A Downhole Passive Sampling System To Avoid Bias and Error from Groundwater Sample Handling

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A new downhole groundwater sampler reduces bias and error due to sample handling and exposure while introducing minimal disturbance to natural flow conditions in the formation and well. This “In Situ Sealed,” “ISS,” or “Snap” sampling device includes removable/lab-ready sample bottles, a sampler device to hold double end-opening sample bottles in an open position, and a line for lowering the sampler system and triggering closure of the bottles downhole. Before deployment, each bottle is set open at both ends to allow flow-through during installation and equilibration downhole. Bottles are triggered to close downhole without well purging; the method is therefore “passive” or “nonpurge.” The sample is retrieved in a sealed condition and remains unexposed until analysis. Data from six field studies comparing ISS sampling with traditional methods indicate ISS samples typically yield higher volatile organic compound (VOC) concentrations; in one case, significant chemical-specific differentials between sampling methods were discernible. For arsenic, filtered and unfiltered purge results were negatively and positively biased, respectively, compared to ISS results. Inorganic constituents showed parity with traditional methods. Overall, the ISS is versatile, avoids low VOC recovery bias, and enhances reproducibility while avoiding sampling complexity and purge water disposal.

Introduction

Two general approaches are used to collect water samples from wells or open boreholes: (i) uphole sampling, with water pumped from depth and collected at the surface and (ii) downhole sampling, with a sampling vessel lowered down the well and the water sample collected at depth. In the 1970s, Tate (1) and Frost et al. (2) reported some of the first downhole groundwater samplers, which were developed for investigation of inorganic groundwater chemistry and employed a sampling vessel open at both ends to allow water to flow through during descent in the well. At the appropriate depth, the vessel ends could be closed by messenger or remote control. In the 1980s, the need arose to detect volatile organic contaminants (VOCs; e.g., chlorinated solvents) and other constituents at very low levels (i.e., µg/L), and it was recognized that uphole sampling could cause sample chemistry to be unrepresentative of in situ chemistry (3, 4). Downhole samplers were further developed to minimize escape of VOCs and dissolved gases (e.g., CH4, CO2). Gillham (5) developed a technique for downhole sampling using modified low-cost polyethylene syringes. The syringe was lowered to sampling depth, and then the plunger (and sample) withdrawn by vacuum applied via a hand pump at the surface. The syringe was then raised to surface and immediately capped. A new syringe was used for every sample, thus avoiding the need for sampler decontamination. This device has been used for studies of redox parameters, metals, and radon (5). Other downhole samplers included small cylindrical cartridges filled with sorbent material (6–8). After lowering to sampling depth, water was drawn through the sorbent material for capture of the contaminant mass; the cartridges were then removed and transferred to the laboratory for analysis. Similar to the syringe sampler, this method avoided sample exposure between sampling and analysis but required a thermal desorption step in the analytical procedure that is not standard in commercial laboratories. Passive downhole dissolved gas sampling approaches have also included syringes as a means of collection (9, 10).

Regulatory guidance in the United States in the 1980s concurrently pushed the groundwater industry toward vigorous well purging to sampling (e.g., removal of 3–5 well volumes) (11). This caused uphole collection to become standard practice, based on the premise that purging removes “stagnant” water from the well prior to sampling (11). However, Robin and Gillham (12) and Powell and Puls (13), among others, have argued (and shown) aquifer water in the screened interval of wells is not stagnant. These investigators illustrated water flows naturally through the screen zone of the well under background gradients, given hydraulic communication between the well and aquifer. The screened interval itself functions as a relatively high permeability zone, as indicated by borehole dilution tests (14). Low flow purging and sampling techniques in many cases also rely on flow-through in wells because the method commonly removes only a portion of the water within the screen interval (15, 16). Passive sampling also generally relies on this phenomenon (17, 18). Overall, well purging has three negative aspects: it generates contaminated wastewater needing treatment or disposal, it creates hydrologic disturbance in the aquifer prior to sampling, and it requires labor. The perception that monitoring wells must be purged prior to sampling is losing its appeal, as the “nonpurge” method (i.e., passive sampling) regularly provides similar data sets (19–23).

