

Standard Guide for Selection of Passive Techniques for Sampling Groundwater Monitoring Wells¹

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1. Scope

1.1 This standard provides guidance and information on passive sampling techniques for collecting groundwater from monitoring wells. Passive groundwater samplers are able to acquire a sample at a discrete depth or interval in a well, without the active transport associated with a pump or purge technique (1).² Passive groundwater sampling is a type of no-purge groundwater sampling method where the samplers are left in the well for a predetermined period of time prior to collecting the sample.

1.2 Methods for sampling monitoring wells include low-flow purging and sampling methods, traditional well-volume purging and sampling methods, post-purge grab sampling methods (for example, using a bailer), passive no-purge sampling methods, and active no-purge sampling methods such as using a bailer to collect a sample without purging the well. This guide focuses on passive no-purge sampling methodologies for collecting groundwater samples. These methodologies include the use of diffusion samplers, accumulation samplers, and passive-grab samplers. This guide provides information on the use, advantages, disadvantages, and limitations of each of these passive sampling technologies.

1.3 ASTM Standard D653 provides standard terminology relevant to soil, rock, and fluids contained in them. ASTM Standard D4448 provides a standard guide to sampling groundwater wells, and ASTM Standards D5903 and D6089 provide guides for planning and documenting a sampling event. Groundwater samples may require preservation (Guide D6517), filtration (Guide D6564), and measures to pack and ship samples (Guide D6911). Standard D7069 provides guidance on the quality control and quality assurance of sampling events. ASTM Standard D5092 provides standard practice for the design and installation of groundwater monitoring wells, ASTM Standard D5521 provides a standard guide for devel-

1.4 The values stated in SI Units are to be regarded as the standard. Values in inches (such as with well diameters) are given in parentheses, and are provided for information. Use of units other than SI shall not be regarded as nonconforming with this standard.

1.5 This guide provides information on passive groundwater sampling in general and also provides a series of considerations when selecting a passive groundwater sampling method. However, it does not recommend a specific course of action, and not all aspects of this guide may be applicable in all field situations. This document cannot replace education or experience and should be used in conjunction with professional judgment. This ASTM standard is not intended to represent or replace the standard of care by which the adequacy of a given professional service must be judged, nor should this document be applied without consideration of a project's many unique aspects. The word "standard" in the title of this document means only that the document has been approved through the ASTM consensus process.

1.6 This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

2. Referenced Documents

2.1 ASTM Standards:

D653 Terminology Relating to Soil, Rock, and Contained Fluids

D3740 Practice for Minimum Requirements for Agencies Engaged in Testing and/or Inspection of Soil and Rock as Used in Engineering Design and Construction

D4750 Test Method for Determining Subsurface Liquid Levels in a Borehole or Monitoring Well (Observation

oping groundwater monitoring wells in granular aquifers, and D6452 provides a standard guide for purging methods used in groundwater quality investigations. Consult ASTM Standard D6724 for a guide on the installation of direct-push groundwater monitoring wells and ASTM Standard D6725 for a guide on the installation of direct-push groundwater monitoring wells with pre-pack screens.

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² The boldface numbers in parentheses refer to the list of references at the end of this standard.

Well) (Withdrawn 2010)³

D4448 Guide for Sampling Ground-Water Monitoring Wells D5092 Practice for Design and Installation of Groundwater

Monitoring Wells

D5521 Guide for Development of Groundwater Monitoring Wells in Granular Aquifers

D5903 Guide for Planning and Preparing for a Groundwater Sampling Event

D6089 Guide for Documenting a Groundwater Sampling Event

D6452 Guide for Purging Methods for Wells Used for Groundwater Quality Investigations

D6517 Guide for Field Preservation of Groundwater Samples

D6564 Guide for Field Filtration of Groundwater SamplesD6724 Guide for Installation of Direct Push GroundwaterMonitoring Wells

D6725 Practice for Direct Push Installation of Prepacked Screen Monitoring Wells in Unconsolidated Aquifers

D6911 Guide for Packaging and Shipping Environmental Samples for Laboratory Analysis

D7069 Guide for Field Quality Assurance in a Ground-water Sampling Event

3. Terminology

- 3.1 For common definition of terms about soil and rock and the fluids contained in them, refer to Terminology in D653.
 - 3.2 Explanation of Terms Specific to this Standard:
- 3.2.1 passive environmental sampling, n—is a group of sampling technologies that were first developed to sample air, were subsequently adapted to sample soil vapor, and now are being used to sample water. In the scientific literature, passive sampling in air, soil, and water has been defined as any sampling technique based on the free flow of analyte molecules from the sampled medium to a receiving phase in a sampling device as a result of a difference between the chemical potentials of the analytes in the two media (2 and 3). These passive sampling devices are usually based on diffusion through a diffusion barrier or permeation through a membrane (2 and 3). Uptake of analytes follows a standard uptake curve where uptake initially is linear, followed by a period of time where uptake is no longer linear (that is, becomes curvilinear), and finally equilibration is reached. Analytes are retained in a suitable medium within the passive sampler, known as a reference or receiving phase, which can be a solvent, chemical reagent, or a porous adsorbent (2 and 3). There are two main accumulation regimes, kinetic and equilibrium, and these are described based on the device's physical basis of operation as defined below.
- 3.2.1.1 *equilibrium samplers*, *n*—passive samplers that have an exposure time that is sufficiently long to permit establishment of thermodynamic equilibrium between the sampled medium and receiving phase (3).
- 3.2.1.2 *integrative or kinetic samplers, n*—passive samplers that work in the linear uptake phase (of a standard uptake

curve) where the rate of desorption of analytes from the receiving phase to the sampled medium is negligible (2 and 3). These samplers provide a total mass for the time they are deployed, which can be converted to concentration values in some cases.

