. (1981) felt that this was because the bubbles of nitrogen or air stripped water of CO_2 . This raised the pH (~1 pH unit) and caused precipitation of hydrous iron oxides and coprecipitation of Zn. Stolzenburg and Nichols (1985) noted that turbulence occurred in the line and at the point of discharge.

Houghton and Berger (1984) found that the air-lift pump had the most pronounced effect on sample chemistry among the seven samplers they tested. They found that samples taken with this type of pump had increased D.O. levels (350%), decreased ammonium levels (35%), decreased nitrate levels (50%), decreased Hg levels (71%), decreased Mo levels (49%), decreased Se levels (30%), and increased temperature (26%) as a result of mixing with hot summer air. They also noted loss of volatile organic constituents and increased pH. They concluded that these pumps should not be used for volatiles. In their laboratory study, Barcelona et al. (1984) also found that samples taken from these types of pumps showed statistically significant losses of purgeable organics under controlled sampling conditions, although losses were less than 8%.

Gas-operated bladder pumps

Although there are several types of bladder pumps (diaphragm, gas-squeeze, and Middleburg-type pumps), most of the literature did not specify which type was used. According to Herzog et al. (1991), pumping rates can be controlled easily with this type of pump, although the minimum flow rate may be higher than ideal for sampling volatiles. Unlike the previous samplers, the gas does not contact the sample with these pumps. Bladder pumps have been fairly extensively tested. While many of these studies conclude that this is one of the better samplers available, some of the field studies show that there also can be problems with this sampler.

In a laboratory study, Barcelona et al. (1984) found no statistically significant difference in the values of dissolved oxygen and methane in samples taken with bladder pumps vs. control values. They also found no significant difference in the accuracy or precision of the results for trihalomethanes taken with bladder pumps when compared with controls. They concluded that bladder pumps are among the best of the ten types of samplers they tested.

In another lab study, Tai et al. (1991) found that the recovery of high concentrations of VOCs was excellent, 98.5 to 100.8% at 92 ft (28 m). However, they discovered it was necessary to take these samples by using the manual control and low gas pressure after they lost their low concentration samples because bubbles were introduced into the sample vial as a result of using a high flow rate. Baerg et al. (1992) also had good

recoveries (99.1% to 111.2%) of five VOCs using a bladder pump (when compared with controls).

Devlin (1987) conducted a field study that compared a peristaltic pump and bladder pump and found that concentrations of all 16 contaminants were 4 to 70% lower with the peristaltic pump. At two field sites, Imbrigiotta et al. (1988) also found that bladder pumps gave one of the better overall performances of the seven samplers they tested. At the one site where its performance was poor, they felt that this was because the height of the water column in the well was insufficient to keep the pump submerged.

In contrast to the two previous field studies, in the first phase of their field study Muska et al. (1986) found that the bladder pump had the poorest recoveries of TCE of the six devices they tested. For example, TCE recovery with the bladder pump was 77% of that found with the mean for the other five pumps. However, it is important to note that two of the grab samplers with which they compared this pump (a surface bomb sampler and a pressurized bailer) were designed specifically for this study to retrieve VOCs at depth without losses due to depressurization.

In the second phase of their study, once again the bladder pump yielded poorer recoveries than several of the other devices at higher concentrations (high ppb- and ppm-range), while the opposite was true for one sample that was taken at a much lower concentration (low ppb range). They concluded that this device was not one of the better devices for sampling VOCs. The reason that Muska et al. (1986) found losses of volatiles in this study while Imbrigiotta et al. (1988) did not may be because the wells used by Muska et al. were much deeper than those used by Imbrigiotta et al.

In a laboratory study, Gossett and Hegg (1987) found that recovery of VOCs with these pumps was less than that achieved with the controls and that lift height (2, 4, and 6 m) had a significant effect on the recovery. At 6 m, recovery of the VOCs ranged from 87.6 to 88.9%.

With respect to inorganics, Stolzenburg and Nichols (1985) found that in-line filtered samples had high iron levels because turbulence broke up the iron-colloidal complexes and because oxidation and precipitation occurred during the transfer step. However, they concluded that high recoveries are possible with this type of pump if samples are handled carefully and are dis-

charged gently. Kearl et al. (1992) also found that bladder pumps can be used with a minimum impact on colloidal density.

