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Division of Drinking and Ground Waters

Technical Guidance Manual for Ground Water Investigations

Chapter 10

Ground Water Sampling

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Director : Chris Korleski

TECHNICAL GUIDANCE MANUAL FOR GROUND WATER INVESTIGATIONS

CHAPTER 10

GROUND WATER SAMPLING

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PREFACE

This document is part of a series of chapters incorporated in Ohio EPA's *Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring* (TGM), which was originally published in 1995. DDAGW now maintains this technical guidance as a series of chapters rather than as an individual manual. These chapters can be obtained at http://www.epa.state.oh.us/ddagw/tgmweb.aspx.

The TGM identifies technical considerations for performing hydrogeologic investigations and ground water monitoring at potential or known ground water pollution sources. The purpose of the guidance is to enhance consistency within the Agency and inform the regulated community of the Agency's technical recommendations and the basis for them. In Ohio, the authority over pollution sources is shared among various Ohio EPA divisions, including the Emergency and Remedial Response (DERR), Hazardous Waste Management (DHWM), Solid and Infectious Waste (DSIWM), and Surface Water (DSW), as well as other state and local agencies. DDAGW provides technical support to these divisions.

Ohio EPA utilizes ***guidance*** to aid regulators and the regulated community in meeting laws, rules, regulations, and policy. Guidance outlines recommended practices and explains their rationale. The Agency may not require an entity to follow methods recommended by this or any other guidance document. It may, however, require an entity to demonstrate that an alternate method produces data and information that meet the pertinent requirements. The procedures used usually should be tailored to the specific needs and circumstances of the individual site, project, and applicable regulatory program, and should not comprise a rigid step-by-step approach that is utilized in all situations.

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Jeff Patzke, DDAGW-CO, who serves as editor and project coordinator for the Technical Guidance Manual

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TECHNICAL CHANGES FROM THE FEBRUARY 1995 TGM

The Ohio EPA Technical Guidance Manual for Hydrogeologic Investigations and Ground Water Monitoring (TGM) was finalized in 1995. This guidance document represents an update to Chapter 10 (Ground Water Sampling). Listed below are the major technical changes from the 1995 version of Chapter 10.

1. Modified the Parameter Selection section to make it more generic and less slanted to a particular regulatory program.

2. Deleted the Sampling Frequency section. Frequency pertains more to the overall monitoring program and will be discussed in future chapters. Information on sampling frequency can be found in Barcelona et al., 1989.

3. Added language discouraging the use of bailers. Provided more guidelines on how bailing, if used, should be completed.

4. Added information on submersible pumps and types that appear acceptable for obtaining a ground water sample.

5. Added information on low flow purging/sampling, diffusion bag sampling, and minimum/no purge sampling.

6. Corrected the stabilization parameter criteria for purging a well. The 1995 document erroneously indicated that the criteria for stabilization for all parameters was 10%. Note that a 10% variation pH would be a significant change. For pH, the stabilization has been corrected to ± 0.1 units. Stabilization criteria have been provided for specific conductance, oxidation-reduction potential, turbidity, dissolved oxygen and temperature based on U.S. EPA guidance and peer-reviewed.

7. Modified the decontamination process. This included removing the reference to using ASTM Type II water for decontaminating equipment.

8. Changed the turbidity criterion from 5 to 10 NTU. Added a recommendation to filter ground water samples using media with 5 micron pore size (when filtration is appropriate and site conditions do not dictate a different size.)

9. Preservatives and holding times: Made the table more generic and based on U.S. EPA Federal Register 40, Volume 69, No. 66, April 6, 2004.

10. Added web addresses to various sites (e.g., U.S. EPA-approved analytical methods).

11. Added an appendix that provides additional considerations when sampling a water supply well.

CHAPTER 10

GROUND WATER SAMPLING

This chapter summarizes procedures for collecting ground water samples from monitoring wells. It focuses on the planning and preparation prior to sampling, types of sampling and purging equipment, field procedures, quality control sampling, and documentation to ensure that samples represent the quality of water obtained from the sampled interval. When selecting protocol, it is important to understand the impacts that removing water from a well can have on the chemistry of the water. Therefore, impacts to sample integrity are also discussed. The chapter also provides some information on the selection of analytical methods and laboratory quality assurance.