- 3.2.2 groundwater sampling, n—most groundwater sampling methods currently involve purging the well prior to sample collection although, samples can be collected without purging the well as long as the data-quality objectives of the investigation are met. Additional information on active sampling methods that involve purging the well can be found in Guides D4448 and D6452.
- 3.2.2.1 no-purge groundwater sampling, n—sampling methods that differ from active purging-and-sampling methods for sampling groundwater (as described in Guide D6452) in that there is no requirement to remove water from the well prior to sampling. Thus, without purging the well, no-purge methods can collect a sample using an active method (such as pumping, suction, bailing) or a passive method.
- 3.2.2.2 passive groundwater sampling, n—a type of nopurge groundwater sampling method where the samplers are deployed in the well at one or more target depths within the well screen or open bore hole and are then left in the well for a predetermined period of time prior to collecting the sample (rather than collecting a sample immediately). These sampling methods do not use pumping, suction, or bailing to collect the sample and thus do not induce stress on the aquifer (Guide D4448).
- 3.2.3 passive-groundwater samplers, n—are deployed in the well for a set period of time prior to sample collection; this is either an equilibration time or a deployment time that is based upon linear uptake of the analytes by the sampler. All of these devices provide a sample from a specific location within the well screen or borehole. Spatial integration, if any, is a result of natural ambient flow of the sampled medium. These samplers can be classified by the mechanism used to collect the sample and include: diffusion samplers (4 and 5), accumulation samplers (1, 6), and passive-grab samplers.
- 3.2.3.1 diffusion samplers, n—usually contain deionized (DI) or distilled water inside a membrane and rely on diffusion of analytes through the membrane to reach equilibrium with concentrations in the well. These samplers are an equilibrium type of passive sampler (as defined in 3.2.3). The length of the equilibration period depends primarily upon the types of analytes, the membrane material, the rate of exchange of water in the well, and temperature of the well water.
- 3.2.3.2 accumulation samplers, n—typically consist of a membrane that houses a sorbent medium, either liquid or particulate, and rely on diffusion and sorption to accumulate analytes in the sampler. Although, these samplers can be used as either an integrative or equilibrium sampler, adsorptive samplers are prone to saturation effects and other reactions which make them less suitable for equilibrium sampling (7). When these samplers are used in the integrative (or kinetic) mode, the sampling time must be within the linear portion of the uptake curve.

³ The last approved version of this historical standard is referenced on www.astm.org.

- 3.2.3.3 passive-grab samplers, n—are grab samplers that collect a whole water sample and require an equilibration period prior to sample collection. Passive-grab samplers should not disturb the water column during sample collection, should be able to collect a sample at the target depth(s) in the well, and should be able to isolate the sample inside the sampler prior to removing it from the well.
- 3.2.3.4 equilibration period, n—the suggested deployment period for all passive-grab and diffusion samplers and accumulation samplers when they are used as equilibrium samplers. The appropriate deployment period depends upon one or more of the following factors: the time needed for environmental disturbances caused by sampler deployment to dissipate and ambient conditions in the well to return, the time needed for equalization of analyte concentrations with surrounding concentrations in the well water, and the time needed to reduce losses due to sorption of the analytes by the sampler materials to negligible levels.
- 3.2.3.5 deployment time, n—a term used for an accumulation sampler that is being used as an integrative (or kinetic) sampler and is a function of the time needed for the sampler to achieve quantitative levels of uptake of the target analytes. For accurate quantitative measurements, the deployment time must be within the linear portion of the uptake curve of the sampler for the analytes of interest.

4. Significance and Use

- 4.1 General—In the past ten (plus) years, the Interstate Technology Regulatory Council (ITRC) has provided several technical and regulatory documents on the use of passive groundwater sampling methods (1, 4-6). Collectively, these documents have provided information and references on the technical basis for their use, comparison of sampling results with more traditional sampling methods, descriptions of their proper use, limitations, and a survey of their acceptance and use by responding state regulators.
- 4.1.1 Because of the large number of passive samplers that have been developed over the past fifteen years for various types of environmental sampling, it is beyond the scope of this standard to discuss separately each of the methods that could or can be used to sample groundwater. Extensive literature reviews on diffusion- and accumulation-passive samplers can be found in the scientific literature (that is, 3, 7-13). These reviews provide information on a wide variety of passive sampling devices for use in air, soil vapor, and water. A review paper on the use of diffusion and accumulation-type passive samplers specifically for sampling volatile organic compounds (VOCs) in groundwater (14) includes information on other passive samplers that are not included in the ITRC documents (1, 6) and discusses their use with respect to measuring mass flux.
- 4.2 *Use*—Passive samplers are deployed at a pre-determined depth, or depths, within a well for a pre-determined period of time and should remain submerged for their entire deployment time. All of the passive technologies described in this document rely on the sampling device being exposed to the groundwater during deployment and the continuous flushing of the open or screened interval of the well by ambient ground-

- water flow (15) to produce water quality conditions in the well bore that effectively mimic those conditions in the aquifer adjacent to the screen or open interval. For samplers that require the establishment of equilibrium, it is important that the equilibration period be long enough to allow the well to recover from any disturbance caused by placing the sampler in the well and to prevent, or reduce, losses of analytes from the water sample by sampler materials due to sorption. For kinetic accumulation samplers (used as kinetic samplers), it is important that the deployment time is long enough that quantitative uptake can occur but not so long that uptake is no longer in the linear portion of the uptake curve (that is, has become curvilinear).
- 4.2.1 As with all types of groundwater sampling methods, the appropriate use of passive methods assumes that the well has been properly located (laterally and vertically), designed, constructed, and was adequately developed (as described in Guide D5521) and maintained (as described in Practices D5092 and D6725, or Guide D6724). These measures are necessary so that the well is in hydraulic communication with the aquifer.
- 4.2.2 Each type of passive sampler has its own attributes and limitations, and thus data-quality objectives (DQOs) for the site should be reviewed prior to selecting a device. For wells in low-permeability formations, diffusive flux may become more important than advective flow in maintaining aquifer-quality water in the well.
- 4.3 Advantages—While passive methods are not expected to replace conventional pumped sampling in all situations, they often offer an easier-to-use (requiring only minimal operator training), alternative "tool" for sampling groundwater monitoring wells when their use meets DQOs and regulatory requirements. Other advantages include that these samplers can be used in most wells and typically have no depth limitation. These samplers are either disposable or dedicated to a well, and this eliminates or reduces the need for decontamination. Passive samplers typically reduce the logistics associated with sampling and are especially useful at sites where it is difficult to bring larger equipment (such as pumps and compressors) onto the site.
- 4.3.1 Passive groundwater sampling techniques typically provide a much lower "per-sample" cost than conventional pumped sampling methods (16-25). This is primarily because the labor associated with collecting a sample is substantially reduced.
- 4.3.2 If there is interest in identifying contaminant stratification within the well, multiple passive samplers can be used to characterize vertical contaminant distribution with depth. Baffles or packers can be used to segregate the sampling zones and often provide better characterization of each zone. (In cases where turbidity is a concern, it is important to deploy the sampling devices as gently as possible.) Profiling contamination with depth in a well can be especially useful when trying to decide where to place a passive sampler within the well screen; placing a sampler at the mid-point of the screen may not yield a sample with the highest contaminant concentrations or one that agrees best with previous low-flow concentrations (for example, 25).