Two studies (Houghton and Berger 1984, Unwin and Maltby 1988) specifically looked at the performance of gas-squeeze bladder pumps. These studies found that they were one of the best devices they tested. In their laboratory study, Unwin and Maltby (1988) found that there was very little loss of even the most volatile organic constituent (tetrachloroethylene) with this pump [although the sampling depth was only 7 meters (23 ft)]. Houghton and Berger (1984) tested this device in the field at depths greater than 250 ft and found that the gas-squeeze pump was best able to deliver the most representative water samples of the seven devices they tested. They felt that this was because it was able to maintain the sample under a pressure equivalent to the native aquifer.

Yeskis et al. (1988) found that, of the devices they tested, the bladder pump was the most difficult sampling device to decontaminate. They had a TCE-contaminated blank in a sample that was taken with a bladder pump that had been used previously to sample TCE in the 240-ppb range. They felt that this pump was difficult to decontaminate because it needs pressure on the bladder in order for the bladder to collapse during the recharge cycle (this is hard to do at the surface without having a long tube filled with water). In their field study, Snow et al. (1992) also had a problem with elevated levels of the pesticide atrazine and one of its metabolites in samples taken with a bladder pump that had been used previously to sample a more contaminated well.

Thus, bladder pumps are able to yield representative samples under certain conditions. However, further testing of these devices would yield better operating and decontamination guidelines.

Gas-operated piston (reciprocating) pumps

Like bladder pumps, the gas used to operate these pumps also does not contact the samples. Although the flow rates can be easily controlled with these devices, there still appear to be some problems associated with their use. According to Nielsen and Yeates (1985), these pumps have an intricate valving mechanism that causes a series of pressure drops in the sample, which can lead to degassing and pH changes. Houghton and Berger (1984) found that samples taken with this

device were slightly warmer and had increased D.O. levels (8 to 36%), presumably due to entrainment of air during insertion and subsequent agitation of the water by the pump hoses during each cycle. They also found that minor degassing affected the solution chemistry. They felt that this was because the sample hose is not maintained under back-pressure. They also found increased levels of barium, cadmium, and strontium (66%, 44%, and 7%, respectively), which they attributed to leaching from the barium-based grease on the piston seals.

However, more recent studies indicate fewer problems associated with this type of pump. Yeskis et al. (1988) found that recovery of VOCs using an air-activated piston pump was comparable to that found using a submersible centrifugal (impeller) pump and a bladder pump. Although the wells were not especially deep in the previous study (depth to water < 85 ft), Knobel and Mann (1993) also found that the ability of a piston pump to recover three VOCs to be equivalent to that of a submersible centrifugal pump (Grundfos) in much deeper wells (600 ft).

Electric submersible pumps

There are three types of electric submersible pumps: a helical rotor pump, a gear-driven pump, and a centrifugal submersible (impeller-driven) pump.

Helical rotor pumps (progressing cavity pumps)

Several studies have shown that the helical rotor pump should not be used to sample for gaseous solutes and VOCs. Barcelona et al. (1984) found that this device caused loss of gaseous solutes (oxygen and methane) when compared with control values. They also found more variability in the results with this pump. Imbrigiotta et al. (1988) found that the ability of the helical rotor pump to recover VOCs varied from site to site. At one site, it was one of the better devices. However, at another site its performance was one of the poorest, although its performance was not significantly different from the other devices. Unwin and Maltby (1988) found that helical rotor pumps (Johnson-Keck) caused significant losses of VOCs when compared with controls. For a well 23 ft deep (7 m), they observed a 7 to 8% loss of the more volatile organics they tested.

Pearsall and Eckhardt (1987) conducted a study to determine if the type of material used in the stator (Viton fluoropolymer vs. EPDM) had

any effect on concentrations of VOCs, but found little difference in concentration.

The mechanism for loss of VOCs with helical rotor pumps is not clear. Nielsen and Yeates (1985) felt that the samples might be subject to pressure changes at the drive mechanism. These pumps are known for their poor flow controllability, and their high pumping rates lead to turbulence (Nielsen and Yeates 1985, Herzog et al. 1991). Nielsen and Yeates (1985) and Herzog et al. (1991) felt that these pumps may not be suitable for chemically sensitive parameters.