The primary objective of most ground water monitoring programs is to collect a sample that represents the in-situ ground water quality. However, the working definition of "representative" is not always the same for all programs. For example, those interested in characterizing ground water for the purpose of evaluating it as a potable water supply may be more interested in volumetric-averaged concentrations in the ground water zone (Nielsen and Nielsen, 2006). Monitoring programs may also be designed to determine "worst-case" conditions. Therefore, prior to starting any monitoring program, the data quality needs should be determined to ensure the collection of data that are of adequate quality to support decision making (See U.S. EPA, Data Quality Objectives Guidance, 2000).

The goal in sample collection is to sample in a manner that results in the least disturbance or change in the chemical and physical properties of the water. The guidelines provided here are intended to assist in choosing the most appropriate methods. Site-specific circumstances may require alternative approaches that are not specified. In these cases, the appropriate regulatory authority should be contacted to establish an acceptable approach. In addition, rules may specify issues such as frequency of sample collection, filtration, frequency and accuracy of water level measurements, and parameters for analysis. Requirements for documentation of field and laboratory procedures may also be specified. Appropriate divisions within Ohio EPA should be consulted when planning a ground water sampling program.

The choice of equipment and methodology should be based on an understanding of the hydrogeology of the area and the purpose of the data collection. Each technique has disadvantages and advantages; therefore, there is no best overall method. Because different techniques may yield different results, the best approach is to be consistent throughout an investigation to facilitate the comparison of data values over time (ASTM D4448-01). When necessary, changes in sampling strategies should be discussed with Ohio EPA prior to implementation.

Although the chapter is intended specifically for the sampling of conventional monitoring wells, the procedures may be useful for other types of ground water sampling, such as direct push technology and water supply wells. Additional information on direct push can be found in Chapter 15-Use of Direct Push Technologies for Soil and Ground Water Sampling. Additional considerations for sampling a water supply well can be found in Appendix A of this chapter.

POTENTIAL EFFECTS ON SAMPLE QUALITY

Many aspects of the sampling process can affect the chemistry of ground water when it is being collected. As a result, a sample may not represent the actual quality of the ground water. Therefore, the potential effects need to be considered in any sampling program.

EFFECTS CAUSED BY WELL CONSTRUCTION AND DEVELOPMENT

The chemistry of a ground water sample may be affected by poor well construction and/or development. Wells that do not have proper filter packs or are improperly grouted may have water that does not represent the quality of ground water flowing through their intakes. This may be due to grout contamination or water seeping down the casing from the surface or other ground water zones. If a well has not been properly developed (See Chapter 8 - Monitoring Well Development, Maintenance, and Redevelopment), then sample quality may be affected by the sediments in the well.

EFFECTS CAUSED BY CHANGE IN SAMPLE ENVIRONMENT

Transfer of ground water from *in-situ* to atmospheric conditions can alter its chemistry significantly unless proper sampling techniques are used. Aeration/oxidation, pressure, and temperature changes are three major causes of chemical alteration.

Aeration/Oxidation

Upon exposure to the atmosphere, the redox state of ground water samples increases due to the addition of oxygen. Dissolved species such as iron (Fe), manganese (Mn), arsenic (As), and cadmium (Cd) may be oxidized from a reduced state (Gillham et al., 1983), which can cause them to precipitate from solution. The oxidation of Fe is particularly important for sample stability. Ground water may contain high concentrations of dissolved Fe due to anoxic (low oxygen) subsurface conditions. Upon exposure, it can oxidize rapidly and precipitate ferric hydroxide, resulting in a decrease in pH that may alter sample integrity further ($4Fe + 10H_2O \rightarrow Fe(OH)_{3(s)} + 8H^+$). Ferric hydroxide is known to remove contaminants from solution including, but not limited to, copper (Cu), zinc (Zn), cobalt (Co), cadmium (Cd), arsenic (As) and lead (Pb). While it may often be difficult to prevent redox changes, acidification of samples being analyzed for metals will prevent metals from precipitating.