- 4.4 Disadvantages—As with any groundwater sampling method, rapid or rigorous deployment of the sampler(s) (or pumps in the case of active sampling methods) can increase turbidity in the well. For passive groundwater samplers, this can be reduced or eliminated if the equilibration time is long enough to allow the return of the natural ambient turbidity in the well. In many cases, passive samplers are deployed at the end of a sampling event and left in the well until the next scheduled sampling event; this practice provides more than enough time for equilibration to occur.
- 4.4.1 It is also possible that some wells where only passive sampling methods are used may require more frequent maintenance than wells that are routinely pumped. However in other instances, sampling methods that utilize pumping can bring fines into the well and the well may need more maintenance than if a passive method is used.
- 4.5 *Limitations*—There are three primary limitations with passive samplers: analyte capability, sample volume, and size (that is, with respect to well diameter). For the diffusion and accumulation samplers, the membrane and sorbent (for accumulation samplers) determine the specificity of the sampler. Although, two or more individual types of samplers can be used simultaneously to sample for a broader spectrum of analyte types. In contrast, passive-grab samplers collect whole water samples and can be used for most analytes.
- 4.5.1 With respect to volume limitations, the passive-grab and passive-diffusion samplers collect a finite sample volume. This volume may not be sufficient when there are several types of analytes to be analyzed or when several water-quality measurements (such as dissolved oxygen (DO), pH, etc.) need to be conducted (that is, surface measurements versus in-situ measurements). Additional samplers or larger volume samplers may be available and can be used to meet the volume requirements. Alternatively, because laboratories typically use only a small portion of the sample collected, it may be possible to provide the laboratory with a smaller sample volume. Table X1.1 provides suggested minimum volumes for several analyte classes. However prior to sampling, the total volume of sample needed to run all of the chemical analyses should be confirmed (for each sampling point) with the laboratory.
- 4.5.2 Finally, the diameter of the sampler or combination of samplers must be able to fit in the well or multi-level sampler.

Note 1—The quality of the result produced by this standard is dependent on the competence of the personnel performing it, and the suitability of the equipment and facilities used. Agencies that meet the criteria of Practice D3740 are generally considered capable of competent and objective testing. Users of this standard are cautioned that compliance with Practice D3740 does not in itself assure reliable results. Reliable results depend on many factors; Practice D3740 provides a means of evaluating some of those factors.

5. Considerations for Passive Groundwater Sampling

5.1 Planning a Passive Sampling Event—As with all sampling activities, it is essential that all parties involved in planning the use of any sampling method identify and agree on the sampling and data-quality objectives, data-evaluation criteria, end use of the data, target analytes, and hydrogeologic concerns before the sampling method is selected. The appropriateness of any method is determined by the data-quality

- objectives (DQOs) for the sampling event and overall site monitoring program, and by the ability of the sampling method to meet them accurately and reliably. Considerations when selecting a passive sampling method can include sampler design, ability of the sampler to collect the target contaminants, well construction (including well diameter, screen and filter pack length, and proper slot size for the screen and filter pack design as described in Practice D5092), vertical and horizontal flow patterns within the well, and contaminant stratification. Additional guidance on the selection of a passive sampling method can be found in Table X2.1.
- 5.2 Analytes of Interest—When deciding whether to use passive sampling or which passive sampling method to use, consideration should be given to the contaminants of concern (COCs) for the site and other analytes or parameters that may be used to evaluate the geochemical processes of interest. Some passive samplers collect only specific analytes, whereas other devices can be used for a broader suite of analyte types.
- 5.2.1 Some samplers collect a limited volume of sample, and this may limit the use of these samplers. The sample volume that can be collected will be determined by the type of passive sampler, the diameter of the well, and the length of the desired sampling interval in the well. A larger total sample volume can be obtained by increasing the number of samplers used within the sampling interval (at the same depth or in series with depth) or, in some cases, by increasing the size of the sampling device (that is, using a longer or wider diameter sampler). However, when samplers are deployed in series with depth, concentrations in the samplers will reflect any stratification that exists in the sampling zone. Also, as mentioned previously, consulting with the analytical laboratory may make it possible to reduce the minimum volume of sample. (See Table X1.1 for suggested minimum volumes.)
- 5.2.2 More specific information on the capabilities of particular sampling devices can be found in 6.1.4, 6.2.4, 6.3.8, and in Table X2.1. For devices that are available commercially, current information can also be obtained by contacting the sampler vendor(s).
- 5.3 Site Considerations—In general, passive groundwater samplers can be used in a wide variety of hydrogeologic settings. Site considerations can include: accessibility of the wells, well diameter, screen length, saturated thickness, the hydraulic connection between the well and aquifer, and the hydraulic gradient that generates flow. Passive samplers are particularly well suited for conditions where active sampling methods can be problematic. These conditions can include low-yield formations where excessive drawdown is unavoidable even at low flow rates, locations that are difficult to access with a vehicle, or where low-turbidity samples are needed but cannot be obtained using other sampling methods such as with a bailer or a pump.
- 5.3.1 However, there can be situations that preclude the use of any sampling method, including standard purged methods. Both passive and active sampling methods may inadvertently collect non-aqueous phase liquid (NAPL). For example, this can occur when a sampler or pump passes through a NAPL zone during deployment or when droplets are drawn down or entrained while pumping the well. In these cases, collection of

water samples from wells containing NAPL may overestimate the risk to human health and may complicate data interpretation. Therefore, the practical effect of this bias on the sampling objectives and project DQOs should be evaluated, and continued collection of the water sample may not be warranted.

