

REPRESENTATIVE SAMPLING OF GROUNDWATER FOR HAZARDOUS SUBSTANCES

Guidance Manual for Groundwater Investigations

July 1995
Revised February 2008

California Environmental Protection Agency
Department of Toxic Substances Control

FOREWORD

The California Environmental Protection Agency (Cal/EPA) was created in 1991 by Governor's Executive Order. Six Boards, Departments, and Office were placed within the Cal/EPA "umbrella" to create a cabinet level voice for the protection of human health and the environment. Cal/EPA's mission is to restore, protect, and enhance the environment, to ensure public health, environmental quality, and economic vitality. Within Cal/EPA, groundwater investigations are mainly conducted under the oversight of the Department of Toxic Substances Control (DTSC), the State Water Resources Control Board (SWRCB) and its nine Regional Water Quality Control Boards (RWQCBs). DTSC's mission is to restore, protect, and enhance the environment, to ensure public health, environmental quality, and economic vitality, by regulating hazardous waste, conducting and overseeing cleanups, and developing and promoting pollution prevention. The SWRCB's mission is to preserve and enhance the quality of California's water resources, and ensure their proper allocation and efficient use for the benefit of present and future generations. The mission of the RWQCBs is to develop and enforce water quality objectives and implementation plans which will best protect the beneficial uses of the State's waters, recognizing local differences in climate, topography, geology and hydrology.

Within DTSC's Emergency Response and Statewide Operations Division (ERSO), the Engineering and Geological Services Branch (EGSB), supports the other programs within DTSC by providing expert technical assistance. As part of the EGSB, the Geological Support Unit (GSU) provides geologic assistance, training, and guidance. This document was prepared by GSU staff and it provides guidelines for the characterization and investigation of groundwater at hazardous substance release and hazardous waste sites. It should be used in conjunction with the two-volume companion reference for hydrogeologic characterization activities:

Guidelines for Hydrogeologic Characterization of Hazardous Substances Release Sites (Cal/EPA 1995a)

Volume 1: Field Investigation Manual

Volume 2: Project Management Manual

Within this document, the terms *hazardous substance release site*, *hazardous waste site* and *toxic waste site*, are used synonymously. However, it should be noted that any unauthorized release of a substance, hazardous or not, that degrades or threatens to degrade water quality may require corrective action to protect its beneficial use.

This document is an updated version of and supersedes the document, *Representative Sampling of Groundwater for Hazardous Substances, Guidance Manual for Groundwater Investigations (Cal/EPA 1995c)*. Additional copies of this document may be obtained from DTSC's web site at www.dtsc.ca.gov.

COMMENT SHEET

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California Department of Toxic Substances Control
 5796 Corporate Avenue
 Cypress, California 90630

Attention: Theodore Johnson, C.E.G., C.Hg., Geological Services Unit

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The preparation of this guidance document was achieved through the efforts of many individuals at DTSC. The following people were responsible for editing and writing:

Steve Belluomini	Senior Engineering Geologist
Kathleen Considine	Engineering Geologist
Marie McCrink	Engineering Geologist
Bill Owen	Engineering Geologist
John Woodling	Senior Engineering Geologist

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1.0 INTRODUCTION

The goal of groundwater sampling is to generate effective, meaningful, and representative groundwater chemistry data. Samples representative of in-situ groundwater conditions are those collected by methods that minimize artifacts caused by sampling equipment or procedures. Groundwater sample collection and handling procedures can cause variability in reported water quality concentrations due to differences in personnel, sampling procedures, and equipment (U.S. EPA 1995). The goal of this document is to promote consistent sampling methods in order to minimize variability in groundwater sampling data caused by equipment or procedures.

No single sampling method is applicable for all sampling objectives. As new methods and/or equipment are developed, additional groundwater sampling protocols should be developed and incorporated into this document. This document was revised to include guidelines on low-flow (minimal drawdown) sampling procedures and the use of passive samplers. Key references are cited within this guidance. A more detailed discussion of sampling procedures, devices, techniques, etc. is provided in various publications by the United States Environmental Protection Agency (U.S. EPA) (Barcelona et al. 1985 and U.S. EPA 1993, 2002 (Yeskis and Zavala)) and the U.S. Geological Survey (Wilde et. al. 1998).

1.1 PURPOSE

This document is intended to provide guidelines for the sampling and analysis of groundwater used for the characterization of hazardous substance release and hazardous waste sites. The purpose of this document is to aid in the selection of sampling devices and analytical methods, provide recommended quality assurance and quality control (QA/QC) procedures, and to provide a standardized approach for the presentation of the resulting data. The recommendations contained herein represent minimum criteria judged necessary to obtain quality data and assure reasonable and independently verifiable interpretations.

The recommendations presented here are a subset of the larger site characterization process. Refer to the *Guidelines for Hydrogeologic Characterization for Hazardous Substance Release Sites* (Cal/EPA 1995a) for additional information on investigative tools for site characterization.

1.2 APPLICABILITY

This guidance is applicable to the characterization and investigation of groundwater associated with hazardous substance release sites, hazardous waste sites, and proposed new or expanding school sites under the oversight of DTSC pursuant to the following statutes:

- Hazardous waste sites - Health and Safety Code, division 20, chapter 6.5 – Hazardous Waste Control
- Hazardous substance release sites - Health and Safety Code, division 20, chapter 6.8 – Hazardous Substance Account
- Proposed new or expanding school sites - Education Code, sections 17210, 172101, 17213.1, and 17213.2

1.3 LIMITATIONS

The recommendations presented here represent criteria that can aid in obtaining quality data and assuring reasonable and independently verifiable interpretations. Some sites may require investigative efforts above and beyond the scope of this document, while at other sites a less rigorous application of this guidance may be appropriate. It is the obligation of the responsible parties and qualified professionals performing site investigations to consult with pertinent regulatory agencies, identify all requirements, and meet them appropriately.

This document discusses broad categories of methods and devices used in sampling groundwater. It does not define specific operating procedures for sampling nor propose guidelines for every available

sampling device. This guidance is not intended to exclude alternate sampling approaches; however, any alternative method should only be used with the concurrence of Department of Toxic Substances Control (DTSC). The qualified professional in charge of the field investigation should specify the sampling methods, equipment, and operating procedures in an appropriate work plan and document any significant departures from the work plan.

This document does not supersede existing statutes and regulations. Applicable or relevant and appropriate federal, state and local regulations, statutes, and ordinances should be identified, and site characterization activities should be performed in accordance with the most stringent of these requirements.

2.0 WORK PLAN

A work plan should be prepared for the investigation to be conducted. The work plan provides the purpose of the investigation, summary of site background information, and a description of the tasks to be performed and should include a sampling and analysis plan (SAP) and health and safety plan (HSP). For groundwater investigations, the SAP should specify all procedures and techniques used for groundwater sample collection, sample preservation and shipment, analytical procedures, and chain-of-custody documentation. Field personnel should follow the SAP while performing, collecting, and analyzing groundwater samples. Project tasks and time lines, dates anticipated for initiating and completing monitoring activities may be included in the SAP.

2.1 SAMPLING AND ANALYSIS PLAN

The SAP consists of a field sampling plan (FSP) and a quality assurance project plan (QAPP). The FSP describes, in detail, the sampling and data-gathering methods to be used in the field on a project. The QAPP describes the policy, organization, activities, and protocols necessary to achieve the data quality objectives dictated by the intended use of the data. The SAP should include the following information:

- Field Sampling Plan (FSP)
 - Site background
 - Sampling objectives;
 - Sample location and frequency
 - Sample designation
 - Sampling equipment and procedures
 - Sample handling and analysis
- Quality Assurance Project Plan (QAPP)
 - Project description
 - Project organization and responsibilities
 - QA objectives for measurement
 - Sampling procedures
 - Calibration procedures
 - Analytical procedures
 - Data reduction, validation, and reporting
 - Internal Quality Control
 - Performance and systems audits
 - Preventative maintenance
 - Data assessment procedures
 - Corrective actions
 - Quality assurance reports

Additional guidance on the preparation of SAPs can be found in the *Guidance for Conducting Remedial Investigations and Feasibility Studies Under CERCLA* (U.S. EPA 1988).

During preparation, the following information specific to groundwater sampling should be considered and incorporated into the SAP:

- Sampling objectives
- Pre-sampling activities;
- Sampling method selection
- In-situ or field analyses
- Sample preservation and handling
- Chain-of-custody documentation and records management
- Analytical procedures and quantitation limits for both laboratory and field methods
- Field and laboratory quality assurance/quality control
- Evaluation of data quality

2.1.1 Sampling Objectives

The specific objectives of a sampling effort should describe the intended use of data and should include the collection of samples “representative” of the current groundwater conditions over a specific volume of aquifer (U.S. EPA 2002). In meeting this objective, sampling equipment, sampling method, monitoring well construction, monitoring well operation and maintenance, and sample handling procedures should not alter the chemistry of the sample. A sample obtained from a poorly constructed well, using improper sampling equipment, using poor sampling techniques, or improperly preserving samples, can bias the analytical results. Biased or unrepresentative samples can lead to misinterpretations of groundwater quality data (Nielson 1991 and Nielsen, 2006)

The sampling program data quality objectives (DQOs) should be thoroughly developed, presented and understood by all parties involved in the sampling. The purpose of the sampling effort and data use(s) should be clearly defined when developing the DQOs. For example, DQOs for site assessment sampling to determine if a contaminant is present may differ from those for determining the nature and extent of a contaminant. Differences in the sampling objectives may dictate the type of sampling equipment used, type of information collected, sampling protocol, and analytical scheme.

A dynamic site conceptual model should be constructed to develop appropriate DQOs. The conceptual model, as it applies to the DQOs, should focus on the contaminant fate and transport processes, such as contaminant migration pathways, influence of geologic materials on contaminant migration (e.g. depositional environments, geologic structure, lithology, etc.), contaminant types (e.g., hydrophobic versus hydrophilic, dissolved versus suspended, and processes that influence concentrations of the contaminants present (e.g. dilution, biodegradation, and dispersion) (U.S. EPA 2002). The detail of the conceptual model is dependent on the information available when the plan is developed. The conceptual site model should be modified as new data becomes available. Initial investigations will have a simpler conceptual site model than previously investigated sites. Specific parameters that should be described or shown in a conceptual model that may impact the design of a groundwater-sampling program include:

- Geologic materials controlling contaminant transport to and from the site.
 - Horizontal (lateral) and vertical (thickness) , extent
 - Horizontal and vertical flow direction
 - Horizontal and vertical hydraulic conductivity and contrasts between different geologic materials
- Types of contaminants to be sampled and factors that could bias sampling results.
- Horizontal and vertical distribution of contaminants.