Pressure Differences

Pressure changes caused by the release of ground water into a well may cause shifts in chemical equilibrium. Ground water may have high partial pressures of carbon dioxide (CO_2) gas and, upon exposure, degas CO_2. This is known to cause increases in pH by up to 0.5 to 1 standard units and may cause various metals to dissolve or precipitate. If volatile organic compounds (VOCs) are present, sudden pressure changes cause their volatilization. This will result in a negative bias with respect to true VOC concentration.

Temperature Differences

The temperature of a sample may change because of differences between ambient air and subsurface conditions. A primary concern is an increase in temperature, which may kinetically favor redox reactions and promote increased biodegradation and volatilization.

EFFECTS DUE TO SAMPLING TECHNIQUE

The method and design of the sampling device potentially can alter samples. Tools that allow air to contact ground water (see equipment section) can potentially aerate samples, as discussed above. Devices can leach contaminants into samples or sorb contaminants from them. Also, improper decontamination of equipment can alter samples.

PLANNING AND PREPARATION

The success of any ground water sampling event hinges on the planning and preparation conducted prior to entering the field. The sampling procedures should be documented in a written plan. What should be included in the written plan is summarized below. Procedures and event planning and preparation should be evaluated carefully and be appropriate for the associated Ohio EPA program and the intended use of the sampling data. This should also include an evaluation of the parameters selected.

WRITTEN PLAN

Written, detailed, site-specific protocol should be developed to document sampling and analysis procedures. The protocol can be incorporated into a single, stand-alone document (sometimes called a sampling and analysis plan) or can comprise a section of a more comprehensive document. Protocol should provide sufficient detail for personnel to properly operate equipment and perform procedures and techniques in a manner that will generate representative data. The circumstances and conditions under which procedures and techniques will be implemented should be clearly described.

The submittal, format, and/or disposition may or may not be specified by rule. In all cases, the plan or other protocol should meet all requirements of the associated Ohio EPA program and provide data appropriate for the investigative purposes. In general, a plan may include (at a minimum) the components listed in Table 10.1

Table 10.1	***GENERAL COMPONENTS[1] OF A GROUND WATER SAMPLING AND ANALYSIS PLAN (SAP)***
Parameter selection	
Sampling frequency	
Field procedures prior to sampling ground water: -well inspection -water level measurements (including meter type and level of accuracy) -total depth of well -detection and sampling of immiscible liquids	
Well purging, including but not limited to: -methods -criteria completion	 - equipment - disposal of water
Field measurements of ground water: - parameters (e.g., pH, temperature, and conductivity) - description and calibration of field equipment - description of field analysis procedures	
Sample withdrawal: - methods - equipment	
Sample handling: - order of collection - preservation (type and when/how added) - holding times	 - filtration[2] - containers with labels - shipping
Decontamination procedures	
Documentation: - field logbook or sampling documentation forms[3] - standardized chain-of-custody forms - sample analysis request sheet - field QA/QC samples	
Laboratory analysis: - analytical methods - detection limits - laboratory QA/QC samples - description of data validation methods - reporting requirements and format	

[1] Additional components may be necessary on a site-by-site basis.

[2] Check whether the regulatory program allows filtering of ground water samples. Note that the Ohio solid waste regulations do not allow filtering at municipal landfills.

[3] See page 10-48 for items that may need to be included.