- 5.4 Acceptability of Passive Groundwater Sampling Methods—Numerous studies have shown that passive-groundwater sampling methods can be valid and viable alternatives to purged sampling methods. (These studies are listed for each type of sampling device in 6.1.4, 6.2.4, and 6.3.8.) As a whole, passive groundwater sampling methods continue to gain acceptance among the regulatory, scientific, and user communities. Much of the acceptance of these methods can be attributed to the publication of guidance documents and free internet training provided by the ITRC Diffusion/Passive-Sampler Team.
- 5.4.1 Questions about the "need to purge" have been largely answered over the course of the last few decades (15, 26, 27). In properly designed, developed, and maintained monitoring wells, adequate hydraulic communication exists between the aquifer and well. With adequate hydraulic gradient, aquifer water flows into and out of the screened or open sections of a well. Passive sampling devices set in such screened or open zones will collect aquifer water that is in dynamic equilibrium with the aquifer without purging. The hydraulics within the well, well bore, and the formation will determine what the sample actually represents. It is not in the scope of this guide to describe how an aquifer is to be represented; that is for the user to determine.
- 5.4.2 There are conditions where a passive sample does not collect a sample from the entire screened zone of a well. This may be due to for example, vertical flow in the well, contaminant stratification, poor hydraulic communication, or a low hydraulic conductivity in the formation (creating a long residence time in the well). However, these conditions can also be problematic for purged sampling methods (28, 29). These conditions do not necessarily make passive sampling an unacceptable alternative because passive sampling can represent the adjacent aquifer differently than a pumped sampling method. In contrast, pumped sampling methods collect a flow-weighted average sample that is more heavily weighted by the more transmissive portions of the adjacent aquifer(s). Recommendations on how to deal with differences between analyte concentrations when comparing passive vs. active sampling methods are given in Appendix X3.
- 5.4.3 In instances where there is poor hydraulic communication between the aquifer and the well, rehabilitation of the well or redevelopment often improves the communication between the aquifer and well. This can be necessary for both pumped and passive methods.
- 5.5 Implementing Passive Sampling Methods—Technical concerns, regulatory concerns, or both should be addressed when selecting a sampling method or changing one, as there are inherent advantages and limitations in every groundwater sampling method. These differences should be examined within the context of the particular project objectives, data needs, and site conditions for each proposed application. A fundamental concern of regulators is that the sampling method

used at a site, or at a particular well, provides results that meet the DQOs for the project.

- 5.5.1 There are many different passive sampling systems, and these technologies vary with respect to the degree of field validation they have received. Methods that can provide good reproducibility among different users, field conditions, and time frames are best suited for long-term monitoring strategies. Two or more passive sampling techniques may be deployed simultaneously and provide samples for a broader range of analytes and thereby meet the site DQOs. Also for well water with a broad range of analyte concentrations, it may be necessary to deploy two or more samplers of the same type in a well.
- 5.5.2 New Sites—In cases where new wells or a new site is under consideration, selection of a sampling method does not rely on historical data continuity, and thus method selection would rely on a rigorous evaluation of the data quality needs for the site. Improved site-characterization methods can yield better designed wells (often with shorter screens) and thereby improve this decision process. Data from passive sampling methods that use multi-level samplers may provide more specific and detailed high-resolution information in terms of aquifer stratigraphy, contaminant fate and transport, and site management.
- 5.5.3 Older Sites—There should be no impediment to switching to a passive method as long as the DQOs of the site are well understood and can be met by the particular sampling method chosen. A number of field and laboratory studies (listed in 6.1.4, 6.2.4, and 6.3.8) have been conducted to determine the comparability of passive methods with conventional sampling methods. These studies reveal that in most situations, passive methods provide samples that have analyte concentrations that are not significantly different (on a statistical basis) from those collected using other conventional sampling methods such as low-flow purging and sampling.
- 5.5.3.1 When considering a change in sampling methods, the question arises how the results of the existing and new methods will compare. When converting to a passive sampling method, a side-by-side comparison test with the site's current method or comparison with historical data may be necessary to understand data differences between sampling methods or may be required by a regulator. Further discussion on how to conduct this type of test, how to analyze the data, and how to best interpret the data are given in Appendix X3.

6. Types of Passive Groundwater Sampling Devices

The three types of passive groundwater sampling devices (that is, passive-grab samplers, diffusion samplers, and accumulation samplers) vary greatly in how they function and each type has its own specific deployment-time requirements.

6.1 Passive-grab Samplers are used to collect a whole water sample from a discrete depth or interval within the well or borehole after a predetermined deployment period in the well. This residence time allows the well to recover from the disturbance caused by inserting the sampler in the well and thus allows the water in the screened interval to return to the ambient flow conditions that existed between the well and the formation. This reduces the possibility of collecting a sample with an artificially elevated turbidity and thus obtaining falsely

elevated concentrations of particle-borne contaminants. This residence time also allows time for the sampler materials to effectively equilibrate with analyte concentrations in the surrounding well water prior to sample collection, and thereby prevents, or reduces, analyte losses due to sorption by the sampler materials (30-34). Sample collection does not occur until the device is triggered or actuated. Passive-grab samplers should not disturb the water column during sample collection, should be able to collect a sample at the target depth(s), and should be able to isolate the sample inside the sampler prior to removing it from the well. These criteria distinguish "passivegrab samplers" from other grab samplers that are used as no-purge samplers, such as various types of bailers including point-source bailers and collapsible bailers (for example, sleeve-type samplers). The ITRC Diffusion/Passive Sampler Team (1, 6) previously categorized grab samplers used in passive sampling as "equilibrated-grab samplers." However, not all of "equilibrated-grab samplers" meet the more restrictive definition for passive-grab samplers" given in this stan-

6.1.1 Advantages—The primary advantage of passive-grab samplers is that typically they can be used to collect samples for a wide range of organic and inorganic analytes. This is because sample collection is not limited by the sampler membrane or the collection media inside the device. These devices do not exclude colloidal particles, and thus can be used to collect samples for analyses of total and dissolved concentrations of analytes. Samples collected with these samplers can be used to measure pH, oxidation-reduction potential (ORP), electrical conductivity, and dissolved gases. Also, these samplers can be used for quarterly, semi-annual, or annual sampling events. After collecting a sample, a new sampler or sample bottle is placed in the well thereby eliminating having to make a second trip to the field. For one passive-grab sampler (that is commercially available), the samples are sealed in a sample bottle in the well. In some instances the sample bottle can remain sealed until the sample is analyzed; this prevents loss of VOCs during transfer in the field or in the laboratory.