Development of passive samplers has more recently included the low-cost polyethylene diffusion bag (PDB) sampler. This flexible bag is filled with analyte-free water and positioned at the sampling depth to equilibrate with fresh formation water in the well screen (24, 25) under ambient/natural aquifer flow conditions. Samples are collected by retrieving the PDB from the well and transferring the water into a container. This method thus requires sample transfer and is limited to hydrophobic VOCs (e.g., benzene, tetrachloroethene) that readily diffuse across the polyethylene membrane.

Passive sampling approaches have since been further developed to increase the analytical capacity of this approach. This paper describes features and results of several field investigations of an “In Situ Sealed” (ISS) downhole sampler, or “Snap Sampler,” with direct comparisons with several standard and accepted alternative sampling approaches for various analyte types and hydrogeologic conditions. The ISS device seals samples downhole in the containers used to transport the sample to the laboratory. Thus, the sampler is
designed to minimize the alteration of groundwater samples from their in situ condition and allows the samples to arrive at the laboratory for analysis without exposure to external influences including: atmospheric air, tubing, or secondary containers.

**Methods**

**Description and Operation of the ISS/Snap Sampler.** The ISS sampler holds specialized double end-opening sample bottles in series to allow collection of multiple sample bottles for laboratory analyses (Figure 1). Samplers can be stacked in different combinations of bottle size and separated vertically to collect samples from multiple depths if desired. The ISS sampler bottle is built with an internal Teflon-coated stainless steel spring retaining two Teflon end-caps (Figure S1). A release pin system holds the bottle caps open during a user-defined downhole equilibration period. The sampler is lowered downhole with a triggering line (polyethylene tube with an internal Teflon-coated stainless steel wireline, which is hung from the well head) that supports the sampler at a specific position and allows the user to close the sample bottles without a messenger system or movement of the sampler. The trigger system retracts the release pins on the sampler downhole, freeing the Teflon caps to close the bottle, thus sealing the sample in situ. Pneumatic and electric triggering systems are available for applications deeper than ~15 m.

Preparation for deployment and sampling consists of inserting sample bottles in the samplers, setting the bottle caps open onto the release pins, attaching the trigger line, and lowering downhole (Figure S1A-E). The samplers are left in the well in an open position to allow restabilization of undisturbed ambient flow in the well. This period can be short if sampling objectives allow it (hours or days) or for the entire period between scheduled sampling events (3–6 months or more).

Deployment interval is largely a function of user logistics, but there are some minimum deployment limitations for certain VOCs. Parker and Mulherin (23) identify a 24 h “rule of thumb” minimum deployment period when sampling for most analytes, with longer periods (72 h) for some highly sorptive organics (e.g., m-xylene). Often times, a data quality objective requiring the well to physically restabilize after insertion of the device is longer than the time required for chemical equilibration. In most cases samplers are deployed for the entire interval between sampling events, avoiding concern about either problem. However, long deployment periods and certain well conditions may impact sampler function. Where ambient silting or substantial biofouling affect the physical function of the device, long deployment intervals may not be appropriate.

Once triggered to close, the sealed samples are retrieved. The bottles are designed to seal with no headspace, and in many cases can be sent to the laboratory without exposure to air. Surface preparation of the sample bottles consists of clipping the release pin tabs on the vial caps and securing a septa cap on each end of the bottle. If acid preservation is required, a cavity on each vial cap is sized to accept 0.5 mL of preservative (Figure S1F–H), which can be added without exposing the sample to air. A septa screw cap is then applied, similar to standard volatile organic analysis (VOA) vial preparation. After sample collection, bottles remain closed at all times in either preserved or unpreserved preparation and can be analyzed in standard laboratory autosampler equipment with no special considerations.

Limitations of the device primarily include sample volume and hydrogeologic or well conditions where communication between the well and aquifer are limited. Otherwise, the ISS sampler can be used for testing any analyte. Maximum sample volume is a limitation of the ISS sampler tested here and depends in part on well diameter. Fifty millimeter (2-in.) wells are a minimum requirement. In 50 mm wells, the maximum sample volume is approximately 750 mL. In larger diameter wells (100 mm or larger), potential sample volume increases to about 2 L. Long analytes lists requiring large sample volume may be problematic for this device, but as laboratory methods improve the volume limitation will diminish in importance. As described above, hydraulic exchange in the screen zone should generally be expected. However, if a well is very poorly yielding due to the geology encountered, or well condition, chemical exchange to the sampling device may be limited. In many cases, a pumped sample is also compromised by these conditions, so caution should be employed using either sampling approach where poor communication between the aquifer and well is present.