Prior to the completion of a groundwater monitoring well installation program, vertical aquifer characterization is strongly recommended. A detailed vertical aquifer characterization program should include field characterization of hydraulic conductivities, determination of vertical and horizontal flow directions, assessment of lithologic and geologic variations, and determination of vertical and horizontal contaminant distributions (U.S. EPA 2002).

2.1.2 Sampling Frequency

In most situations, sampling frequency should be based on the hydrogeology of the site. There is no minimum or maximum sampling frequency set by DTSC for all sites. Groundwater analytical results should be reviewed periodically, and sampling frequency modified according to data needs, historical water quality trends, and regulatory goals. To track potential seasonal changes in concentration, at least two sampling rounds should roughly coincide with maximum and minimum water table or potentiometric surface elevations. DTSC recommends sampling at least quarterly for a minimum of one year to track seasonal changes and establish water quality trends. The document *Statistical Analysis of Groundwater Monitoring Data at RCRA Facilities, Addendum to Interim Final Guidance* (U.S. EPA 1992a) suggests a method for choosing a sampling interval that will reflect site-specific hydrogeologic conditions. The method uses the Darcy equation to determine the horizontal component of the average linear velocity of

groundwater flow for confined, semi-confined, and unconfined aquifers. This value is used to determine a sampling interval that will yield an independent sample of groundwater. Research performed in the area of groundwater sampling frequency (Barcelona et. al. 1989) indicates that groundwater monitoring data should be carefully collected over long periods of time (i.e. greater than two years) to determine optimal sampling frequency and to delineate seasonal trends in groundwater monitoring results. In this research, groundwater samples were collected biweekly for 18 months and analyzed for 26 water quality and geochemical constituents. The researchers determined that for the study site, groundwater sampling performed four to six times per year would result in an estimated data/information loss below 20 percent and would minimize redundancy. The researchers concluded that by using careful sampling and analytical procedures, sampling and analytical errors can be controlled to approximately ± 20 percent of the annual mean inorganic chemical constituent concentration in groundwater.

2.1.3 Pre-Sampling Activities

The following activities should be conducted before each sampling event.

2.1.3.1 WELL-HEAD INSPECTION

Well-head conditions (e.g., condition of well casing, well lock, marking, standing water at surface, condition of surface pad, and annular seal) and any suggested maintenance should be assessed and documented in the field notes. The SAP should describe procedures and schedules for performing routine well maintenance. Incidental maintenance should be documented and conducted in a timely manner. A well-head maintenance checklist should be included in the SAP. The well-head inspection should include gas monitoring in and around well-heads and well vaults.

2.1.3.2 STATIC WATER LEVEL ELEVATION MEASUREMENT

The SAP should include provisions for measuring the static water elevation in each well prior to each sampling event. Measurement of water level elevations on a continuing basis is important to determine whether horizontal and vertical components of the hydraulic gradient change over time. A change in groundwater flow may necessitate modification to the design of the groundwater monitoring system. The following methods for determining water level elevations are suggested:

- Electric water level sounders
- Pressure transducers

These devices and other methods are described in more detail in U.S. EPA (1987), Aller et al. (1989), Nielsen (1991), and ASTM D4750 (2001). The SAP should specify the device to be used for water level measurements, procedure for measuring water levels, and accuracy of the measuring device.

The following criteria should be met when determining water level elevations in monitoring wells or piezometers:

- The top of the well casing should be surveyed and tied into a known vertical datum.
- Each well should have a permanent, easily identified reference point from which all depth measurements are taken. The reference point (the top of the inner casing, outer casing, or security/protective casing) should remain constant through all measurements, should be clearly marked on the casing and its description recorded. The inner casing should be used as a reference point, since the outer casing and surrounding area may be affected by other phenomena (e.g., general instability of outer casings due to frost heaving, and vehicular damage) which could cause movement of casings. The elevation of this reference point should be known and clearly marked at the well site (Nielsen, 1991 and Nielsen, 2006). This reference point should also have a known latitude and longitude consistent with the Regional and National Minimum Data Elements requirements. The elevation of the reference point should be surveyed relative to Mean Sea Level (MSL) using the NAVD 88 datum (U.S. EPA 2002).

- After well construction and development, water levels should be allowed to stabilize for a minimum of 24 hours prior to measurement. Low yield aquifers may take longer, and several water level measurements should be made over a period of several days to ensure that adequate recovery has occurred.
- Water levels (the depth to standing water) should be accurately measured with a precision of ± 0.01 foot from the survey datum on the top of the well casing. The method or device used to measure water levels should be sufficiently sensitive so that a measurement to 0.01 foot can be reliably obtained.
- Water level measurements used to establish a water table (the surface of the zone of saturation) or any single potentiometric surface should be collected as soon as practicable (e.g., within less than one day). This practice is adequate if the magnitude of change is insignificant over a specific time period. In certain situations, small water level changes could be significant or site-specific variables may warrant collecting water level measurements within a short time interval. These situations may include:
 - tidally influenced aquifers
 - aquifers affected by river stage, bank storage, impoundments, and/or unlined ditches
 - aquifers stressed by intermittent pumping of production, irrigation or supply or remediation wells
 - aquifers being actively recharged because of recent precipitation
 - aquifers that demonstrate significant water level fluctuations in response to barometric pressure changes
- Water level and well depth measurement equipment should be constructed of chemically inert materials not prone to sorption or desorption.
- Water level and well depth measurement equipment should be decontaminated prior to use at each well to ensure sample integrity and prevent cross-contamination of groundwater.
- Devices used to measure water levels and well depths should be periodically calibrated.
- Total well depth measurements should be made periodically using a weighted tape measure or marked cable. The purpose of these depth-to-bottom measurements is two-fold. The first is to determine the length of the water column for purposes of well volume purging calculations. The second is to determine if the well is filling with sediment over time indicating the need for periodic removal of bottom sediments and/or well redevelopment. The weight should be heavy enough to keep the tape measure straight and it should be blunt so that it will not penetrate soft materials on the bottom of the well. The deeper the well, the heavier the weight has to be to "feel" the bottom of the well. Standing water level measuring devices may not be appropriate for making well depth measurements. For wells with dedicated equipment, the total depth should be measured anytime the pump is removed for repair or maintenance or when indicated by elevated turbidity measurements.

Note: When using a well volume purge procedure, depth-to-bottom measurements should be made *before* purging and calculating the purge volume. For other sampling methods, where the well volume calculation is not critical (e.g., low-flow sampling), the depth-to-bottom measurement should be conducted *after* sampling to avoid generating artifact turbidity and to minimize the possibility of introducing contaminants before sampling.

2.1.3.3 DETECTION OF IMMISCIBLE LAYERS

The SAP should include provisions for detecting and measuring the thicknesses of immiscible liquid contaminants, such as light non-aqueous phase liquids (LNAPLs) and dense non-aqueous phase liquids (DNAPLs), if present or likely to be present each time the water level is measured. LNAPLs, also known

as "floaters", are organic liquids, less dense than water, that tend to spread across the water table (in unconfined aquifers). DNAPLs, also known as "sinkers", are relatively insoluble organic liquids that are denser than water. DNAPLs tend to migrate downward and accumulate on underlying lower impermeable intervals. The detection of immiscible layers requires specialized equipment that should be used before a well is evacuated for conventional sampling. The SAP should specify the device(s) to be used to locate and determine the thickness of LNAPLs and DNAPLs, as well as the procedures to be used for detecting and sampling these contaminants.

Extra health and safety precautions should be taken when asphyxiates, LNAPLs or DNAPLs are expected in a well, and the lead regulatory agency should be notified when they are detected.

2.1.3.3.1 LNAPL Detection/Collection

The SAP should specify the following procedures for detecting the presence of LNAPLs. These procedures should be followed before the well is purged for conventional sampling.

1. Open the well vault and sample the air in the vault for target vapors using an appropriate testing device capable of detecting the contaminant; typically, a photoionization detector or an organic vapor analyzer is used for common organic contaminants. Record the measurement results. The air above the well head should be monitored to determine the potential for fire, explosion, or health and safety hazards. Air monitoring also serves as a first indication of the presence of LNAPLs. The presence of LNAPLs precludes the exclusive use of water level sounders to make a determination of static water level.
2. Inspect the well vault and the well head to observe evidence of infiltration or danger.
3. If it is safe to do so, and the lid can be opened without introducing non-native materials into the well, remove the locking and protective caps.
4. Sample the air in the well head for target vapors using an appropriate testing device and record the measurements.
5. Two possible methods to determine the presence of LNAPL are:
 - a. Gently lower a clear disposable bailer into the well to just below the fluid level and retrieve a sample. Use of a clear bailer is best for visually determining the presence of very thin or sheen-type layers.
 - b. Alternatively, lower an interface gauging probe or a weighted tape coated with commercially available reactive indicator into the well to determine the depth to the air/LNAPL and the LNAPL/water interfaces. The interface probe serves two related purposes. First, as it is lowered into the well, the probe registers when it is exposed to an organic liquid and thus identifies the presence of LNAPLs. Secondly, after passing through the LNAPL layer, the probe indicates the depth to water. Careful recording of the depths of the air/LNAPL and LNAPL/water interfaces establishes a measurement of the thickness of the LNAPL in the well casing.
6. The approach to collecting LNAPL samples depends on the depth to the floating layer surface and the thickness of the layer. A sample of the LNAPL should be collected without purging the well. To collect an LNAPL sample, a bottom valve bailer is the equipment of choice. The bailer should be lowered slowly until contact is made with the surface of the LNAPL. The bailer should then be lowered to a depth less than that of the LNAPL/water interface depth, determined beforehand using the interface probe.

2.1.3.3.2 DNAPL Detection/Collection

The SAP should specify the following procedures for detecting the presence of DNAPLs. These procedures should be followed before the well is evacuated for conventional sampling:

1. Open the well vault and sample the air in the vault for target vapors using an appropriate testing device capable of detecting the contaminant; typically a photoionization detector or an organic vapor analyzer is used for common organic contaminants, but specialized equipment should be employed where potentially dangerous volatiles are suspected. Record the measurement results. The air around and below the well head should be monitored to determine the potential for the accumulation of dense gases or low oxygen conditions. Air monitoring also serves as a first indication of the presence of DNAPLs. A water interface probe may be used to locate the depth to water, but the presence of DNAPLs can not be determined through the exclusive use of water level sounder.
2. Inspect the well vault and the well head to observe evidence of infiltration or danger.
3. If it is safe to do so, and the lid can be opened without introducing non-native materials into the well, remove the locking and protective caps.
4. Sample the air in the well head for target vapors using an appropriate testing device and record the measurement results
5. Determine the static groundwater level using a water level sounder or other device listed in Section 2.1.3.2.
6. Two possible methods to determine the presence of DNAPL are:
 - a. lower an interface probe (conductivity or resistivity sensor) to the well bottom to determine if an organic liquid is present; or
 - b. lower a transparent, double check-valve bailer to the bottom of the well and withdraw a sample to visually check for the presence of DNAPL. DNAPLs should be collected by slowly lowering and raising the bailer within the well or leaving the bailer in the bottom of the well for an extended period (i.e., overnight).