EVENT PLANNING AND PREPARATION

Before any sampling begins, planning and preparation should be a high priority. All personnel should be familiar with site-specific written protocol and trained in the proper use of the equipment. All equipment and paperwork should be organized. Instruments should be in working order and properly decontaminated. Field logs, sheets, or other documents used to record notes should be organized. Arrangements with the laboratory should be made to ensure that samples can be handled and analyzed within the required holding times and to obtain labels, appropriate containers, and preservatives. The following are general checklists for preparation procedures and equipment:

Preparation Procedures

- Determine sampling date, time, and location.
- Estimate total sampling and travel time to insure appropriate lab arrangements.
- Determine the number and type of analyses needed from each location.
- Determine purge water management practices.
- Determine decontamination procedures.
- Determine safety procedures.
- Determine the number of field, equipment, and trip blanks and duplicates needed.
- Determine sample volumes needed, total number of samples, and container type.
- Review the construction, sampling history and recharge rate of each well.
- Be aware of any nearby production wells that may affect measured water levels.
- Determine samples to be filtered (if appropriate) and secure appropriate equipment.
- Check to see that the equipment is working properly.
- Calibrate all instruments and calculate bailer volume (if necessary).
- Collect containers and all necessary preservatives if containers not pre-preserved.
- Review and understand all transportation and chain-of-custody procedures.

General Supply and Equipment Checklist

- SAP.
- Keys to locks on wells.
- Map of site and well locations.
- Field notebook, logbook, and/or field sampling forms.
- Indelible marking pens.
- Appropriate lab analysis and chain-of-custody forms.
- Preservatives.
- Filtration equipment.
- Ice.
- Coolers for ice and samples.
- Purging and sampling devices.
- Appropriate tubing.
- Appropriate sample containers and labels.
- Field monitoring meters (e.g., water level, pH, specific conductance, temperature, etc.).
- Calibration instructions and standard testing solutions for field monitoring equipment

- Calibrated bucket (to determine volume of purged water).
- Tool box.
- Extra batteries.
- Safety equipment.
- Calculator.
- Plastic sheeting for ground cover.
- Decontamination solutions and equipment.
- Flashlight.
- Photoionization detector (PID) or organic vapor analyzer (OVA).
- Equipment for detecting immiscibles (e.g., interface probe or clear bailer).
- Contact information for site, facility, and laboratory.
- Emergency contact information.

PARAMETER SELECTION

Parameter selection depends on whether the purpose of sampling is to quantify the general quality of the ground water or identify the presence of any contamination.

Parameters to Characterize General Quality

Parameters used to characterize general quality can include: pH, alkalinity, total dissolved solids (TDS), turbidity, dissolved oxygen, oxidation/ reduction potential (ORP), fluoride (F^-), hydrogen sulfide (H_2S), total hardness and non-carbonate hardness, specific conductance, chloride (Cl^{-1}), nitrate (NO_3^{-1}), sulfate (SO_4^{-2}), phosphate (PO_4^{-3}), silicate (SiO_2), sodium (Na^{+1}), potassium (K^{+1}), calcium (Ca^{+2}), magnesium (Mg^{+2}), ammonium (NH_4^{+1}), total iron (Fe), and manganese (Mn). The results can provide an overall picture of ground water geochemistry that is useful to site characterization. For example, an understanding of geochemistry can help in determining chemical species present (e.g., AsO_3^{-2} versus AsO_4^{-3}) and mobility in the subsurface. Certain parameters (e.g., anions, cations, pH, TDS, specific conductance) are helpful in evaluating releases of inorganic contaminants, while other parameters (chloride, iron, nitrate, sulfate, dissolved oxygen, ORP, and alkalinity) can be used to evaluate changes in ground water chemistry caused by the release and biodegradation of organic contaminants**.** Regulated entities (such as municipal or hazardous waste landfills) may be required to establish a sampling program that may include some the above-mentioned parameters.