Sampling with this method is relatively rapid compared to purge sampling and is accomplished with little equipment. In dedicated applications, items brought to field site are minimal and include replacement bottles, a water level meter, a cooler, and documentation forms. No wastewater is generated from purging or extra sample waste; all water collected is submitted with the bottles to the laboratory. The method avoids the open air transfer step. Time to trigger, retrieve, and redeploy the ISS sampler is typically 10–20 min per well (Figure S2).

**Field Investigations.** Six field-based studies were conducted to compare the ISS sampler to traditional approaches, with data sets representing a wide range of chemical classes and hydrogeologic conditions (Table 1; detailed site and sampling information provided in the Supporting Information).
Results and Discussion

Each field site yielded results illustrating one or more data-quality advantage of the sealed-in situ sampling approach. Overall, results from the ISS method and purge or alternate passive methods were very highly correlated. For the Guelph and Morgan Hill sites, PDB and purge sample VOC concentration data were, on average, slightly lower than from the ISS sampler (y > 1, positive relative percent difference [RPD]; Figures 2 and 3). At Chatsworth and Morgan Hill, y-slope and RPD are very close to neutral for VOCs and perchlorate, respectively. Across all sites, VOC concentrations were usually higher using the in situ approach (e.g., Guelph, Morgan Hill, McClellan sites); for nonvolatile constituents, concentration equivalence between the purge samples and ISS samples was very good (Hillside, Morgan Hill, McClellan).

The passive approaches collect either a time-weighted sample in the case of the PDB or an instantaneous sample in the case of the ISS sampler. As such, the passive samples collect water at (or very near) the deployment position in the well at the time of collection. Early time purge samples (i.e., low flow/low volume purging) collect water from nearly the same position in the well when the pump is placed at the same position. Longer purge times and larger purge volumes interrogate larger portions of the well and eventually the formation adjacent to the well and beyond (Figure S3).

However, water delivered to the well under ambient flow-through conditions may be effectively the same in many cases, yielding similar results for this sampling approach (26). The comparisons highlight similarities and differences among methods and analyte type. For constituents not substantially affected by air or polymer exposure (e.g., perchlorate), or collected using low-bias methods (e.g., predeployed bladder pump using Teflon bladder and tubing), results are remarkably similar. In other cases, the purge method (e.g., peristaltic pump, bailer), and/or collection method (bailer, pouring), and/or exposure to unequilibrated plastics (tubing, bailer) contributed to the low bias for VOCs in the more traditional methods.

For the McClellan study site in Sacramento, CA, data previously reported by Parsons (22) were reanalyzed (27) to find additional clues about VOC recovery apparent in the data. The McClellan data are extensive and allow comparisons among a variety of sampling methods. The ISS/Snap sampler and low flow method consistently yielded the highest and lowest VOC concentrations, respectively (22, 27). The low bias of the low flow method compared to other methods at this site was attributed to multiple influences: an electric submersible pump was employed using new polyethylene tubing in each well; the tubing was not Teflon lined and was deployed immediately in advance of purging; and depth to sampling positions were often well over 100 ft (30 m) so