2.1.4 Sampling Method Selection

Sampling method selection should be based on site-specific conditions and site-specific DQOs. DQOs for the data collection activity include the overall level of uncertainty that a decision-maker is willing to accept in results derived from environmental data. This uncertainty is used to specify the quality of the measurement data required, usually in terms of objectives for precision, bias, representativeness, comparability, and completeness. As described in Chapter One of SW-846, DQOs should be defined prior to the initiation of the field and laboratory work (U.S. EPA 1992b).

Field and laboratory organizations performing the work of the DQOs should be informed so their personnel may make informed decisions during the course of the project to attain those DQOs. The procedures used to characterize the hydrogeology of a site, to design and construct a monitoring network, to collect and analyze environmental samples, and to evaluate analytical results should ensure that the data are of the type and quality necessary to allow for the detection of contamination when hazardous substances have migrated from the waste management area (U.S. EPA 1992b). Please refer to Section 2.1.1, Sampling Objectives, for additional information.

Method selection refers to the type of sampling method that will be used at the site, such as low-flow, bailer, or passive samplers. Implementation of each method will differ at each site and at specific wells. Some criteria to be considered when selecting a sampling method include location of the sampling intake, purge completion measurements, the general composition of the groundwater, recharge rates, and

degree of screen submersion. Each of these and other site-specific conditions should be considered when selecting a groundwater sampling method for a site. Regardless of the sampling method used at the site, detailed step-by-step procedures and rationale for the proposed sampling method should be included in the SAP.

Sampling method selection should take into consideration that water in a well screen and surrounding filter pack is generally in a state of flux, while water in the blank casing above the screen tends to stagnate (Robin and Gillham 1987, Powell and Puls 1993, U.S. EPA 2002, and ASTM 2002). Groundwater sampling methods that purge relatively large volumes from the well to achieve a representative sample must ensure that the blank casing water is effectively removed before sample collection. Methods that do not remove multiple casing volumes must ensure the sampling location is within the screen interval to assure formation water is sampled. Non-pumping sampling methods, also known as passive sampling, relies on a constant state of flux in the screen zone and that samples are collected from the actively flushed portion of well (i.e. the screen zone).

The following sections include details of several common sampling methods. However, other methods may be applicable to a groundwater monitoring program. Methods not included here can be proposed to the regulatory agency, detailing the proposed method. Alternate methods, meeting site data quality objectives, are encouraged.

2.1.4.1 CHANGING SAMPLING METHODS

Cal-EPA recognizes sampling technologies or methods will evolve. During the site investigation or remediation, new technologies or sampling methods may be proposed. Maintaining the same sampling method throughout the life of a project, provided the method is carried out the same way every time (e.g., pump inlet depth), removes a variable that may impact sample results. However, a new method may be proposed as being more cost effective and capable of providing a representative sample. In cases where a new sampling method is proposed to replace a previous sampling method, some type of comparison evaluation is necessary. When applicable, comparisons should include conversion between volume-based purging and sampling and low flow purging and sampling.

Comparison between two sampling methods can be in the form of side-by-side evaluations (collection of water samples using the two different sampling methods over a period of time, trend evaluations (change sampling method and provide the trend plots from the previous and new sampling method on the same graph), or a combination of methods. How the method(s) will be compared and evaluated should be established prior to initiation of the new sampling method and presented in an appropriate workplan or SAP. Results of the comparison sampling can be provided in either a separate groundwater sampling report or incorporated into an existing routine groundwater report (e.g., quarterly groundwater monitoring report).

2.1.4.2 WELL PURGING METHOD SELECTION

Water standing in a monitoring well casing may not be representative of in-situ formation groundwater quality. Water in the blank (unscreened) portion of the well is generally considered “stagnant” and non-representative. Studies have shown that water within the screened section of a well can be representative of adjacent groundwater (Robin and Gillham 1987, Powell and Puls, 1993, U.S. EPA 2002, ASTM 2002). In cases where water from the “stagnant” casing cannot be separated from the screen zone water (e.g. during bail sampling, or due to drawdown during pumping), purging of well water is conducted to assure screen zone formation water is collected.

Well purging and the requirements for completion criteria were updated and revised in the groundwater literature over the last 20 years. This guidance incorporates findings of available research and field practice, as well as allowing for new findings and new technologies, and includes discussion and rationale for several well sampling procedures. No judgment is made about what purging methodology is most appropriate in every scenario because different sampling approaches may be applicable for different sampling needs. The overarching purpose of the guidance is to outline the requirements of several sampling protocols and to help the user choose a protocol appropriate for site-specific DQOs. For

methods not specifically discussed, it is recommended that the user incorporate elements of a similar method/protocol in the SAP and discuss variances with the site's lead regulator for concurrence on the sampling methodology prior to sampling.

The SAP should include detailed, step-by-step procedures for the selected purge method including the purge method rationale. Depending on the type of purge method chosen, the SAP should contain descriptions of the equipment to be used for pumping, the instrumentation used to quantitatively measure water quality indicator parameters (including calibration methods), intervals between parameter readings, well drawdown, the location of the pump in relation to the well screen and water table, and the purge pump rate.

2.1.4.3 PURGE METHODS

Well purging methods are as follows:

1. Purge a Minimum of Three to Five Well Casing Volumes. This approach is based on the removal of a sufficient volume of water from the well prior to sample collection to assure "stagnant" or non-representative water is removed and formation water is being sampled. The minimal volume is cited as three to five casing volumes (U.S. EPA 1987, Wilde et. al. 1998) reportedly based on engineering calculations used to determine effective flushing. For enforcement purposes, U.S. EPA recommends the collection of water quality stabilization parameters (U.S. EPA 1998) during purging. As technology and experience with the practice of well sampling advanced, the collection of indicator parameters to document parameter stabilization with this method became routine. In such cases, many SAPs stipulate well purging will cease when one of the two criteria first occurs, either removal of the minimal purge volume (usually three casing volumes) or the attainment of the parameter stabilization criteria.
2. Purge to Stabilization. This approach is referred to as "Purging to Stabilization" or "Well Volume Approach" (U.S. EPA 2002). This method evolved from the traditional three to five well volume/parameter stabilization approach, but without purging a fixed minimum number of well volumes. The method is based on continuously monitoring groundwater indicator parameters during purging until they have stabilized within an acceptable range, at which point stagnant water is presumed to be removed and steady-state conditions achieved. When parameter stabilization occurs, the sample is presumed to be representative. This approach became possible with the development of flow-through cell water quality indicator parameter measurement instruments with continuous data recording capability, which greatly enhanced the ability to determine parameter stabilization characteristics and assurance of steady state conditions. The critical issue with this purge method is to define the criteria for indicator parameter stabilization (e.g., the time interval between measurements, minimal purge time, purge rate, and parameter selection.) Refer to U.S EPA 2002b for an example protocol for this purge method.
3. Low-Flow Purging ("Low-Stress Approach", "Micro-Purge Method" or "Minimal Drawdown Method"). Low-flow purging practices (Puls and Barcelona 1996) were the culmination of numerous observations and studies, in the late 1980s and early 1990s, that groundwater generally flows through the monitoring well screen with sufficient velocity to maintain an exchange with formation water surrounding the screen. If water is removed from a well at rate minimizing stress to the groundwater system, as measured by drawdown in the well, then the pumped water should be representative of formation water after water level and parameter stabilization. In low-flow purging, the pump intake must be situated within the screened portion of the well, and well drawdown must be minimized (Puls and Barcelona 1996). This approach effectively isolates the screened interval from the overlying (stagnant) casing water which the more traditional methods remove by purging. Groundwater indicator parameters are measured during low-flow purging and purging is considered complete, regardless of the amount of water removed from the well, when the indicators parameters have stabilized. During purging, careful measurement and documentation of water levels and pump rate are required to assure that this

method is being effectively performed. Puls and Barcelona recommend this method not be used with well screen intakes greater than ten feet. Refer to U.S EPA 2002a for an example protocol for this purge method.

DTSC recommends the type of sampling method chosen be determined on a well-by-well basis, depending on the hydraulic properties of the monitored zone, the physical nature of the contaminants, and the hydraulic performance of the well (Barcelona et al. 1990, Barcelona, 1985). DTSC will consider the following recommendations and requirements when evaluating monitoring well purge methods:

- Some purge method strategies may be better suited to specific site conditions than others. For example, purging three to five well volumes may detect contamination, while a low-flow method, at the same well, may not. This may be due to the differing hydraulic influence (i.e. radius of influence) of each method. At sites where characterization is limited or uncertain, where well characteristics are not fully known, or where specific constituents are sensitive to certain purge methods, side-by-side comparisons between purging protocols should be considered to determine which method should be used to yield the most representative data or to meet the site-specific DQOs.
- The use of purging equipment which can excessively disrupt the well and potentially affect sample quality, such as bailers or vacuum systems, are discouraged. The use of a dedicated pump is recommended to minimize turbulence during sampling and eliminates the need for equipment decontamination.
- Pump placement within the well may be critical to effective purging. The depth of pump placement should be determined based on the selected purge method, pump design, aquifer characterization, well characteristics, and the nature of contaminants. Comparative sampling at various depths within the screen interval may be required to avoid missing zones of contamination or preferential contaminant pathways.
- Wells should be purged at rates below those used to develop the well. This is to prevent excessive stress on the well (i.e. inducing high turbidity), to prevent damage to the well, and to avoid disturbing accumulated corrosion or reaction products in the well (Puls et al. 1990; Puls and Barcelona 1989a, Puls and Barcelona 1989b, Barcelona et al. 1985). A low purge rate will also reduce the possibility of stripping volatile organic compounds (VOCs) from groundwater, and will reduce the likelihood of mobilizing solids in the subsurface that are immobile under natural flow conditions. However, purge rates should not be purposefully kept low to mask deficiencies in well design or development, as shown by excessively high turbidity. Water quality parameters should be resampled at the lower sampling rate to ensure water quality parameters are stable.
- Water levels should be monitored during purging and sampling to ensure the proper pump flow rate is used to provide minimum drawdown and/or water level stabilization.
- Water quality indicator parameters should be measured in all cases to document stabilization and steady-state conditions. Parameters should include temperature, specific conductance, pH, oxidation-reduction potential (ORP), and dissolved oxygen (Puls and Eychaner 1990, Puls et al. 1990; Puls and Barcelona 1989a, Puls and Barcelona 1989b). In general, the order of parameter stabilization is pH, temperature, specific conductance, ORP, dissolved oxygen, and turbidity. In-line flow-through cells instruments are preferred, and are considered essential for the purge to stabilization method. Turbidity measurements should be collected during purging, and should be used to evaluate the need to redevelop monitoring wells.
- Parameter stabilization should be based on the criteria shown in Table 1, at the end of this section. The intervals between parameter readings should be based on either a set time interval or a specified volume of water purged. These intervals (time or water volume) should be of

sufficient spacing and quantity to assure true stabilization trends are achieved before sampling. At a minimum, four parameter stabilization measurements should be recorded while purging.