Parameters to Characterize Contamination

When ground water contamination is known, suspected, or being investigated as part of a monitoring program, parameters specific to the waste material, history of the site/facility, or chemicals of concern (COCs) usually are necessary. Rules may also dictate specific parameters. When ground water contamination is known or suspected, entities may be required to monitor additional site-specific parameters[4]**.**

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[4] It is suggested that, in some cases (e.g., characterizing known ground water contamination), that the laboratory be requested to report all constituents listed in a methods target analyte list whether they are detected or quantified or not. This ensures that breakdown products are also considered.

Past waste constituents and handling practices should be considered. Because waste released to the environment may chemically change through time, potential breakdown products should be considered. If accurate disposal records are available and waste constituents are well documented, the list of parameters can be relatively limited. The list should be more extensive if handling practices are poorly understood. Monitoring suites of parameters (e.g., volatiles, semi-volatiles, metals, etc.) may be necessary when specific waste constituents are not known. Where rule/policy allows, lists may be narrowed as the investigation progresses and waste constituents and chemicals of concern become better defined.

SAMPLING AND PURGING EQUIPMENT

A variety of sampling and purging equipment is available. Depending on the situation, all types have advantages and disadvantages. There is no device that can be used in every situation. Site-specific hydrogeology, geochemistry, types of contaminants, and well design may affect equipment performance. Ultimately, the ideal scheme should employ inert material, should not subject samples to negative pressures or high positive pressures, and should minimize exposure of samples to the atmosphere (ASTM, Method D4448-01).

CRITERIA FOR SELECTION

In general, the choice of a device should be based on the ***characteristics of the device*** in combination with the ***characteristics of the site/project***. The following paragraphs discuss these characteristics and the criteria that should be considered.

Device Characteristics

Characteristics of devices are:

- ***Device composition*** - The chosen device should have sample-contacting parts made of "inert" materials that limit the potential for bias through sorption or leaching of contaminants, degradation, or corrosion. For components requiring rigid material (casing, screen, bailers etc.), the acceptable materials are fluorocarbon polymer (e.g., Teflon®), stainless steel (316 and 304), and PVC. Disposable bailers can also be composed of polyethylene and polypropylene. When sampling for organics, pump tubing should be composed of flurocarbon polymer, or flurocarbon polymer-lined polyethene. Polyethene tubing is also acceptable for sampling for inorganics (U.S.G.S, U.S.EPA, 2002, ASTM 4088).

- ***Device design and technique of use*** - The device should deliver samples with minimal atmospheric exposure, should not apply negative pressures (vacuum), and should limit agitation, both in the well and in the transfer process. Furthermore, the tool should not introduce air or non-inert gas into samples as part of its lift mechanism.

- ***Flow rate control and capacity*** - When pumps are used, low flow rates are desirable to limit agitation and turbulent flow, especially for VOCs (Barcelona et al., 1985, U.S. EPA, 1986a). The ability to maintain a steady low flow varies significantly. If the device is

being used for purging and sampling, then it should be capable of being operated at variable flow rates suitable for both applications. Flow control that involves "valving" should be avoided, since it can cause pressure changes and subsequent sample alteration. Instead, a mechanism that directly controls the rate (i.e., a rheostat to vary the power supplied to an electric submersible pump) should be utilized.

- ***Operation and Maintenance*** - The device should be easy to operate and maintain. If personnel are not properly trained, the margin of potential error is greater. The device should be designed for in-field maintenance. Mechanically simple equipment that can be easily repaired with inexpensive, replaceable parts is preferable. If decontamination is necessary, the device should be easy to decontaminate. Devices that are constructed to minimize the surface area contacting ground water samples and that are easy to disassemble and reassemble are best. Use of dedicated or disposable equipment at each well or sampling point eliminates the need for decontamination, saving valuable field time and reducing the potential for cross contamination of samples.

- ***Device reliability, durability, and portability*** - The device should operate reliably for extended periods and be able to withstand a variety of chemical and physical environments. Dedicated equipment may need to withstand extended contact with ground water and any existing contamination. Equipment that is transported into locations where access is limited should be sufficiently portable. Excess weight and volume of battery packs, generators, air compressors, tubing, etc. can limit portability.