### TABLE 1. Site Information for Field Deployments

<table>
<thead>
<tr>
<th>site location</th>
<th>geology</th>
<th>sampling depth (m)</th>
<th>depth to water (m)</th>
<th>number of wells</th>
<th>sample intervals</th>
<th>analytes compared to</th>
<th>notes</th>
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<td>fractured sandstone</td>
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<td>6 to 35</td>
<td>3</td>
<td>1</td>
<td>VOC, gases</td>
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<td></td>
<td>1 week deployment</td>
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<tr>
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<td>fractured dolostone</td>
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<td>2 to 5</td>
<td>5</td>
<td>1–2</td>
<td>VOC</td>
<td>low flow, PDB pull trigger</td>
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<td>3 to 10</td>
<td>14</td>
<td>1–2</td>
<td>VOC, perchlorate</td>
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<td></td>
<td>pull trigger</td>
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<td>9 to 12</td>
<td>17</td>
<td>1–3</td>
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**FIGURE 2.** ISS/Snap sampler, diffusion sampler (PDB), and low flow comparison of VOCs at Guelph site (left panel); ISS/Snap sampler and low flow purge comparison at Santa Susanna Field Laboratory (SSFL) site (right panel). Slight positive offset of trendline (y > 1) indicates y-axis comparator is slightly higher on average. Very good correlation coefficients relate tight correspondence among the methods. SSFL shows closer correspondence (y = 1.02) with the use of a predeployed bladder pump rather than a peristaltic pump. Specific VOCs are listed in the Supporting Information.
extensive exposure to the tubing occurred. Parker and Ranney (28) showed exposure to polymer tubing, especially at low flow rates, tends to promote sorptive VOC loss. Handling of the low flow and other passive samples in the study added to the low relative recovery as the ISS sampler experienced neither exposure to tubing nor any bottle-filling transfer steps.

Examination of the chemical-specific VOC recovery differentials among methods used at the McClellan site (22) supports the proposition that bias is due to exposure to air and exposure to sorptive polymer materials. In all comparisons, the Snap Sampler yielded the highest VOC recovery. Based on that observation, the ISS sampler results were treated as a baseline comparator (assumed 100% recovery), and all comparisons were normalized to the ISS.

The plot of percent recovery vs octanol–water partitioning coefficient ($K_{ow}$) of VOC components (Figure 4, top panel) indicates poorer VOC recovery percent is associated with higher $K_{ow}$, suggesting sorption contributed to the difference among methods. Similarly, a plot of percent recovery vs Henry’s vapor partitioning coefficient suggests volatilization contributed to the difference among methods as poorer percent recovery was associated with a higher Henry’s constant (Figure 4, bottom panel). To the authors’ knowledge, this is the only data set to date that allows such chemical-specific analysis of field data. Differentials of this magnitude are rare, with these by far the largest identified. Chemical-specific associations could be developed due to the high differential recoveries and large size of the overall database. Differences are statistically significant at the 99% confidence level. For 6 of the 7 chemical/sampling method pairs where statistical significance was not demonstrated, few comparison pairs (4 or fewer) were available for the evaluation. Britt (27) spoke at length about individual constituent differences and the statistical tests employed. Tables S1 and S2 include statistical details.

The primary contaminant of concern at the Hillside New Jersey site was arsenic. Sampling for metals in groundwater has been historically problematic due to entrainment of a nonmobile fraction (e.g., sediment) during purging (29), and samples are commonly filtered to remove the artifact solids. Multiple filtration methods have been employed to delineate the mobile colloidal fraction, and some regulatory jurisdictions prohibit this procedure. Unfortunately, filtration also removes the mobile colloidal fraction, and samples are commonly filtered to remove the artifact solids. Unfortunately, filtration also removes the mobile colloidal fraction, and some regulatory jurisdictions prohibit this procedure. Multiple filtration methods have been employed to delineate the mobile fraction from artifact (30) but are rarely employed in the field. The closure action of the ISS sampler does not mobilize normally immobile formation particulates because no pumping is involved and therefore allows collection of naturally mobile colloidal contaminant load closer to that of ambient groundwater flow. Purge samples were collected, acidified, and analyzed in both filtered (0.45 µm) and unfiltered preparation; ISS/Snap samples were simply acidified after collection without filtration. Arsenic levels in filtered purge samples tended to...
be lower on average than unfiltered ISS samples, while unfiltered purge samples tended to be higher than unfiltered ISS samples (Figure 5). This is expected as the ISS sampler captures naturally mobile colloidal material, while unfiltered purge sample incorporates this colloidal material plus artifact particulates due to the disturbance caused by purging; a filtered purge sample removes (nearly) all particulates, including the mobile colloid fraction. Application to other colloid-borne or colloid-like constituents is implied by these findings; however, further work is required to test the applicability to bacteria, pathogens, or other colloidal constituents of concern.