- At a minimum, wells with screens below the water table should be purged of a volume of water equivalent to the volume of water standing in the blank casing of the well above the screened interval.
- For wells screened in media with low hydraulic conductivities, special considerations apply. If development data or pump tests show a well will either pump to dryness or that pumping will expose a significant portion of the saturated screen interval, the well recharge rate should be quantitatively determined to evaluate if water is entering the well with excessive turbulence. Turbulent flow can cause a significant loss of volatile contaminants and may affect water chemistry. Once identified and characterized, such wells should be purged at sufficiently low pump rates to avoid turbulent flow (low-flow).
- The purging/sampling method should ensure formation water does not cascade (i.e. flow vertically down the screen) down the sides of the well screen (this may occur when the water level in the well is lowered into or below the screened interval). Laboratory experiments have shown that unless cascading is prevented, up to 70 percent of the volatiles present could be lost before sampling. At no time should a well be purged to dryness if recharge causes formation water to cascade down the sides of the screen, as this may cause an accelerated loss of volatile constituents, resulting in a sample not representative of actual groundwater quality. This problem should be anticipated; water should be purged from the well at a rate that does not cause recharge water to be excessively agitated.
- Wells recharging at a slow rates should be sampled as soon as a sufficient volume of groundwater has entered the well to enable the collection of the necessary groundwater samples. Re-purging should be performed if a well is inactive for more than 24 hours after full recharge.
- Purged water should be stored in appropriate containers until analytical results are available, at which time proper arrangements for disposal or treatment should be made.

TABLE 1. Stabilization Criteria with References for Water-Quality-Indicator Parameters

Parameter	Stabilization Criteria	Reference
Temperature	± 3% of reading (minimum of ± 0.2° C)	SAM 2002
pH	+/- 0.1	Puls and Barcelona, 1996; Wilde et al., 1998
specific electrical conductance (SEC)	+/- 3%	Puls and Barcelona, 1996
oxidation-reduction potential (ORP)	+/- 10 millivolts	Puls and Barcelona, 1996
dissolved oxygen (DO)	+/- 0.3 milligrams per liter	Wilde et al., 1998

2.1.4.4 PUMP INTAKE POSITION

There are two positions for pump intake placement, within the screened interval or the blank casing above the screen. Each of these positions has advantages and disadvantages based on the portion of the screen sampled, data reproducibility, and potential purge volumes (U.S. EPA 2002).

The vertical location within the well where the pump is placed during an assessment is of primary concern. Unless adequate precautions are taken to lower the pump into the exact position used in previous sampling rounds, or a dedicated system is used, the position of the sampling pump intake may vary between sampling rounds potentially resulting in sampling different zones within the aquifer. When the pump intake location varies along the well screen, reproducibility of the sampling results can be reduced. The variability of sample collection points along the well screen length can be reduced by using dedicated sampling pumps or a premeasured sampling pump hose.

To minimize the contact time between groundwater and the well construction materials during sampling, and ensure the evacuation of the stagnant water above the screen, Keely and Boateng (1987) suggested that the sample pump be gradually lowered through the submerged blank casing while purging. This would minimize contact time between the groundwater and the well construction materials while sampling, as well as ensure the evacuation of the stagnant water above the screen. (U.S. EPA 2002).

DTSC recommends placing the pump intake location during sampling within the well screen, instead of above it, to minimize potential mixing of stagnant water, to minimize the required purge time, and to keep the intake off the bottom of the well where accumulated sediment may be disturbed and drawn into the sample. Locating the pump intake centrally within the well screen provides the best opportunity to collect samples representative of water across the entire well screen (Varljen 2006). Shorter well screens are preferred to reduce concentration averaging across large profiles of the aquifer and to reduce time required for water to reach the pump intake from portions of the screen distant from the pump intake.

2.1.4.5 PASSIVE METHODS

Passive Sampling. Passive sampling approaches do not incorporate purging or pumping as part of the groundwater sampling method. These include diffusion samplers such as polyethylene diffusion bags (PDB), or rigid porous pipe samplers (RPP); *equilibrated* grab samplers such as the Snap Sampler or Hydrasleeve; and sorptive samplers such as the Gore sampler. These devices are placed in the screened section of wells for a device-specific equilibration period. Most devices can be left downhole between sampling events. Passive methods rely on ambient aquifer flow-through to deliver groundwater to the sampling device. The operation of these devices includes exposure and diffusion of contaminants of concern into the sampling device, or collection of a whole water sample at a user-identified collection event.

2.1.4.6 GROUNDWATER SAMPLING EQUIPMENT SELECTION AND USE

The following is a list of the most common categories and types of groundwater sampling devices (Nielsen 2006, Pohlmann and Hess 1988, ITRC 2007):

- Active
 - Grab samplers (e.g. bailers and syringe devices)
 - Positive displacement pumps (e.g. gear drive, bladder, helical rotor, piston, and centrifugal)
 - Suction lift pumps (e.g. peristaltic)
 - Gas contact pumps
- Passive
 - Polyethylene Diffusion Bags
 - Rigid Porous Pipe Samplers
 - Dialysis Membrane Sampler
 - Snap Samplers
 - Hydrasleeve

- Gore Sampler

DTSC prefers all sampling equipment be dedicated to a particular well. To encourage innovation, DTSC may allow the use of other devices that are not specifically mentioned above if it can be demonstrated that the device will yield “representative” groundwater samples.

The following criteria should be considered when selecting sampling equipment:

- Sampling equipment should be chosen based on the analytes of interest and the characteristics and depth of the saturated zone from which the sample is withdrawn. For example, the choice of sampling equipment should reflect consideration of the potential for LNAPLs and DNAPLs.
- Sample collection equipment should not alter analyte concentrations, such as by sorption or desorption, degradation, or corrosion.
- Sampling equipment should cause minimal sample agitation and should be selected to reduce/eliminate sample contact with the atmosphere during sample transfer. Sampling equipment should not allow volatilization or aeration of samples that may alter analyte concentrations.

Appendix A briefly discusses each category and various types of sampling devices, including their appropriateness for use and relative advantages and disadvantages.

2.1.4.7 DECONTAMINATING SAMPLING EQUIPMENT

When dedicated equipment is not used for sampling (or purging), or when dedicated equipment is stored outside of the well, the SAP should include procedures for disassembly and cleaning of equipment before each use at each well.

Disposable items such as rope and low-grade tubing should be properly disposed between wells. Thoroughly cleaning equipment parts that come into contact with well water is especially important. In addition, a clean plastic sheet should be placed adjacent to or around the well to prevent surface debris from coming in contact with the purging and sampling equipment. Clean sampling equipment should not be placed on the ground or on other contaminated surfaces prior to insertion in the well. The effects of cross-contamination can be minimized by sampling the least contaminated well first and progressing to more contaminated ones. Equipment blanks to document the effectiveness of the decontamination procedures should be collected on a regular basis from non-dedicated equipment. The frequency depends on the SAP and regional protocols.

The following cleaning procedure is recommended for organic constituents:

1. Wash the equipment with a non-phosphate detergent
2. Rinse with tap water
3. Rinse with organic-free reagent water or deionized water

If separate phase or hydrophobic contaminants are present (such as LNAPL, DNAPL, high levels of contaminants, etc.), additional decontamination steps may be added. For example, an organic solvent, such as reagent-grade isopropanol or acetone may be added as a first spraying/bucket prior to the soapy water/tap, water/deionized rinse procedure/buckets.

The following cleaning procedure is recommended for inorganic constituents:

1. Wash the equipment with a non-phosphate detergent/soap mixture
2. Rinse with dilute (0.1Mole) hydrochloric or nitric acid
3. Rinse with tap water

4. Rinse with reagent water. Dilute hydrochloric acid with a reagent water rinse is preferred when cleaning stainless steel because nitric acid may oxidize the steel.

The waste decontamination fluids should be containerized and characterized to determine whether they should be treated or disposed of as hazardous waste.

2.1.4.8 COLLECTING GROUNDWATER SAMPLES

Monitoring well sampling should always progress from the well expected to be least contaminated to the most contaminated, to minimize the potential for cross-contamination of samples that may result from inadequate decontamination of sampling equipment. Samples should be collected and containerized according to the volatility of the target analytes. The preferred collection order for some of the more common groundwater analytes is as follows:

- Volatile organic compounds (VOCs)
- Semivolatile organic compounds (SVOCs)
- Major water quality cations and anions
- Stable isotopes (e.g. oxygen, hydrogen, nitrogen, lead)
- Metals
- Cyanide
- Turbidity
- Radionuclides

The following guidelines should be adhered to while using and operating groundwater sampling equipment:

- Check valves should be designed and inspected to ensure that fouling problems do not reduce delivery capabilities or result in aeration of samples.
- Sampling equipment (especially bailers) should never be dropped into the well, as this will cause degassing of the water upon impact.
- Sampler contents should be transferred to sample containers in a way that will minimize sample agitation and aeration.
- Clean sampling equipment should not be allowed to come into contact with the ground or other contaminated surfaces prior to insertion into the well.
- The rate at which a well is sampled should not exceed the rate at which the well was purged. Sampling rates of less than one liter per minute are suggested for wells that have historically yielded turbid samples (Puls et al., 1990). Wells are routinely sampled at rates as low as 100 to 500 milliliter per minute (Puls, et al., 1990; Puls and Barcelona, 1989a).
- Water levels should be monitored during purging and sampling to ensure the proper pump flow rate is used to provide minimum drawdown and/or water level stabilization.
- If the rates of purging and sampling are different, the sample water should be verified as stable by collecting additional field parameters and utilizing the stabilization criteria herein.
- If a flow through cell is used, groundwater samples should be collected before the flow-through cell, between the flow-through cell and the well head. Installation of a Y-fitting approximately 1 foot from the inlet to the flow-through cell will facilitate sampling without interrupting flow.

2.1.5 In-Situ or Field Analyses

Physically or chemically unstable analytes should be measured in the field, rather than in the laboratory. Examples of unstable parameters include pH, redox potential, chlorine, dissolved oxygen, ferrous iron, alkalinity, and temperature. It is suggested that dissolved oxygen, turbidity, and specific conductance be determined in the field as soon as practicable. Although the specific conductance (i.e. electrical conductance) of a sample should be relatively stable, DTSC recommends that this analyte also be measured in the field. Most conductivity instruments require temperature compensation; therefore, the temperature of the samples should be measured at the time conductivity is determined unless the instrument automatically makes this compensation.