However, in three recent studies, recoveries have been good using this device. Tai et al. (1991) found good recovery and precision of five VOCs with these pumps in their laboratory study. At 92 ft (28 m), recovery was 99.4 to 100.6% of the control values and the relative standard deviation was 0.43 to 0.82%. However, they noted that a variable flow controller would help in collecting samples with this type of pump. Rosen et al. (1992) compared the recovery of VOCs in samples that were taken downhole by passing the sample through a sorbent cartridge (Tenax) (which was subsequently thermally desorbed onto a GC column) with samples that were processed the same way after being pumped to the surface (20 m) using this type of pump. They concluded that, where outgassing is not a significant problem, pumping to the surface can be done reliably under many circumstances (using a pumping rate of one L/min).

Gibs et al. (in prep.) compared recovery of 13 VOCs using a helical rotary pump, a point source bailer (without using a bottom-emptying device), and a specially designed USGS downhole isobaric sampler. They found no significant difference in recovery in samples taken with the isobaric sampler vs. those taken with the helical rotor pump. The mean recovery was 8% lower in samples taken with the point source bailer.

The results from later studies do not agree with earlier findings. It is not clear why recent authors have had better results with this type of pump. Sampling rate is most likely an important factor. Again, further studies would yield clarification and more specific guidelines.

Gear-driven pump

These pumps are reported to be easy to operate, clean, and maintain in the field, although the gears will wear out if the pump is used in waters with high levels of suspended solids (Herzog et

al., 1991). There has not been much testing of this type of pump. Imbriotta et al. (1988) found the gear-driven pump was one of the better devices they tested at two sites, while its performance at the other site was intermediate. According to Nielsen and Yeates (1985) and Herzog et al. (1991), there is no control over flow rates, and thus it is not possible to go from high pumping rates used for purging a well to the low flow rates required for sampling volatiles. Also, they claim that pumping can lead to problems with turbulence with this device and that its use should be limited to depths of 125 ft and less. Herzog et al. (1991) felt that the potential for pressure changes (cavitation) exists at the drive mechanism.

Additional testing of this device would be useful.

Submersible centrifugal pumps

Submersible centrifugal pumps are also known as impeller-driven pumps (USEPA, 1992). In their field study, Houghton and Berger (1984) observed similar changes in the chemistry of samples pumped with a submersible centrifugal pump to those they observed with a peristaltic pump. Temperature increased 14%, alkalinity decreased 4.9%, and they observed substantial losses of a number of metals (25% loss of Ba, 60% loss of Hg, and 50% loss of Cr). They concluded that submersible centrifugal pumps should not be used when monitoring for constituents that are volatile or subject to degassing because they create a partial vacuum in the lines.

They also noted that samples taken using this device were enriched with lead (133%) and cadmium (83%), which they attributed to corrosion and flaking of paint from the surface. Stolzenburg and Nichols (1985) evaluated a 4-in. submersible centrifugal pump and found that these pumps significantly reduced dissolved iron levels. They felt that it was likely that oxidation-precipitation reactions were occurring because of the turbulent discharge and felt that a 2-in. pump should operate better. Muska et al. (1986) also concluded that submersible centrifugal pumps may not be suitable for sampling low concentrations of VOCs.

However, in a more recent study, Yeskis et al. (1988) had as good or better recovery using an impeller submersible pump compared with a helical rotor submersible pump, a bladder pump, and an air-driven piston pump, and much better

recovery than using a bailer. It is not clear why these results do not agree with previous studies.

A relatively newly developed submersible impeller pump (e.g., the Grundfos pump) has a variable flow rate that allows one to purge a well at high flow rates (> 20 L/min.) and sample a well at relatively low flow rates (0.1 L/min.). Gass et al. (1991) conducted a laboratory study to determine the ability of this pump to recover high (200 ppb) and low (20 ppb) concentrations of six VOCs (methane, 1,1-dichloroethylene, t-1,2-dichloroethylene, benzene, trichloroethylene, and toluene). They also tested the ability of this pump to recover several inorganic species (total Fe, total Cr, sulfate, and nitrite plus nitrate). (The lift height for the pump was approximately 20 ft.) Generally, recoveries of the VOCs were very good in both studies, except for the recovery of TCE in the low level study (89.19%). Recovery of the other VOCs in the low level study ranged from 99.4% to 101.02%, and recovery ranged from 99.49% to 101.86% for all six of the VOCs in the high-level study. Similarly good recoveries were seen for the inorganic constituents. Recovery ranged from 98.2% for total Cr to 100.7% for sulfate. For the volatile organics, there was no apparent correlation between the percent recovery and the substance's Henry's constants. Among the inorganic species, sulfate and nitrite plus nitrate might have increased as a result of oxidation, but did not.