- ***Capital, operation, and maintenance costs*** - These should be considered, however, they should not be overriding factors. Obtaining a sample that is representative of site conditions should be of more importance than cost, particularly when the costs of well installation, chemical analysis, and possible litigation resulting from discrepant analytical results are considered. These costs often far outweigh equipment purchase costs (Nielsen and Yeates, 1985).

Site/Project Characteristics

Characteristics of sites/projects that should be considered are:

- ***Monitoring Well Diameter*** - The device should be compatible with the diameter of the well. Most sampling equipment is not designed to be used in all wells.

- ***Well Obstructions or Constrictions*** - These can hinder the entry and retrieval of sampling equipment. For example, casing joints may not be flush and could prevent insertion. Also, a well that is not plumb can restrict access.

- ***Depth to the Sampling Interval*** - Deeper zones require greater lift capacity and generally increase sampling times, which may limit the desirability of labor-intensive devices. Options generally become limited as depth increases.

- ***Parameters of Interest*** - The suitability of various devices may depend on the parameters of greatest concern. Some devices perform better for inorganics, while some are more suitable for VOCs.

- ***Presence of Non-Aqueous Phase Liquids (NAPLs)*** - The equipment should be capable of detecting the presence of either light or dense NAPLS if they are potentially present.

- ***Saturated Zone Characteristics and Ground Water Chemistry*** - The equipment should be appropriate for the saturated zone yield, the screen or open borehole length, the presence of stratification (causing vertical variation in yield) within the screened saturated zones, and the available water column in the well. Additionally, the sampling equipment should be compatible with ambient ground water chemistry, unusually low (<5.5.U.) or high (>9.5.U.) pH conditions, the presence of gas, etc.

- ***Temporal (Seasonal) Variations*** - The sampling equipment should be operable over seasonal variations in saturated zone temperature, yield and water level elevation.

TYPES OF EQUIPMENT

The following is a discussion of some of the sampling equipment available. Table 10.3 (at the end of this section) summarizes the recommended devices. Devices not mentioned may be acceptable if they are peer-reviewed and have been demonstrated to be capable of collecting representative samples. For additional information, see ASTM D4448-01, ASTM D6634-01, Barcelona et al. (1985), Nielsen and Yeates (1985), Electric Power Research Institute (EPRI, 1985, 1987), Gillham et al. (1983), Nielsen and Nielsen (2006), Parker (1994), Pohlman and Hess (1988), and U.S. EPA (1992), Yeskis and Zavala (2001).

Grab Samplers

Grab samplers collect a sample at discrete depths without being pumped or lifted to the surface by gas or air. Grab samplers commonly used to collect ground water include bailers and syringe samplers.

Bailers

Bailers are the most portable of all sampling devices. A bailer can be constructed of virtually any rigid or flexible material, including materials that are inert to chemical contaminants. For sampling ground water, acceptable compositions include Teflon®, stainless steel, PVC, polyethylene, and polyprolyene. Disposable bailers are often the choice of the environmental industry. The cord used to raise and lower the bailer should be of non-reactive substance (e.g., stainless steel, teflon-coated wire/rope, polypropylene).

Bailers are readily available in a variety of diameters. Their diameter should be 75% (or less) of the inside diameter of the well casing to allow for adequate clearance.

There are several types of bailers (ASTM D 6634-01, D6699-01):

- A ***top filling*** bailer is designed such that water flows through its top. Because of the agitation of the sample, this bailer is only appropriate for sampling light, non-aqueous phase liquids (LNAPL).

- A ***single check*** valve bailer (open bailer) has a valve at its bottom that seals the sample chamber when the bailer is withdrawn.

- A ***double check*** valve bailer (point source bailer) is designed to sample discrete zones in a water column. Water flows through valves at both ends as the bailer is lowered. When the desired level is reached, the bailer is pulled back, both valves close, and water from the interval is retained. However, if appropriate procedures are not carefully followed, samples collected may not be representative of the depth interval of interest. The double check valve bailer is also effective in collecting dense, non-aqueous phase liquids (DNAPLs).