Three methods can be employed for measuring unstable field parameters:

- Specially designed meters with probes that may be lowered down into the well.
- In-line flow-through monitoring chamber with ports for probe attachment, allowing continuous readings during purging
- Collect a sample in a clean bottle or beaker in the same manner that a sample for laboratory analysis would be collected, and then to analyze the sample using field test kits or meters.

Unstable parameters should be measured in samples collected from the well after the well has been purged and before samples are collected for laboratory analysis. If down-hole probes (pH electrode, specific ion electrode, and thermistor) are used to measure unstable parameters, the probes should be decontaminated in a manner that prevents the probe(s) from contaminating the water in the well. In no case should field analyses be performed directly on samples that will be submitted for laboratory analysis. Monitoring probes should not be placed in shipping containers containing groundwater samples for laboratory analysis. Dissolved oxygen should only be measured with a flow-through cell or downhole instrument.

The SAP should list the specific parameters that will be measured in the field, types of instruments (e.g. downhole probes, meters) that will be used to make these measurements, and describe the procedures for operating the instruments and recording the measurements. The SAP should describe all instrument calibration procedures, including the frequency of calibration. The description of calibration procedures should include: discussion of initial calibration, multi-level calibration for determination of usable range, periodic calibration checks, conditions that warrant re-calibration of instruments, acceptable control limits, and the maintenance of calibration records in the field log book. All instruments should be calibrated with standards that have not exceeded their expiration dates. At a minimum, all field instruments should be calibrated at the beginning of each use and in accordance with the frequency suggested by the manufacturer. Field instruments should be calibrated using at least two calibration standards spanning the range of results anticipated during the sampling event. For example, the pH meter should be calibrated at 4 and 7 pH, or at 7 and 10 pH, dependent if the anticipated pH of the groundwater is either acidic or basic, respectively.

2.2 SAMPLE PRESERVATION AND HANDLING

The procedures employed for sample preservation and handling are nearly as important for ensuring the integrity of the samples as the collection device itself. Detailed procedures for containerization, preservation, packaging, and handling (e.g. shipped daily by overnight courier) should be provided in the SAP. Samples collected from a well should never be composited in a large container for subsequent transfer to the appropriate smaller bottles. Regardless of the analytes of concern, exposure of the samples to the ambient air should be minimized.

Splitting of samples is sometimes required for quality assurance/quality control purposes. When sampling for VOCs, the procedure is changed slightly. For non-VOC samples, one half of the sample is emptied from the sampling device into one container, and one half is emptied into the other, with the procedure being repeated until the containers are full. For VOCs, however, the first volatile organic analysis (VOA) container should be completely filled and sealed, and then the VOA container into which the other split sample will be placed should be completely filled and sealed.

2.2.1 Sample Containers

The SAP should identify the type of sample containers to be used to collect samples, as well as the procedures used to ensure that sample containers are free of contaminants prior to use. The SAP should refer to the specific analytical method that designates an acceptable container and sufficient sample quantity.

The most important factors to consider when choosing sample containers are compatibility with the contaminant or waste, cost, resistance to breakage, and volume. Containers must not distort, rupture, or leak as a result of chemical reactions with constituents of concern. The containers must have adequate wall thickness to withstand handling during sample collection and transport to the laboratory. Containers with wide mouths are often desirable to facilitate transfer of samples from samplers to containers.

New containers should be prepared based on the analyte of interest; used containers are to be discarded. The cleanliness of a batch of precleaned bottles should be verified in the laboratory. The residue analysis should be available prior to sampling in the field.

2.2.2 Sample Preservation

The SAP should identify the sample preservation methods that will be used. Methods of sample preservation are relatively limited, and are generally intended to 1) retard biological action, 2) retard chemical reactions such as hydrolysis or oxidation, and 3) reduce sorption effects. Preservation methods are generally limited to pH control, chemical addition, refrigeration, and protection from light.

Most sample containers provided by a laboratory have pre-added preservative if the analyte of interest requires preservation. If these are not available, then preservatives should be added in the field. Samples should not be brought back to the laboratory for preservation. For pH control, test strips should be used to verify that samples have attained the appropriate pH range for sample preservation.

Most commercial shipping containers ("coolers") leak when the interior water level reaches the lid-body interface and may result in the carrier refusing to ship the container. For this reason, DTSC recommends using two water-tight sealable polyethylene bags for shipping. The first will contain the sample bottles, the second the ice needed to keep the samples at 4 ± 2 °C. Glass containers should be protected from breakage using holders bubble wrap and/or vermiculite. The vermiculite will also absorb any spills or melted ice. The number of samples in the cooler should not prevent effective sample preservation (i.e. cooling). Blue ice should only be used if the samples are pre-cooled before shipping, since blue ice may not chill the samples sufficiently for the duration of the trip to the laboratory. Care should also be taken with the VOC samples to prevent freezing in transit.

As specified by U.S. EPA (1998), a temperature history of the samples should be maintained as a quality control measure. This is done by recording the temperature on the chain-of-custody record (Section 2.3.4) before the sample containers are sealed for shipment. Upon receipt of the shipment, the laboratory is required to record the temperature at receipt on the chain-of-custody record. A temperature blank should be included in the cooler (i.e. a vial or container filled with clean water and marked as such, which is measured by the laboratory upon receipt).

Holding time refers to the period that begins when the sample is collected from the well and ends with its extraction or analysis. Holding time is not measured from the time the laboratory receives the samples. Any laboratory submission to DTSC should contain the date/time sampled, the date/time received, the date/time extracted, and the date/time analyzed.

2.2.3 Special Handling Considerations

During groundwater sampling, every attempt should be made to minimize changes in the chemistry of the samples so that data representative of subsurface hydrogeochemistry are collected. DTSC agrees with the following U.S. EPA protocols that will assist in preserving the natural chemistry of groundwater samples:

- Do not routinely filter groundwater samples in the field.
- Do not transfer samples from one sample container to another.
- Do not allow headspace in the containers of samples that will be analyzed for volatile organic compounds, alkalinity, and dissolved gases.

2.2.3.1 SAMPLE FILTRATION

Decisions to filter samples should be dictated by sampling objectives rather than as a fix for poor sampling practices. Field-filtering of certain compounds should not be the default. Evaluation of what the application of field-filtration is trying to accomplish should be considered (Puls and Barcelona 1996) and included in the SAP.

Groundwater samples used to determine if there is statistically significant evidence of groundwater contamination by organic compounds should not be field-filtered. Data generated from filtered samples provide information on only the dissolved constituents that are present, as suspended materials are removed by the filtration process. The analytical results of both filtered and un-filtered groundwater samples are used to determine if hazardous constituents were released to groundwater. As discussed in greater detail below, current research in groundwater sampling protocol indicates that hazardous constituents are mobile in the subsurface in both the aqueous (dissolved) phase and the solid phase. The research of Puls and Barcelona (1989a), Puls and Barcelona (1989b), Penrose et al. (1990), Backhus et al. (1993) and West (1990) are the primary sources of the discussion of field filtration that follows.

During groundwater sampling, every attempt should be made to minimize changes in the chemistry of the sample so the data is representative of site conditions. A sample that is exposed to the atmosphere or changes in ambient conditions as a result of field filtering is very likely to undergo chemical changes (e.g. volatilization, precipitation, chemical flocculation) that alter constituent concentrations. These reactions can change the concentrations of organic compounds and metals if they are present in the sample. VOCs may partition to the atmosphere if exposed, thereby resulting in groundwater monitoring data that are not representative of in-situ concentrations. Further, precipitated and emulsion trapped constituents migrating in the aquifer are lost through field filtering, because they are unable to pass through a standard 0.45 micron field filter.

For metals analysis of groundwater samples, however, the situation is not as clear. The argument against filtering is that it will not provide accurate information concerning the mobility of metal contaminants. Metals may move through the aquifer matrices not only as dissolved species, but also as precipitated phases, and/or polymeric species; some metals may be adsorbed to, or encapsulated in, organic or inorganic particles (e.g. colloid-size particles), that are likely to be removed by filtration. In addition, field filtration may introduce oxygen into the sample, which can oxidize dissolved ferrous iron to form a ferric hydroxide precipitate ($\text{Fe}(\text{OH})_3$); this may enmesh other metals in the sample, removing them from solution. Precipitated and entrapped constituents would be removed by field filtration.

The argument for filtering samples prior to analysis for inorganic constituents is that small differences in sample turbidity can mean very large differences in analytical results. Sample turbidity is an indirect measurement of the amount of particulate matter suspended in a sample, and is highly dependent on the nature of the aquifer material. In aquifers containing significant silt or clay, turbidity can be reduced through proper well design, construction and development, and by use of appropriate sample collection methods. However, turbidity is rarely eliminated. Since sample turbidity is not directly related to sources of contamination, resulting values from unfiltered samples do not necessarily provide direct evidence of metals contamination, and are generally not a useful indication of contaminant load in an aquifer.

Based on these arguments, the following recommendations are provided as a guide to sampling groundwater for the analysis of trace metals:

- For risk assessment, unfiltered samples should be analyzed if the potential for colloidal transport is suspected.
- Field filtered samples may be collected at the same time for comparison purposes, but field filtering is not a substitute for properly constructed, developed and sampled wells.
- Samples should never be filtered when a water supply well is sampled.

Since significant differences in water quality may be attributed to contamination, it is critical to control other variables that may affect groundwater quality. In addition to factors already discussed in this document, these recommendations, where applicable, should also be followed:

- Monitoring wells should be designed, constructed and developed to minimize turbidity; well construction is discussed in *Monitoring Well Design and Construction for Hydrogeologic Characterization* (Cal/EPA 1995b), and in the Department of Water Resources Bulletin 74-90 (DWR 1990).
- Whenever possible, well purging and sampling should be performed with dedicated pumps at low discharge rates.
- As previously stated throughout this document, wells should be purged until measured values for the stabilization criteria in Table 1 are achieved.
- In-line, positive-pressure filters should be used at all times; vacuum filtration is not acceptable.
- Manufacturer's recommendations for the volume of water to be flushed through the filter prior to sampling should be followed; if guidelines are not available, a volume of groundwater equal to twice the capacity of the filter should be flushed through the filter and discarded before collecting samples.
- There are certain circumstances where it is necessary to filter or centrifuge the sample under controlled laboratory conditions prior to analysis to prevent instrument damage. Sample filtration in the laboratory is permissible if insoluble materials that could damage laboratory equipment (e.g., silicates) remain after acid digestion of the sample. If this step is necessary, the filter and the filtering apparatus should be thoroughly cleaned and pre-rinsed with dilute nitric acid before use. Laboratory personnel should refer to SW-846 (U.S. EPA 1998) for information concerning these procedures. The analytical reports submitted to DTSC should clearly state that groundwater samples were laboratory filtered.
- Samples should not be transferred from one sample container to another. Transferring samples between containers may result in losses of organic material onto the walls of the container or sample aeration.
- To minimize the possibility of volatilization of organics, no headspace should exist in the containers of samples containing volatile organics. Field logs and laboratory analysis reports should note the headspace, if present, in the sample container(s) at the time of receipt by the laboratory, as well as at the time the sample was first transferred to the sample container at the wellhead.