6.1.2 Disadvantages—For passive-grab samplers, inadvertently agitating or aerating the well or dislodging particles from the inside of the well casing or well bore during sampler deployment can alter some analyte concentrations including dissolved gases, metals subject to oxidation/precipitation reactions, and particle-borne or colloid-borne contaminants. However, entraining particles that are not part of the total mobile load moving through the aquifer under ambient conditions can also occur with pumped sampling methods. Therefore, the length of the equilibration period should be sufficient to provide time for the well to recover from any disturbance caused by inserting the sampling device in the well. The extent of recovery in the well depends upon the flow rate in and out of the screened interval and the condition of the well. In instances where entraining extraneous particles is a problem, this can be mitigated in some cases by redeveloping the well.

6.1.3 *Limitations*—The primary limitations with these samplers are their size and the sample volume collected. Typically, these samplers do not fit in wells less than 5 cm (2 in.) in

diameter. In instances where a larger sampler volume is needed, a larger sampler may be available or, it may be possible to place several samplers at the same depth in larger diameter wells or in series with depth in smaller diameter wells. However, placing multiple samplers in series with depth extends the length of sampling interval, and this longer sampler could also dislodge particles from the wall of the well, which could become entrained in the sample.

6.1.4 Additional Information—There are several field and laboratory studies that have evaluated the performance of these types of groundwater samplers include peer-reviewed reports and papers (that is, 21-24, 34, 35) and other reports (16, 36). Also, several of these reports (16, 23, 24) include cost analyses that demonstrate the cost savings that can be achieved using these types of passive samplers when compared with conventional pumped sampling methods.

6.2 Diffusion Samplers rely on diffusion of analytes of interest through a membrane into distilled or deionized (DI) water contained inside the sampler. Polymeric materials commonly used for the membranes include low-density polyethylene (LDPE), regenerated cellulose (or dialysis membrane), nylon, and polymethylsulfone. Typically, a minimum of two weeks is recommended for equilibration (1, 4-6) but a longer period may be needed for some analytes such as explosives (17-19). Diffusion samplers provide a time-weighted average concentration that is weighted most heavily towards concentrations in the well over the last few days the sampler is in the well; the degree of this weighting depends on the equilibration rates for the analytes of interest for the membrane being used (that is, the type and thickness), the water temperature, and rate of recharge (flow rate) in the well.

6.2.1 Advantages—Diffusion samplers are easy to use and can be quickly deployed and retrieved. Waste disposal is limited to a small amount of unused water from the samplers and the spent disposable samplers, and thus little or no decontamination is required. Most of these samplers can be used for quarterly, semi-annual, or annual sampling events.

6.2.1.1 Depending upon the membrane used in the sampler, it may be possible to collect samples that can be used to measure pH, ORP, electrical conductivity, or dissolved gases. Some diffusion samplers can be used to collect samples for a variety of organic and inorganic analytes, and some membranes provide unique advantages. As an example, the LDPE membrane used in some samplers will prevent alkalinity exchange of the aquifer water with the (DI) water in the sampler (37). This can be an advantage when collecting VOC samples from alkaline aquifers where addition of the sample to the acid preservative in the vial (or vice versa) results in effervescence and subsequent loss of the VOCs.

6.2.1.2 Several of these samplers are available commercially and generally are relatively inexpensive to purchase. However, even using samplers that aren't commercially available (and thus have to be constructed) has still been shown to be cost effective (16-24). [For more information on commercial availability, see the ITRC Diffusion/Passive Sampler Team's publications (1, 5, 6).]

6.2.2 *Disadvantages*—These samplers exclude all particles bigger than the pore size of the membrane and thus they cannot



be used to collect samples for analytes that are particle-borne or colloid-borne such as total metals or hydrophobic organic analytes (for example, polycyclic aromatic hydrocarbons (PAHs) and polychlorinated biphenyls PCBs). Another disadvantage is that some of these samplers are not commercially available and therefore have to be constructed in a clean environment such as a laboratory.

6.2.3 Limitations—The primary limitations associated with using diffusion samplers are that: 1) their use is limited to only those analytes that will diffuse through the membrane (depending upon the type of membrane), 2) their use is limited to analytes in the dissolved form, 3) the sample volume is limited to the size of the sampler, 4) depending upon the size of the sampler, deployment may be limited to 5-cm (2-in.) diameter or larger wells, and 5) depending upon the sampler membrane, the maximum deployment time may be limited. In instances where a larger volume is needed, longer samplers often can be custom made. Smaller-diameter samplers can also be custom made.

6.2.3.1 While most samplers can be deployed after a sampling event and left until the next sampling event, some membranes, such as the regenerated-cellulose membrane, may undergo biodegradation if left in some wells for more than two weeks (6, 37). In those instances, two trips to the field are typically required (one to deploy the sampler and one to collect it). However even with two trips to the field, these samplers have been shown to provide substantial cost savings over low-flow sampling methods (16-20). Also, samplers that are left in the well for a long time (such as between quarterly sampling events) should be examined to determine that biofouling has not occurred. The presence of a biological film can affect the transport of analytes through the sampler membrane or can affect sorption by sorbents that are directly exposed to the water column.

6.2.4 Additional Information—Besides those reports and papers already cited, there are several other peer-reviewed reports and journal papers (7, 8, 21-24, 27, 35, 38-44) that provide additional information on passive-diffusion groundwater samplers.

6.3 Accumulation Samplers rely on diffusion through a membrane and then sorption by sorbent media within the sampler that accumulates the analytes of interest within the sampler (1, 6). The sorbent is typically a sorbent powder but can be a liquid. These samplers include nonporous, semipermeable, or permeable membrane devices that allow either direct diffusion of the analytes in the groundwater through the membrane, or there can be direct partitioning into the membrane or partitioning to the vapor phase with subsequent diffusion through the membrane. The analytes accumulate in solid or liquid sorbent material housed within the sampler. The membranes control the type, uptake rate and size of the analyte molecules that reach the adsorbent (for example, hydrophilic compounds), while protecting the integrity of the sample. Alternatively, the sorbent can be directly exposed to the water column and utilize materials such as those used in solid-phase extraction (SPE) materials. Stationary phases can include extraction cartridges and disks.