The Los Angeles site data analysis compared long-term consistency of the sealed in situ method vs a traditional purge and bail-sample approach. Over two years, ISS sampling and traditional purge sampling yielded 181 comparators of individual VOC concentrations from one calendar quarter to the next. Overall, median purge results changed from one event to the next approximately 30% more than the ISS samples. Take, for example, a concentration of 100 that changes to 140 from one event to the next for the ISS, and a concentration of 100 changes to 152 for purge. That differential is a 30% greater change for the purge result (52/40 = 1.30). However, the actual groundwater concentration underlying the measured concentration changed by an unknown amount. If the actual concentration changed from say, 100 to 135, the difference between 135 and 140 (or 152) is the real measure of error. This translates to a true error of 5 for the ISS vs 17 for purge (140–135=5, 152–135=17): a 340% difference. Because the actual groundwater concentration cannot be isolated, the difference in concentration change is the closest proxy. This proxy is a minimum error estimate and reflects all factors influencing concentration, including the actual change in ambient contaminant concentration at the well plus any artifacts of either sampling procedure.

Changes in trichloroethene (TCE) concentration over the course of the comparison (Figure 6) were more pronounced than VOCs overall. Both sampling approaches result in event-to-event changes in the same direction, but the magnitude is reduced with the downhole in situ approach. The overall concentration range in the Figure 6 example was smaller for the ISS (0.0379–0.103 mg/L) compared to purging (0.0056–0.134 mg/L). The median RPD from event to event for purge sampling was 94% but only 35% for the ISS sampler, a substantial reduction indicative of an approach that reduces sources of data variability that are often unknown, uncontrollable, or uncontrollable.

These field investigation findings point to potential improvements in sampling methodology and data quality that can be achieved through in situ collection and sealing of samples. Data quality, which includes precision, accuracy, consistency, and repeatability, should be a controlling factor in selecting groundwater sampling methods. The evolution from strong-purge sampling to low flow sampling was prompted by the desire to improve data quality by reducing...
mobilization of normally immobile particles into the pumped sample and to improve consistency in sampling methods (15, 29). Passive, nonpurge, ISS/Snap sampling minimizes mobilization of particles and adds consistency to the sampling procedure. It also avoids handling and disposal of contaminated waters and the time and costs associated with pumping and field parameter measurements. Moreover, given the overarching goal of groundwater sampling is to collect samples that are the closest feasible representation of in situ conditions in the aquifer (31), the ISS sampler improves data quality by limiting exposure of sample to air or multiple sample vessels. Indication of the importance of atmospheric exposure and exposure to plastics is evident in the field studies and shows VOC losses may be chemical-specific and dependent on Henry’s vapor partitioning coefficient or $K_{ow}$ (27, 32, 33). The method reduces reliance on the operator for pump placement, purge times, purge parameter measurement, and bottle fill technique; avoids data quality problems due to tubing sorption loss and in-well mixing effects during purging; and limits the effect of uncontrollable aspects of field sampling, such as ambient temperature, humidity, or precipitation. Overall, the ISS approach retains many of the advantages while eliminating most of the disadvantages of diffusion-based sampling and can benefit nearly all categories of analytes, including field parameters, volatile organics, gases, metals, and dissolved inorganics.

Millions of monitoring wells are used worldwide to track temporal trends in natural groundwater and at contaminated sites; however, results are influenced by many factors associated with the sampling procedures themselves. These influential factors cause error in individual sample results and diminish the value of long-term trend monitoring. The In Situ Sealed sampler described here imparts the least degree of differential influence of any of these factors from one sampling event to the next through elimination of procedures and sample handling. As such, its use can most reliably focus interpretation of time-series data on the influences caused by the hydrologic system rather than the sampling process.

Acknowledgments

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Supporting Information Available

Details regarding field site geology, history, and sampling procedures as well as illustrations of the ISS/Snap sampler and steps for its deployment and retrieval and additional detail on the statistical significance of Figure 4 data are included as well as additional plots of inorganic constituent data comparisons of the ISS sampler and low flow purging and sampling techniques. This material is available free of charge via the Internet at http://pubs.acs.org.

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