2.3 CHAIN-OF-CUSTODY AND RECORDS MANAGEMENT

A chain-of-custody procedure should be designed to allow for the reconstruction of how and under what circumstances a sample was collected, including any problems encountered. U.S. EPA (1998) provides a complete description of chain-of-custody and records management. The chain-of-custody procedure is intended to prevent misidentification of the samples, to prevent tampering with the samples during

shipping and storage, to allow easy identification of any tampering, and to allow for the easy tracking of possession. Groundwater samples should always be stored in a secure area.

To avoid water damage of the chain-of-custody form during transport in the sample cooler, the form should be placed into a water-tight sealable bag and placed on top of the cooler contents.

2.3.1 Sample Labels

To prevent sample misidentification, labels should be affixed to each sample container at the time of sampling. The labels should be sufficiently durable to remain legible even when wet and should contain, at a minimum, the following information:

- Site designation
- Sample identification number
- Name and signature of collector
- Date and time of collection
- Place of collection
- Parameters requested (if space permits)

Samples can be labeled by recording the above information directly on the sample containers. Alternatively, multiple-part labels consisting of a unique identification number that is placed on the container and at least two copies of the descriptive information for the samples (referenced to the identification number) may be used. One copy should be kept in a separate file or logbook, and a second copy is shipped inside the cooler with the samples to the laboratory.

2.3.2 Sample Custody Seal

In cases where samples leave the samplers immediate control (e.g. shipment to laboratory), a custody seal should be placed on the shipping container or on the individual sample bottles. Custody seals provide prevention or easy detection of sample tampering. The custody seal should bear the signature of the collector and the collection date. It can be placed on the front and back of a cooler, around the opening of sealable polyethylene bags or on the lid of each sample container before it is taped shut for shipping. Caution should be exercised in doing any of the above. Experience has shown that the seal may not always adhere to some plastic coolers, and the cooler may arrive at the destination without the appropriate seal. Sometimes the sample containers become wet from melting ice or condensation; thus, while their labels will stick, their custody seals may not. Taping over the seal with a transparent tape generally solves this problem and can be similarly applied to cooler lids (Note: Some tapes contain chemicals which may be chemicals of concern).

2.3.3 Field Logbook or Log Sheets

If a sample analysis produces an unexpected or unexplainable result, it will be necessary to determine if the circumstances of sample collection, rather than a change in the groundwater quality, are responsible. Examination of the field logbook or log sheets is critical in this process. The field logbook or log sheets should document the following:

- Well identification
- Condition of well and surface completion
- Top of casing surveyed elevation
- Well depth from top of casing
- Static water level depth and measurement technique
- Presence and thickness of immiscible layers and detection method
- Well purging procedure and equipment
- Purge volume and pumping rate
- Time well purged
- Well yield (high or low)

- Well recovery after purging (slow, fast)
- Collection method for immiscible layers
- Sample withdrawal procedure and equipment
- Date and time of collection
- Measurement of groundwater stabilization parameters
- Well sampling sequence
- Types of sample bottles used and sample identification numbers
- Preservatives used and pH verification
- Parameters requested for analysis
- Field observations of sampling event
- Name of collector
- Climatic conditions, including air temperature
- Internal temperature of field and shipping containers

The field logbook or log sheets for well purging and sampling should be included within reports submitted to DTSC.

2.3.4 Chain-of-Custody Record

Sample possession should be clear from the chain-of-custody record sheet. A chain-of-custody sheet should be filled out and should accompany all samples. It should also contain enough copies so that each person possessing the shipment receives his/her own copy. At a minimum, the record should contain the following information:

- Site designation
- Site address
- Sample number
- Sample description and location
- Signature of collector
- Date and time of collection
- Sample matrix (e.g. groundwater)
- Identification of sampling point (well)
- Number and types of containers
- Parameters requested for analysis
- Preservatives used
- Signature of persons involved in the chain of possession
- Inclusive dates and times of possession
- Internal temperature of shipping container when samples were sealed into the container for shipping
- Internal temperature of container when opened at the laboratory
- Remarks section to identify potential hazards or to relay other information to the laboratory

2.3.5 Sample Analysis Request Sheet

This document should accompany the sample(s) on delivery to the laboratory and clearly identify which sample containers have been designated for each requested parameter. It may be included in the chain-of-custody record. Addition of preservatives should also be noted. This document should include the following types of information:

- Name of person receiving the sample
- Name and addresses of analytical laboratory
- Laboratory sample number (if different from field number)
- Date of sample receipt
- Analyses to be performed
- Internal temperature of shipping container upon opening in the laboratory

- Preservatives added in the field

2.3.6 Laboratory Logbook

Once the sample has been received in the laboratory, the sample custodian and/or laboratory personnel should clearly document the processing steps that are applied to the sample. All sample preparation techniques and instrumental methods used should be identified in the logbook. Experimental conditions, such as the use of specific reagents, temperatures, reaction times, and instrument settings, should be noted. The results of the analyses of all laboratory quality control samples should be identified, specific to each batch of groundwater samples analyzed. The laboratory logbook should include the time, date, and name of the person who performed each processing step.

2.4 ANALYTICAL PROCEDURES

The SAP should describe in detail the analytical procedures that will be used to determine the concentrations of constituents or parameters of interest. These procedures should include suitable analytical methods, the associated analytical detection limits, as well as proper quality assurance and quality control protocols.

The SAP should identify a method that will be used for each specific parameter or target analyte that can achieve the required detection limits. The following should be addressed:

1. For SW-846 analytical methods, reference SW-846 and the analysis methods (by method number), including all sample preparation methods (U.S. EPA 1998).
2. For analysis by modified- or non-SW-846 methods, the analytical procedure and method detection limits to be used should be documented in the format of a Standard Operating Procedure (SOP).

2.5 FIELD AND LABORATORY QUALITY ASSURANCE/QUALITY CONTROL

It is important to establish programs to ensure the reliability and validity of field and analytical laboratory data, as part of the overall groundwater monitoring program. Refer to SW-846 (U.S. EPA 1998) for requirements and guidance on establishing and maintaining field and laboratory quality control programs. In general, laboratory quality assurance and quality control (QA/QC) programs should address the following areas:

- Control samples
- Acceptance criteria
- Deviations
- Corrective action for sampling and analysis procedures
- Data handling
- Laboratory control samples
- Method blanks
- Matrix-specific effects

The SAP should explicitly describe the QA/QC program that will be used in the field and laboratory in the Quality Assurance Project Plan (QAPP). The QAPP describes the quality assurance and quality control (QA/QC) protocols necessary to achieve the objectives dictated by the intended use of the data. Control protocols include the procedures for sample collection, preservation, chain-of-custody, and transport, calibration and maintenance of instruments, processing verification, storage, and reporting of data, and other relevant QA/QC procedures required to maintain precision and accuracy of the data. The DQOs of the project should be described in terms of precision, accuracy, completeness, representativeness and comparability for both field activities (sampling, measurements and screening) and laboratory analyses, including the project required acceptance limits and means to achieve these QA objectives. Refer to U.S. EPA 1992b, for a discussion of DQOs. In addition, the preventative maintenance procedures to be used for the field and laboratory instruments and the groundwater monitoring system should be described. A

table showing the type of maintenance to be performed and the frequency is appropriate. Many groundwater samples are analyzed at commercial laboratories. In these cases, the SAP should be used by the laboratory analyzing samples.

Both field and laboratory QC samples should be prepared during the sampling event. The following samples in Table 2 should be analyzed with each batch of samples (generally every 20 samples):

TABLE 2. Quality Control Samples

Type	Typical Frequency	Purpose
Field duplicate	1 per 10 samples	Evaluate precision of sampling and analysis procedures.
Matrix spike	1 per 20 samples or 1 per analytical batch	Evaluate accuracy of analytical procedures.
Matrix spike duplicate	1 per 20 samples or 1 per analytical batch	Evaluate accuracy of analytical procedures.
Equipment blank	1 per set of equipment cleaned. Collect one sample at the beginning of sampling and one each day after decontamination.	Evaluate cross-contamination caused by non-dedicated equipment.
Field blank	1 per day	Evaluate whether contaminants introduced by ambient air during sample collection.
Trip blank	1 per sample cooler containing VOCs	Evaluate whether VOC contamination introduced during sampling, storage, or shipment.
Temperature blank	1 per sample cooler	Evaluate whether sample preservation requirements are achieved.

The matrix-specific detection limit should be determined. This determination does not need to be made on a sample batch basis, but should be made whenever the matrix is suspected to have altered, or as frequently as necessary to document that the matrix has not altered. For an aquifer with relatively static hydrogeological characteristics, this may mean making a matrix-specific detection limit determination twice annually.

2.5.1 Field QA/QC Program

The SAP should provide for the routine collection and analysis of QC samples. Various types of QC samples and blanks should be used to verify that the sample collection and handling process has not affected the quality of the samples. Blanks are to be subjected to the same analysis as the groundwater. Contaminants found in the blanks may be the result of: (1) inter-action between the sample and the container, (2) contaminated rinse water, (3) contaminated preservatives, or (4) a handling procedure that alters the sample analysis results. The concentrations of any contaminants found in the blanks should not be used to correct the groundwater data. The contaminant concentrations should be noted, and if the concentrations are more than an order of magnitude greater than the field sample results, groundwater should be re-sampled. All field QC samples should be prepared exactly as regular investigation samples

with regard to sample volume, containers, and preservation. The QC samples should be prepared and analyzed for all of the required monitoring parameters.

Other QA/QC practices such as sampling equipment calibration and decontamination procedures and chain-of-custody procedures should be described in the SAP. Refer to the previous sections in this document for a discussion of these practices.

2.5.2 Laboratory QA/QC Program

The SAP should provide for the use of control samples, as defined in SW-846 (U.S. EPA 1998). Appropriate statistical procedures (U.S. EPA 1992a) should be used to monitor and document performance and to implement an effective program to resolve testing problems (e.g. instrument maintenance, operator training). Data from control samples (e.g. spiked samples, duplicates and blanks) should be used as a measure of performance or as an indicator of potential sources of cross-contamination. When contaminants are detected in QA/QC samples (field, trip, or lab blanks), the accompanying sample results should be appropriately flagged. All sample results shall be reported unadjusted for blank results or spike recoveries. All QA/QC data should be submitted to DTSC with the groundwater monitoring sample results.