6.3.1 These samplers are placed at the desired depth in the well and left for an exposure period that allows the sorbent to accumulate a detectable level of the target analytes. Exposure periods are a function of the sampler design and target analyte capability, estimated contaminant concentrations, temperature of the well water, and the rate of exchange of water in the well. Thus, the recommended exposure time can range from a time scale of minutes or hours to months, depending on whether they are being used as a kinetic (integrative) or equilibrium sampler. Typically, the exposure time for kinetic (accumulation) samplers ranges from minutes to several hours and the exposure time of equilibrium (accumulation) samplers ranges from days to months. Sampler design ranges from complex (in terms of assembly and adsorbent housing) to relatively simple designs that require minimal handling.

6.3.2 As a group, these samplers can detect a wide range of volatile and semi-volatile organic compounds. Examples include fuel-related and chlorinated compounds, PAHs, organochlorine pesticides, dioxins and furans, PCBs, and pharmaceutical compounds. Other samplers have been developed for sampling for inorganic compounds including some metals.

6.3.3 While other passive groundwater samplers provide a water sample that is analyzed, it is the sorbent material in these samplers that is analyzed. Particulate sorbents may be extracted with water (or some other aqueous solution), an organic solvent, or thermally desorbed. Samplers containing an organic solvent do not require further extraction but may require additional cleanup prior to analyses.

6.3.4 Typically, the results of these analyses are given in a total mass for each of the analytes for the exposure time. However, there is an extensive body of research on passive, sorbent-based methods which can allow one to estimate concentrations in water by measuring sampler uptake rates. The total mass measured (per exposure time) and the measured uptake rate of the analytes by the sampler can be used to calculate analyte concentrations present in the well water. Monitoring well-specific data may be needed to calibrate the measured uptake rate of the samplers. This data can include water pressure (that is, sampler depth in water column), water temperature, groundwater velocity, and the performance of reference compounds incorporated in the sampler.

6.3.5 Advantages vary with sampler design. These samplers can be designed to target a specific class, type, or species of analytes. Common advantages associated with using these samplers result from not having to handle and transport vials and bottles (especially glass) containing aqueous samples, reduced shipping weight, easier handling in the field, and in some cases not having to refrigerate the samples during storage or shipping.

6.3.6 Disadvantages vary considerably depending upon the sampler design, sample handling procedures, extraction methods, and the analytical methods used. Depth below the water table may limit sampler placement, if the water entry pressure of the sampler membrane is overcome or if the sealing of the membrane to the housing is breached due to pressure. Also, some regulators may balk at using calculated concentration values.

6.3.6.1 Those samplers that contain an organic solvent as the sorbent medium may require special handling because of concerns with flammability, and regulatory agency approval should be obtained prior to placing them in a groundwater environment.

6.3.7 Limitations are a function of the sampler design and handling. Typically accumulation samplers are limited to certain types of analytes. For metals, depending upon the DQOs, it may be important to know whether a particular sampler provides total or dissolved concentrations of these analytes. Kinetic (accumulation) samplers rely on a brief exposure (so that uptake of the analytes remains in the linear portion of the uptake curve) and thus they cannot be left in the well between sampling events. In contrast, the exposure time for equilibrium (accumulation) samplers is much longer and some of these samplers can be left in the well between sampling events, depending upon the sampler design and well conditions.

6.3.8 Additional Information—Several sources (1, 6, 14) provide more specific information on the use of accumulation

samplers for sampling groundwater. Other review papers (for example, 2, 3, 7, 9-13) discuss the use of these samplers for aqueous sampling in general. One recently published peer-reviewed technical report (25) provides the results from a demonstration that used an accumulation sampler at two Department of Defense sites and presents data on the associated cost savings that can occur when this sampling method is used (when compared with conventional low-flow sampling).

7. Selecting a Passive Sampling Method

Table X2.1 provides a matrix table that can aid the user when selecting a passive sampling method.

8. Keywords

8.1 accumulation sampler; diffusion sampler; equilibratedgrab sampler; equilibrium sampler; groundwater sampling; integrative sampler; kinetic sampler; passive diffusion sampler; passive-grab sampler; passive groundwater sample; passive groundwater sampling; passive sampler; sorptive sampler; time-integrated passive sampler

APPENDIXES

X1. SUGGESTED MINIMUM SAMPLE VOLUME NEEDED FOR ANALYSES

TABLE X1.1 Suggested Minimum Sample Volume Needed for Analyses (6)

Preservation Type	Analytes	EPA Method Reference	Normal volume (mL) requirement for SW 846	"Easily accepted" minimum vol. (mL) for one analysis	Common number of reruns	Comments
Unpreserved (Must be collected in separate bottle)	Alkalinity	310.1*	200	10	1	Titration to pH 4.5
Unpreserved (Can be combined in one container)	Anions by IC (Cl, Br, NO ₃ , SO ₄)	300/9056A	50	5	3	For IC, all samples start at 1/10 dilution. Thus, standard curve concentrations are lower by a factor of 10.
	BOD, using 60 mL bottles	405.1	100	100	1	Assumes use of 60-mL bottles, set at 1/1, 1/3, 1/30 and 1/100 dilutions and DO meter/probe. PQL is based upon the minimum amount of D.O. uptake required by the method (2.0 mg/L) multiplied by sample dilution factor.
	Hex Chromium	7196 M	96 M 300 5 1	1	Sequential or flow-injection colorimetry using 4-m sample cups.	
	Perchlorate	314	50	25	1	Must have enough sample to run conductivity tes and filter sample in cases of high chloride, sulfate etc.
	Perchlorate	9058	50	10	1	No conductivity test required.
	Perchlorate	6850	10	10	1	
	TDS	160.1	200	100	1	Gravimetric
	TDS	160.1	200	20	1	Gravimetric