Paul and Puls (1992) compared a low flow-rate submersible centrifugal pump with a bladder pump and a peristaltic pump and concluded that the submersible centrifugal pump was able to deliver the most representative and reproducible groundwater samples at their site.

In their field study, Clark et al. (1992) reported that samples collected with this type of pump (Grundfos) were more turbid and had higher concentrations of iron, lead, manganese, and zinc than samples collected with bladder pumps. They felt that this was most likely due to differences in the pumping rate. (The flow rates for the bladder pump were 0.5 to 4 L/min vs. 15 to 53 L/min for the centrifugal pump, which was reduced manually at the sampling port to achieve nonturbulent flow.)

Knobel and Mann (1993) found that the recovery of four VOCs using a submersible centrifugal pump (Grundfos) was equivalent to, or better than, the positive displacement piston pump.

INERTIAL-LIFT PUMP

In a field study, Barker and Dickout (1988) found that the inertial-lift pump and the bladder pump had similar recoveries of five of six VOCs from wells where the water was gas charged. Recovery was substantially better with these devices than with the peristaltic pump. In a lab study, they found recovery of halocarbons was 13 to 19% higher in samples taken with this pump than those taken with a bladder pump. These recoveries were also substantially higher than the control samples (taken with a syringe).

In a laboratory study, Baerg et al. (1992) found that the ability of the inertial-lift pump to recover five VOCs was poorest of the eight samplers they tested. Recoveries ranged from 65.95% to 99.85%. However, they felt that this poor performance may have been due to sorption by the polyethylene tubing used in this experiment. This explanation does seem plausible because losses did correlate with octanol water partition coefficients rather than the Henry's constants of the five organics. They planned further testing with more inert tubing material.

There are almost no published studies on the effects of these devices on turbidity or D.O. However, because of the surging action required to operate these devices, it seems likely that these devices can cause mixing with stagnant water and increased turbidity. There is some preliminary evidence to support this. Iles et al. (1992) observed higher dissolved solid contents in samples taken from two wells using an inertial-lift pump vs. three other samplers (submersible centrifugal pump, bladder pump and bailer). In one of these samples, alkalinity was also much higher (175 mg/L vs. ~120 to 150 mg/L).

CONCLUSIONS

It is clear from this review that there can be significant problems with degassing and loss of oxidizable and volatile inorganics and volatile organics under certain circumstances with almost all the samplers reviewed, including bailers, syringe samplers, peristaltic pumps, surface centrifugal pumps, air-lift and nitrogen-lift pumps, gas-operated bladder pumps, and submersible helical rotor, gear-driven, and centrifugal (or impeller) electrical pumps. There is general agreement among all the studies that certain devices should not be used when sampling for these sen-

sitive constituents. The devices with the poorest performances in these studies are gas-lift pumps, older types of submersible centrifugal pumps, and suction-lift devices, especially the surface centrifugal pumps.

While most studies show that there are serious losses of volatile and oxidizable constituents with peristaltic pumps also, there is some recent evidence that, if a flow controller and low flow rates are used with this pump, more sensitive constituents may be monitored with this device. However, the use of all suction-lift devices is limited to wells where the water table is less than 20 to 25 ft.

Among the grab samplers, recovery of sensitive constituents such as VOCs appears to be best when a point source bailer is used in conjunction with a bottom-emptying device. The overall performance of syringe samplers was poor in these studies. There is not much information available on the performance of Kemmerer samplers. However, they are not recommended for sampling organics because of their rubber end caps. Better guidelines for using the bailer are needed so that impact on sample quality can be minimized.