2.5.3 Groundwater Data Quality Evaluation

A groundwater sampling and analysis program produces a variety of hydrogeological, geophysical, and groundwater constituent concentration (GWCC) data. This section pertains primarily to the evaluation of GWCC data. The GWCC data may be presented to the owner or operator via electronic transmittal or on reporting sheets. These data then should be compiled and statistically analyzed prior to submittal to the lead regulatory agency. If data are to be transmitted electronically, the procedures should be discussed with the lead regulatory agency staff to ensure that all software and hardware being used are compatible with the electronic data formats for integration in the agencies database.

The following guidelines should help to ensure that units of measure associated with data values are reported consistently and unambiguously:

- The units of measure should accompany each target analyte. Laboratory data sheets that include the statement "values are reported in ppm unless otherwise noted" should generally be discouraged, and at least should be examined in detail by the technical reviewer.
- The units of measure for a given target analyte should be consistent throughout the report.
- Data should be reported correctly for the results to be valid. Chemical analysis, laboratory reporting, computer automation, and report preparation data should be generated and processed to avoid mistakes and ensure completeness and full documentation.

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APPENDIX A

Sampling Devices

GRAB SAMPLERS

The four main varieties of bailers are the single check valve, double check valve, messenger, and syringe bailers. Bailers are among the simplest groundwater sampling devices. A bailer is simply a rigid tube that fills with water when lowered into the well; when raised back out of the well, it is sealed on one or both ends by some mechanism. The groundwater sample is subsequently transferred into sample containers from the bailer. Bailers are relatively inexpensive to purchase or fabricate (especially the single and double check valve bailers), easy to clean, portable, simple to operate, and require no external power source (U.S. EPA, 1983).

Disadvantages are that their use can be time consuming and labor intensive and that the transfer of water to a sample container may significantly alter the chemistry of groundwater samples due to degassing, volatilization or aeration. Use of a bailer may also result in an increase of turbidity that may affect analysis results. Bailers should not be used to sample groundwater that will be analyzed for volatile organic compounds, unless a bailer is the only available method, or the bailer is used for sampling LNAPL or DNAPL or the use of a bailer is approved by the lead regulatory agency.

Bailers used to collect groundwater samples and the cable used to raise and lower the bailer should be constructed of material (e.g., fluorocarbon resin, Teflon®, stainless steel, HDPE, or PVC) which does not cause analyte concentrations alteration or cause loss of analytes via sorption. Ideally the bailer should be easy to disassemble to facilitate cleaning and decontamination.

Bailers should never be dropped into a well and should be removed from the well in a manner that causes as little agitation to the sample as possible. For example, the bailer should not be removed in a jerky fashion or be allowed to continually bang against the well casing as it is drawn up. To ensure consistent samples, DTSC recommends that the bailer be submerged only to a depth necessary for filling, except when the bailer is being used to sample a DNAPL. When transferring the sample from a bailer to a container, a bottom emptying device with a valve to allow the water to slowly drain from the bailer should be used. The sample should be allowed to run down the sides of the collection bottle to avoid excessive agitation of the sample.

POSITIVE DISPLACEMENT (SUBMERSIBLE) MECHANISMS

Positive displacement mechanisms for groundwater sampling include gear drive electric submersible pumps, bladder pumps, helical rotor electric submersible pumps, gas-drive piston pumps, and centrifugal pumps. The following sections briefly describe each of these types of pumps and their applications and limitations with regard to collecting groundwater samples.

Bladder Pumps

Bladder pumps (also referred to as gas squeeze pumps) consist of a flexible membrane often enclosed in a rigid stainless steel housing. A strainer or screen attaches below the bladder to filter any material that could clog either of the check valves located above and below the bladder. Water enters the membrane through the lower check valve; compressed gas is injected into the cavity between the housing and bladder. The sample is transported through the upper check valve and into the discharge line. The upper check valve prevents water from reentering the bladder. The process is repeated to cycle the water to the surface. Bladder volumes (e.g., volume per cycle) and sampler geometry can be modified to increase the sampling abilities of the pump. Automated control systems are available to control gas flow rates and pressurization cycles. Bladder pumps prevent contact between the gas and water sample and can be fabricated entirely of fluorocarbon resin and stainless steel. A nearly continuous flow can be attained with

the proper cycles. Pohlmann and Hess (1988) determined that bladder pumps can be suitable for collecting groundwater samples for almost any given organic or inorganic constituent. Disadvantages of bladder pumps include the large gas volumes required to actuate the pump (especially for sampling deep groundwater), and potential bladder rupture. Hence, gas cylinders or air compressors are needed to power the pumps. If using a gasoline or diesel powered air compressor, the compressor should be placed downwind of the wellhead.

If a bladder pump has been chosen as the sampling device, it should be operated at a discharge rate of 100 ml/min or less when collecting samples for volatiles analysis. Higher flow rates can increase the loss of volatile constituents and can cause fluctuation in pH and pH-sensitive analytes. Bladder pumps should be operated in a continuous, non-pulsating manner so that they do not produce samples that are aerated in the return tube or upon discharge. Once the portions of the sample reserved for the analysis of volatile components have been collected, a higher pumping rate may be used, particularly if a large sample volume will be collected. The pump lines should be cleared at a low rate before collecting samples for volatiles analysis, or else the sample collected will be from when the pump was rapidly operating. Running the pump at a low flow rate will take time and may deter the use of a bladder pump when the wells are deep and the lines are long.

Helical Rotor Electric Submersible Pumps

The helical rotor electric submersible pump consists of a sealed electric motor that powers a helical rotor. The water sample is forced up a discharge line by an electrically driven rotor-stator assembly by centrifugal action. Submersible pumps provide relatively high discharge rates for water withdrawal at depths beyond suction lift capabilities. Pumping rates vary depending upon the size of the motor and sampling depth. Heat buildup should be monitored when low (less than 1 gpm) pump rates are used. Heat shields or pump shrouds may be used to aid in heat buildup. A submersible pump provides higher extraction rates than the majority of other methods. However, considerable sample agitation in the well results from operating at high rates, and this may cause alteration of the sample chemistry. In addition, high pumping rates can introduce sediments from the formation into the well that are immobile under ambient groundwater flow conditions, resulting in the collection of unrepresentative samples for metals due to potential partitioning upon contact with the sediment. Further, the potential exists for the introduction of trace metals into the sample from the pump materials. Steam cleaning of the unit followed by rinsing with unchlorinated, deionized water in between sampling is recommended. Where the submersible pump is used for sampling, those parts of the pump in contact with water should be constructed of stainless steel.

Gas-drive Piston Pumps

A piston pump uses compressed air to force a piston to raise the sample to the surface. A typical design consists of a stainless steel chamber between two pistons. The alternating chamber pressurization activates the piston, which allows water entry during the suction stroke of the piston, and forces the sample to the surface during the pressure stroke. Pumping rates of 500 ml/min have been reported from 30.5 meters; sampling depths of 150 meters are possible. The piston pump provides continuous sample withdrawal at depths greater than is possible with most other approaches. Nevertheless, contribution of trace elements from the stainless steel and brass fittings is a potential problem. Pumping rates at depths less than 150 meters are generally slower than with other pumps.

Centrifugal Pumps

A centrifugal (sometimes called impeller) pump is similar to the direct line pump except that a centrifugal pump is connected to the tubing at the surface rather than a vacuum pump. A foot valve is usually attached to the end of the well tubing to assist in priming the extraction tube. A centrifugal pump is capable of delivering large quantities of water, against high as well as low head conditions, with good efficiency. Under field conditions a centrifugal pump has an average suction lift capability of 20-25 feet (6.1-7.6 meters) (Driscoll, 1986). Although relatively high pumping rates can be attained, centrifugal pumps cause sample agitation.

SUCTION LIFT PUMPS

Suction lift pumps can be categorized as direct line and peristaltic. The direct line pump requires lowering one end of a plastic tube into a well or piezometer. The surface end of the tube is connected to a two-way stoppered bottle, and a manually or auxiliary powered vacuum pump is attached to a second tube that leads from the bottle. A check valve is attached between the second tube and the vacuum pump to maintain a constant vacuum control.

A peristaltic pump (also called rotary peristaltic) is a self-priming, low-volume suction pump consisting of a rotor and three ball bearing rollers. Plastic tubing inserted around the pump rotor is squeezed by the rollers as they revolve in a circle around the rotor. One end of the tubing is placed into the well while the other end is connected directly to a two-way stoppered flask. As the rotor revolves, water is drawn into the sampling tube and discharged into the collection vessel. A drive shaft connected to the rotor head can be extended so that multiple rotor heads can be attached to a single drive shaft. The withdrawal rate of peristaltic pumps can be carefully regulated by adjusting the rotor head revolution. The system can be arranged so that the sample contacts only fluorocarbon resin tubing prior to entering the sample container. A limiting factor is the depth of sampling; the depth of sample collection is limited to situations where the potentiometric level is less than 25 feet below land surface (Nielsen, 1991). The suction lift approach offers a simple retrieval method for shallow monitoring wells. However, the method can result in sample mixing and oxidation. Degassing and loss of volatiles also occur to some extent. A peristaltic pump provides a lower sampling rate and less agitation than direct line or centrifugal pumps. Hence, when sampling for VOCs, the sampling results will be biased low. Accordingly, sampling with suction lift pumps should be done for screening purposes only.

GAS CONTACT PUMPS

Gas contact sampling devices include gas-lift and gas-drive devices.

Gas-Lift Pumps

An air or gas lift pump allows collection of groundwater samples by bubbling air or gas at depth in the well. Sample transport occurs primarily as a result of the reduced specific gravity of the water being lifted to the surface. Water is forced up a discharge pipe, which may be the outer casing or a smaller diameter pipe inserted into the well. Air or gas lift methods can result in considerable sample agitation and mixing in the well, and are not permitted for collecting samples for chemical analysis. The considerable pressures required for deep sampling can result in significant redox and pH changes.

Gas-Drive Pumps

Gas drive (gas displacement) pumps are distinguished from air lift pumps by their method of sample transport. Gas displacement pumps force a column of water under linear flow conditions to the surface without extensive mixing of the pressurized gas and water. A vacuum can also be used to assist the gas. The disadvantages of a gas drive pump are that the drive gas comes into contact with the water and therefore, can be a source of contamination; also, the pump can be difficult to clean.

Gas control pumps should not be used for the collection of groundwater samples at hazardous substances release sites due to the potential for sample alteration.