TABLE X1.1 Continued

Preservation Type	Analytes	EPA Method Reference	Normal volume (mL) requirement for SW 846	"Easily accepted" minimum vol. (mL) for one analysis	Common number of reruns	Comments
Sulfuric Acid	COD	410.4	100	5	1	Hach COD digestion tubes (p/n 21259-15: high level, 21258.15: low level) using 2 mL/tube.
	NH3, w/out dist.	350.1	100	5	1	Sequential or flow-injection colorimetry, using 4 or 8-mL sample cups, assuming no distillation required
	TKN	351.2	500	20	1	Up to ~5 dilutions from 1 distillation, but no repeat distillations. Block digestion using 20 mL of sample, followed by sequential or flowinjection colorimetry using 4 or 8-mL sample vials.
	Phenols, distilled	420.2	100	50	1	In-line sequential-flow distillation followed by colorimetry.
	Dissolved gases (Methane, ethane, ethene)	RSK 175	120	40	1	Using GC FID TCD
Sulfuric Acid	TOC	415.1	120	50	1	UV or heated-persulfate TOC analyzer, with 40-mL VOA vial autosampler
Nitric Acid	Total Hardness	130.2	100	10	1	Titration to sky-blue endpoint
	RCRA or CAM Title 22	6010	250	25	1	
	RCRA or CAM Title 22	6020	250	25	1	
	RCRA or CAM Title 22	700 Series	250	25	1	
	Mercury	7470	250	50	1	Hot-block digester
Sodium Hydroxide	Total Cyanide	335.4/9012	500	50	1	Please note 335.4 and 9012 are the same procedure. Differences are in the QC requirements. (335.4 ICV acceptance: 90-110 and LCS: 90-110; 9012 ICV: 85-115 and LCS: 74-123). Midi distillation of 50-mL sample, followed by sequential or flow-injection colorimetry.
Zinc Acetate +	Total Sulfide	376.1	100	60	1	No headspace, 60-mL BOD bottle.
Sodium Hydroxide		9030B	100	100	1	Midi distillation requires 100-mL sample.
Hydrochloric acid	Volatile Organics	8260	140	20	1	If separate 40-mL vials are used for each 20 mL aliquot, inert material is need to occupy the remaining 20 mL. Approved inert material should be used. Alternatively, 20-mL vials can be used.
Unpreserved (SVOCs)	(SVOCs) BNAs	8270	1000	250	1	Can use 100 mL, but RLs will be higher than AFCEE 3.1 QAPP
	Pesticides	8081	1000	100	1	
	PCBs (1016,1221, 1232, 1242, 1248. 1254, & 1260)	8082	1000	100	1	100 mL extracted by separatory funnel (3510) and concentrated to 1.0 mL, 2 µL injection dual column GC/ECD analysis.
	Herbicides	8151	1000	100	1	

Acronym	Meaning
AFCEE	Air Force Center for Engineering and the Environment
BNA	Base Neutral and Acid Extractable SVOC
BOD	Biological Oxygen Demand
CAM	California Assessment Manual
COD	Chemical Oxygen Demand
DO	Dissolved Oxygen
ECD	Electron-Capture Detector



EPA US Environmental Protection Agency

FID Flame-Ionization Detector
GC Gas Chromatography
IC Ion Chromatography
ICV Initial Calibration Verification

ITRC Interstate Technology and Regulatory Council

LCS Laboratory Control Sample
PCB Polychlorinated biphenyl
PQL Practical Quantitation Limit
QAPP Quality Assurance Program Plan
RCRA Resource Conservation and Recovery Act

RSK175 Method for Dissolved Gases (methane, ethane, etc.) in Water

SVOC Semi-volatile Organic Compound

SW864 US EPA Test Method for Evaluating Solid Waste

TCD Thermal Conductivity Meter
TDS Total Dissolved Solids
TKN Total Kjeldahl Nitrogen
TOC Total Organic Carbon

UV Ultraviolet

VOA Volatile Organic Analysis VOC Volatile Organic Compound

X2. DECISION MATRIX

TABLE X2.1 Decision Matrix

		Applicability of Passive Sampler Technologies					
Type of Consideration	Consideration	Passive-	Diffusion	Accumulation	Comments		
Type of Consideration Sample volume and	Need to collect a whole water	grab yes	no	N/A ^A	¹ These samplers do not collect water samples but rather sorb		
analyte type	sample	you	110	14/71	specific analytes.		
	Need to collect a large volume of sample	probably ¹	possibly ¹	N/A	¹ May have to use multiple samplers, larger samplers, or less sample volume.		
	Need to sample for a number of organics and inorganics	yes ¹	possibly ²	possibly ²	¹ In most cases but sampler volume dependent. ² Depends on the sampler; may have to use more than one sampler type.		
	Need to collect sample for water quality measurements	yes	possibly ¹	N/A ²	¹ Depends on sampler design ² Would have to make these measurements in-situ.		
	Only need to sample for limited analyte types	yes	yes	yes			
	Need to determine concentrations of only dissolved constituents	yes	yes	yes/no ¹	¹ Depends on sampler design. May need more than one type of sampler.		
	Need to determine both total and dissolved analyte concentrations	yes	no	possibly ¹	¹ Depends on sampler design		
Internal diameter (ID) of well or multi-level sampler	Sample a well with an ID of 5 cm (2 in.) or more	yes	yes	yes			
	Sample a well with an ID of 2.5 cm (1 in.) but less than 5.1 cm (2 in.)	possibly ¹	possibly ¹	yes	¹ May be able to make or have made smaller diameter sampler		
	Sample a well or multi-level sampler with an ID between 0.6 cm (1/4 in.) and 2.5 cm (1 in.)	no	possibly ¹	yes ²	¹ May be able to make or have made smaller diameter sampler ² Depends on sampler design		
Hydrogeology	Profile contaminants with depth in well screen or open borehole	yes	yes	yes			
	Determine the average contaminant concentrations over a longer period of time	no	no	yes/no ¹	¹ Yes if uptake is in the linear portion of the uptake curve; otherwise samplers left for an extended period of time will reach equilibrium.		
	Do not want to miss a flush of contaminants	no	no	yes			
	Sample a formation where the hydraulic conductivity is low	yes	yes	yes			

TABLE X2.1 Continued

Require analyte concentrations at a specific point in time (vs. timeaveraged concentrations)

no

ves

yes1

¹If used as a kinetic sampler where sample is collected during linear portion of uptake curve.

^AN/A = Not applicable for this technology

X3. COMPARATIVE STUDIES BETWEEN PASSIVE AND CONVENTIONAL SAMPLING METHODS

At sites where the transition from conventional sampling to passive sampling methods is proposed, some form of comparison study of the two methods can be enlightening or may be required by the regulator. There are two basic approaches to these studies: a side-by-side comparison field test or a comparison of initial passive sampling results with historical data. For a well that has exhibited relatively low variability in temporal concentrations, comparing the passive sampler results to historical data may provide enough information to determine whether conversion to the use of passive samplers is desirable or appropriate. In other instances, direct comparison may be needed to satisfy site requirements.