With respect to positive displacement type of samplers, gas-operated piston (reciprocating) pumps also performed poorly. Generally, bladder pumps gave the best overall recovery of sensitive constituents of all devices tested. However, even with these devices there were losses of sensitive constituents and problems with cross contamination if not properly decontaminated. Much of the earlier literature indicates that there will be losses of sensitive parameters with helical rotor pumps and submersible centrifugal pumps. However, recent studies indicate that these devices can yield good recovery of VOCs if a flow control device (rheostat) is used for controlling flow rate for the helical rotor pump and if the new variable flow submersible centrifugal pump (e.g., Grundfos) is used.

There is very little information on the performance of gear-driven pumps. Clearly, further testing would yield more information regarding the performance of those devices that have not been well evaluated and would yield better operational guidelines for those devices where results appear to be conflicting.

While studies on inertial-lift pumps indicate that this device can be used successfully to recover VOCs, further testing is needed, especially to determine their effect on D.O. and turbidity.

An important consideration for future studies, which was not addressed in many of the studies that are reviewed here, is pumping rate. Several studies have stressed that the pumping rate should be slow, around 100 mL/min (Barcelona et al. 1984, Puls and Powell 1992, Kearn et al. 1992). However, many of the studies reviewed here have used much higher flow rates or do not state what flow rates they did use.

Other issues that need to be addressed by future studies include the use of a rheostat as a flow control mechanism and dedication of samplers. Kearn et al. (1992) recommended using a rheostat to control flow over mechanisms that involve "throttling down" because this introduces the potential for partial pressure changes. They also recommended that sampling pumps be dedicated, because they found that inserting sampling devices mobilized colloids that previously were sorbed to the surrounding foundation.

For comparative purposes, future studies should include the following information: type of sampler, manufacturer, model, construction materials (including any lines and tubing), sampling depth, lift height, important aspects of the solution chemistry (e.g., high levels of dissolved solids or gases, low pH, etc.), and pumping rate.

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REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestion for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE October 1993		3. REPORT TYPE AND DATES COVERED	
4. TITLE AND SUBTITLE The Effects of Groundwater Samplers on Water Quality: A Literature Review				5. FUNDING NUMBERS MIPR 1133 30 July 1993	
6. AUTHORS Louise V. Parker					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Cold Regions Research and Engineering Laboratory 72 Lyme Road Hanover, New Hampshire 03755-1290				8. PERFORMING ORGANIZATION REPORT NUMBER CRREL Report 93-18	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) U.S. Army Environmental Center Aberdeen Proving Ground, Maryland 21010-5401 (formerly USATHAMA)				10. SPONSORING/MONITORING AGENCY REPORT NUMBER ENAECS-TS-CR-93107	
11. SUPPLEMENTARY NOTES					
12a. DISTRIBUTION/AVAILABILITY STATEMENT Approved for public release; distribution is unlimited. Available from NTIS, Springfield, Virginia 22161.				12b. DISTRIBUTION CODE	
13. ABSTRACT (Maximum 200 words) This report reviews both field and laboratory studies that test or compare the ability of various types of samplers to deliver representative groundwater samples. Several types of grab samplers, positive displacement devices, and suction-lift devices are evaluated. It was found that most of these devices can, under certain circumstances, alter the chemistry of a groundwater sample. Gas-lift pumps, older types of submersible centrifugal pumps, and suction-lift devices are not recommended when sampling for sensitive constituents such as volatile organics and inorganics that are subject to oxidation/precipitation reactions. Generally, of the devices reviewed in this report, bladder pumps gave the best recovery of these sensitive constituents. However, better performance could be achieved for several devices if better operational guidelines were developed by additional testing. Clearly, further research is warranted. Issues that need to be addressed in future studies include pumping rate, use of flow control mechanisms, and dedication of samplers.					
14. SUBJECT TERMS Grab samplers Groundwater samplers Groundwater sampling devices Inertial-lift pump Positive displacement samplers Suction-lift pump				15. NUMBER OF PAGES 19	
				16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT UNCLASSIFIED	18. SECURITY CLASSIFICATION OF THIS PAGE UNCLASSIFIED	19. SECURITY CLASSIFICATION OF ABSTRACT UNCLASSIFIED	20. LIMITATION OF ABSTRACT UL		