PASSIVE SAMPLERS

The effectiveness of a single passive sampler in a well is dependent on groundwater flow through the well screen and whether the water quality directly adjacent to the sampler is representative of the entire screened interval. If there is intrabore flow, multiple intervals contributing to flow, or varying concentrations of contaminants vertically within the screened interval, then multiple passive samplers within a well may be more appropriate for sampling the well. (Vroblesky, D.A., 2001a, Vroblesky, D.A., 2001b).

Passive samplers are classified on the basis of sampler mechanism and nature of the collected sample. A more detailed discussion of these samplers can be found at www.itrcweb.org/Documents/DSP_4.pdf.

1. *Devices that recover a grab well water sample.*

Samples are an instantaneous representation of conditions at the sampling point at the moment of sample collection.

- HydraSleeve™ Samplers
- Snap Sampler™

2. *Devices that rely on diffusion of the analytes for the sampler to reach and maintain equilibrium with the sampled medium.*

Samples are time-weighted toward conditions at the sampling point during the latter portion of the deployment period. The degree of weighting depends on analyte and device-specific diffusion rates. Typically, conditions during the last few days of sampler deployment are represented.

- Regenerated-Cellulose Dialysis Membrane Samplers
- Nylon-Screen Passive Diffusion Samplers (NSPDS)
- Passive Vapor Diffusion Samplers (PVDs)
- Peeper Samplers
- Polyethylene Diffusion Bag Samplers (PDBs)
- Rigid Porous Polyethylene Samplers (RPPS)

3. *Devices that rely on diffusion and sorption to accumulate analytes in the sampler.*

Samples are a time-integrated representation of conditions at the sampling point over the entire deployment period. The accumulated mass and duration of deployment are used to calculate analyte concentrations in the sampled medium.

- Semi-Permeable Membrane Devices (SPMDs)
- GORE™ Sorber Module
- Polar Organic Chemical Integrative Samplers (POCIS)
- Passive In-Situ Concentration Extraction Sampler (PISCES)

HYDRASLEEVE™ SAMPLERS

HydraSleeve™ samplers are designed to recover groundwater from monitoring wells without purging and can be used to sample a wide spectrum of analytes (e.g., VOCs, semi-volatile organics, and metals) and can also be used to sample low-yielding wells. HydraSleeve™ samplers allow recovery of discrete samples from the screened zone where the sampler is activated, with no drawdown and minimal agitation of the water column. The reed valve design keeps the device closed except during sample collection, thereby assuring that the sample is collected from the desired interval within the screened zone.

SNAP SAMPLER™

The Snap Sampler™ is designed to collect groundwater samples in situ without purging. The Snap Sampler™ utilizes specialty double-ended bottles closed while submerged in the well. A well re-equilibration period is recommended for passive deployments. The Snap Sampler™ VOA vial can be used directly in common laboratory auto sampler equipment, so samples are not exposed to ambient air during retrieval, field preparation, or analysis at the lab unless manual dilutions or re-analyses are required. Utilizing minimum sample volume requirements, this sampler can be used for analyzing many different physical and/or chemical water quality parameters, including VOCs and metals.

REGENERATED-CELLULOSE DIALYSIS MEMBRANE SAMPLERS

Regenerated-cellulose dialysis membrane samplers collect groundwater samples for inorganic ionic constituents as well as organic constituents using a diffusion-type sampler. Dialysis membrane samplers can be used to sample a wide spectrum of water-quality parameters.

NYLON-SCREEN PASSIVE DIFFUSION SAMPLERS (NSPDS)

NSPDS are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler. Larger volumes can be obtained by using a stack of bottles in the same mesh sleeve.

PASSIVE VAPOR DIFFUSION (PVD) SAMPLERS

Passive-vapor-diffusion (PVD) samplers have been used successfully as reconnaissance tools at many hazardous waste sites. The primary use of PVD samplers is to identify locations where VOC contaminated groundwater is discharging into surface water. PVD samplers also have been used as passive-soil-gas samplers in the unsaturated zone. USGS Water-Resources Investigations Report 02-4186 provides detailed guidance for construction and use of PVD samplers.

PEEPER SAMPLERS

Peeper samplers (a.k.a. Hesslein In-situ Pore Water Sampler) are rigid structures, which can hold volumes of water separated from the environment by porous membranes to monitor constituents in saturated environments. Peeper samplers rely on diffusion of the analytes to reach equilibrium between the sampler and the pore water. Peeper samplers (i.e., dialysis cells) have been used for in situ monitoring of dissolved constituents in saturated sediments. The Peeper sampler measures pore water analyte concentrations. Peeper samplers can be stacked in a specially designed corer so that they sample discrete near-surface depths.

POLYETHYLENE DIFFUSION BAG (PDB) SAMPLERS

The Polyethylene Diffusion Bag (PDB) sampler was developed in the late 1990's and has become a widely accepted technique for determining concentrations of VOCs in groundwater monitoring wells. PDBs are installed in groundwater monitoring wells, at one or more intervals below the water surface in the well screen, and left in place under natural flow conditions. PDBs are also used in saturated sediments in and around surface water to approximate VOC discharge to the surface.

RIGID POROUS POLYETHYLENE SAMPLERS (RPPS)

Rigid porous polyethylene samplers (RPPSs) are diffusion based samplers developed to sample for a broader range of analytes than can be collected by the PDB sampler. The RPPS is constructed from thin sheets of foam-like porous polyethylene with pore sizes of 6 to 15 microns. The sampler is filled with water free of the target analytes, capped at both ends, and placed inside a mesh liner, which is subsequently attached to a deployment rope using cable-ties and deployed in a well.

SEMI-PERMEABLE MEMBRANE DEVICES (SPMDS)

Semi-permeable Membrane Devices (SPMDs) are designed to sample chemicals dissolved in surface water, mimicking the bioconcentration of organic contaminants into the fatty tissues of organisms. The SPMD enables concentration of trace organic contaminant mixtures for analysis, toxicity assessments, and toxicity identification evaluation. It is designed to sample lipid or fat-soluble (nonpolar or hydrophobic) semi-volatile organic chemicals from water and air. The SPMD is an integrative sampler which accumulates analyte mass over a deployment period ranging from days to months. SPMDs provide a highly reproducible means for monitoring contaminant levels, and are largely unaffected by many environmental stressors affecting biomonitoring organisms.

GORE™ SORBER MODULE

The GORE™ Sorber Module relying on diffusion and sorption to accumulate analytes in the sampler. These modules yield a total mass of analytes that can be correlated with analyte concentrations in water

or air. This device can be utilized to sample soil gas in the vadose zone and dissolved organic analytes in water saturated soils or in groundwater monitoring wells. This device has been used in both fresh and saltwater environments, including sampling sediments in marshes, streams, river embankments, and coastal settings.

POLAR ORGANIC CHEMICAL INTEGRATIVE SAMPLER (POCIS)

The Polar Organic Chemical Integrative Sampler (POCIS) is designed to sample water-soluble (polar or hydrophilic) organic chemicals from aqueous environments. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from weeks to months. The POCIS samples chemicals from the dissolved phase, mimicking the respiratory exposure of aquatic organisms. The POCIS also concentrates trace organic contaminants for toxicity assessments and toxicity identification evaluation (TIE) approaches.

PASSIVE IN-SITU CONCENTRATION EXTRACTION SAMPLER (PISCES)

The Passive In Situ Concentration Extraction Sampler (PISCES) is designed to sample non-polar or hydrophobic organic chemicals in surface water. This device relies on diffusion and sorption to accumulate a total mass of analytes. The residence period ranges from one day to one month. PISCES consist of a membrane, typically low-density polyethylene (LDPE), forming one end of a metal container filled with an organic solvent, typically hexane or isooctane (2,2,4- trimethylpentane). Analyte uptake is driven by the preferential partitioning of nonionic organic chemicals from water to the solvent. The membrane excludes ionic, high molecular-weight natural organic matter, and particulates.

Where site conditions are not fully characterized, side-by-side comparisons between multiple well-volume purge, low flow groundwater sampling, and diffusion bag sampling methods may be necessary to determine which method should be used to yield the most representative data. The sampling method ultimately used should be discussed with the lead agency before implementation.

Additional information on the use of these samplers can be found at www.itrcweb.org/Documents/DSP_4.pdf

PACKER ASSEMBLAGES

A packer assembly provides a means by which to isolate and sample a discrete interval in the subsurface. Hydraulic- or pneumatic-activated packers are wedged against the casing wall allowing sample collection from an isolated portion of the well. The packers deflate for vertical movement within the well and inflate when the desired depth is attained. Packers are usually constructed from some type of rubber or rubber compound and can be used with submersible, gas lift, and suction pumps.

If pumps are operated at a low rate, a packer assembly allows sampling of low-yielding wells, and wells that would otherwise produce turbid samples. A number of different samplers can be placed within the packers depending upon the analytical specifications for sample testing. One disadvantage is that vertical movement of water outside the well (e.g., if used in the screened interval) is possible with packer assemblages, depending upon the pumping rate and formation properties. Another possible disadvantage is that the packer material may contribute undesirable organic constituents to the water sample.

TABLE A1. Generalized guide for selection of groundwater sampling devices. Modified from U.S. EPA (1991).

Device Type	Device	Groundwater Parameters														
		Inorganic							Organic					Radioactive		
		EC	pH	Redox	Major ions	Trace metals	Nitrate/Fluoride	Dissolved gases	Non-Volatile	Volatile	TOC	TOX	Coliform bacteria	Radium	Gross alpha and beta	
Portable Sampling Devices	Grab	Open Bailer	!	G	G	!	!	!	G	!	G	G	G	!	!	G
		Point Source Bailer	!	!	!	!	!	!	G	!	G	!	!	!	!	G
		Passive Diffusion Bags	G	G	G	G	G	G	G	G	Limited constituents	G	G	G	G	G
		Bat Sampler	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Hydropunch	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Geoprobe	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Syringe Sampler	!	!	!	!	!	!	G	!	!	G	G	!	!	!
	Positive Displacement (Submersible)	Gear-drive	!	!	!	!	!	!	!	!	!	!	!	G	!	!
		Bladder Pump	!	!	!	!	!	!	!	!	!	!	!	!	!	!
		Helical Rotor (electrical)	!	!	!	!	!	!	!	!	!	!	!	G	!	!
		Piston Pump (gas drive)	!	G	G	!	!	!	G	!	!	G	G	G	!	!
		Centrifugal (low-rate)	!	!	!	!	!	!	!	!	!	!	!	!	!	!
	Suction Lift	Peristaltic	!	G	G	!	!	!	G	!	G	G	G	!	!	!
		Pneumatic	!	!	!	!	!	!	G	!	G	G	G	!	!	!

Acronyms and Abbreviations

EC electroconductivity TOC total organic carbon
 Redox oxidation/reduction potential TOX total organic halides

Symbols

! Device is generally suitable for application (assuming device is properly operated and is constructed of suitable materials).
 G Device may be unsuitable or untested for application.