X3.1 Conducting a Field Comparison Test

X3.1.1 For field-comparison tests, the results from the passive samplers are compared with the results from the conventional sampling method that is being used at the site. Typically the conventional method is a pumped method that involves purging the well prior to collecting the samples; for example, low-flow purging and sampling. For these comparisons, it is important that the passive samples are collected first and then the samples from the conventional pumped method are taken as immediately after as possible. The passive sampler should be deployed at the same depth as the pump (or tubing) inlet. If the well does not already contain dedicated equipment then, if possible, the passive sampler should be deployed at the same time as when the pump (or tubing) is placed in the well. The sampler design and well diameter will dictate whether the passive sampler and the pump can be deployed in the well at the same time. It is important that the passive sampler be fully submerged and left in the well for the proper deployment (or equilibration) period prior to sampler retrieval. When removing the passive sampler from the well, try not to disturb the water column because this can increase turbidity in well and prolong purging prior to collecting low-flow samples.

X3.1.1.1 If the passive samplers and pump equipment cannot be deployed in the well at the same time, then the passive samplers should be carefully removed from the well prior to placing the pump (or tubing) in the well. The former approach reduces potential concentration differences between the two methods that may result from additional well disturbance during equipment deployment or removal at the time of sampling (6).

X3.2 Data Analyses

X3.2.1 While this section provides some general recommendations on how to compare conventional and passive sampling methods, this section is not intended to be an exhaustive explanation of statistical analysis.

X3.2.1.1 The statistical analyses should be conducted on each analyte independently. This approach is preferable because different analytes can behave differently and one analyte may be impacted more by a particular sampling method than another. Also, if the data for different analytes is combined into one data set, there can be concerns whether each data pair (that is, the analyte concentrations for the conventional and passive samples) are truly independent given that the results for multiple analytes were obtained from the analysis of the same samples.

X3.2.1.2 When comparing data from these studies, the quality of the data needs to meet all the DQOs for the site. Therefore, it is important to determine if both sampling methods yield reproducible results. If the relative percent difference or relative standard deviation is used to evaluate the precision of the data-quality results, it is important to remember that the variability between duplicate samples typically increases as concentrations approach the laboratory detection or reporting limit. Data sets where many of the analyte concentrations are near the detection limit can make either of these metrics difficult or impossible to interpret. It is also important to remember when comparing the variability of a passive method with a conventional pumped sampling method that while the passive samples are true co-located duplicate samples, the duplicate pumped samples are taken one after the other without stopping or starting the pump and thus have been defined by some regulators as subsample field duplicates (45).

X3.2.1.3 When comparing the two sampling methods, a paired-t test (or its non-parametric equivalent such as the Wilcoxon Signed Rank test) can be used to determine if there is a statistically significant difference between the two methods (that is, if there is a consistent difference associated with one sampling method versus the other). It may be that the concentrations are significantly higher (or lower) using a passive method. This will be discussed more in the next section.

X3.2.1.4 However, a more useful approach is to simply plot the data for the two sampling methods on an X-Y scatter plot in relation to a 1:1 concentration line. This approach allows for meaningful visual observation of the data. Wells exhibiting outlying data on these plots can be noted and, if need be, later examined to determine the cause(s) of this difference. Linear regression analyses can then be used to determine whether the relationship is linear (on a statistically significant basis) and whether the slope of the regression line is significantly different from 1.0 (assuming a y-intercept of 0). The slope of the line is useful in determining the degree of agreement or difference between the two sampling methods; a slope of 1.0 indicates a 1:1 correlation between the two sampling methods.



X3.3 Interpretation of Comparison—Study Data

X3.3.1 While the majority of the comparisons between pumped and passive methods have shown agreement between the two methods for the majority of analytes and wells, it can be difficult to decide how to proceed in cases where the two methods produce different results. Differences can be expected in some cases because each sampling method represents the aquifer in its own way. Sampler or pump position in the well and aquifer flow regimes, with or without pumping, can affect the two sampling methods differently.

X3.3.1.1 Thus passive samplers may provide data that does not agree with the existing sample database. This can occur when the water sample has undergone some degree of mixing during purging, sampling, or both, and represents a different (often larger) aquifer volume. Also, passive-sampler data taken from multiple depths in a well may provide more specific and detailed high-resolution information in terms of aquifer stratigraphy and contaminant fate and transport.

X3.3.1.2 While different sampling methods may produce different individual sample results (for individual wells), substantial systematic differences (that is, consistent differences or biases) may be cause for concern and should be evaluated with respect to the DQOs of the project and the possible cause(s) for these difference(s). If the differences between the sampling methods (either for the entire site or individual wells) are outside of an acceptable range, follow-up work is needed to explain the reason(s) for the poor correlation. This work can include vertical profiling, bore-hole flow testing, review of the hydrology and well construction information, evaluation of the pumped sampling method, etc.

X3.3.1.3 Variations in the results from different sampling methods sometimes can be attributed to wells that connect zones of significantly different hydraulic head or contaminant concentrations. With passive sampling, analyte concentrations reflect the groundwater concentrations at the sampler location

in the well screen or open borehole. With pumped methods, water from areas not adjacent to the screened interval can be drawn in; for example, water may come from an adjacent zone of higher permeability, along inadequate well seals, or through fissured clay or fractured rock. If the water that is drawn into the pump contains higher (or lower) contaminant concentrations than the ambient water in the well, then the passive sampler results probably will differ. The difference may be due to a variety of factors, including head differences, hydraulic and chemical heterogeneity within the screened or open interval of the well, and the relative permeability of the well bore and well screen. In the absence of ambient vertical mixing in a well, passive samplers can help identify whether chemically stratified zones are present, although the exact location of the stratigraphic interface cannot always be determined. In contrast, pumped methods can combine water from multiple zones, potentially resulting in different mixed concentrations than those found using a passive method.

X3.3.1.4 A borehole flowmeter, multiple passive samplers, or both may help determine how and why passive and pumped methods differ. A borehole flowmeter can assess whether intra-borehole flow is present and multiple passive samplers can be used to determine if contaminant stratification is present. For most of the passive samplers discussed in this document, multiple samplers can be placed at narrow, discrete depths throughout the well screen or borehole, thereby profiling contamination with depth in the well. In those cases, the use of baffles or packers can be used to separate the different sampling intervals.

X3.4 Data Handling

X3.4.1 Because long-term monitoring (LTM) programs generally emphasize evaluating trends, records and reports should clearly identify the date when a change in sampling method occurs (5).

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