- A **differential pressure** bailer consists of a sealed canister body with two small diameter tubes of different heights. The bailer is rapidly lowered into the well. When the descent has stopped, differences in hydrostatic pressure between the two tubes allow the bailer to fill through the lower tube as air is displaced through the upper tube. This minimizes the exposure of the sample to air, especially if the bailer is fitted with internal 40 ML vials for direct sample bottle filling. However, because the bailer is lowered rapidly, it will agitate the water column.

The use of bailers is discouraged. Current research indicates that bailers generally <u>are not</u> the best available technology to collect ground water samples. Various studies (laboratory and field) have been conducted to investigate the potential differences in VOC analytical results between samples collected by bailing and low-flow techniques. Some studies have demonstrated that levels of VOCs in samples obtained with bailers are statistically lower than in samples obtained with other devices (Imbrigiotta et al. 1988; Tai et al. 1991). In addition, bailing can cause increased turbidity (Puls and Powell, 1992; Puls et al., 1992; Backhus et al., 1993). In contrast, a literature survey by Parker (1994) found that bailers can recover representative samples under certain circumstances and that loss of volatile and oxidizable analytes can be reduced by careful use of bottom-emptying devices. In addition, a Wisconsin Department of Natural Resources study comparing results from a bottom-emptying bailer and a Keck® helical-rotor pump operated at low flow pumping rates determined that differences in VOC concentrations were relatively small (Karkins, 1996).

Though current research indicates that bailers generally <u>are not</u> the best available technology, they may be the only practicable option for sampling some ground water zones. Bailers may be preferred where the water column is small or the saturated zone is very deep. They may be preferred when concentrations of contaminants are extremely high because they are easier to decontaminate and are less expensive to replace than pumps. Disposable bailers eliminate the need to decontaminate. Personnel sampling with bailers need to be properly trained since the results are highly dependent on the skill, care, and consistency of the operator. This training should be documented in the SAP.

If bailers are used, ***double check valve bottom-draining*** bailers are recommended. This allows for lessened sample disturbance during transfer to the container. The bailer should be composed of Teflon®, stainless steel, PVC, polyethylene, or polyprolyene. Either fluorocarbon polymer-coated or colorless (white) polypropylene cord should be used to lower and raise the bailer. Polypropylene cord is inexpensive enough to be discarded after one use. A bailer should always be lowered and raised slowly to minimize sample agitation

associated with degassing, aeration, and turbidity and to the extent possible, avoid hitting the sides of the well. A tripod and pulley may be used to remove the bailer.

Pouring water from the top of a bailer either directly into a container or to a transfer vessel may agitate/aerate the sample and alter its chemistry; therefore, the pouring should be done with care.

Syringe Samplers

Syringe samplers may be used for low-volume sampling for inorganics and non-volatile organics. These samplers can operate at great depths to provide discrete samples from specific intervals or zones. A sample container is pressured or evacuated and lowered into a well. The sample is collected by opening the container or releasing the pressure, drawing water into the sampler (Nielsen and Nielsen, 2006). The syringe sampler is withdrawn and the sample is transferred to a collection bottle, or alternatively, the syringe sampler can be utilized as the sample container.

Syringe devices cannot be used for purging large volumes and are ineffective for collecting large samples. In addition, ground water containing high concentrations of suspended solids may cause the syringe device to leak (U.S. EPA, 1992). Researchers have concluded that these samplers are inferior in comparison to other devices when sampling for VOCs (Imbrigiotta et al., 1988). Therefore, syringe samplers are not recommended.

Bladder Pumps

A bladder pump consists of a flexible bladder inside a rigid housing. Water enters the bladder from the bottom and is squeezed to the surface through a discharge line by gas pressure applied to the outside of the bladder. An air compressor and regulator turn the pressure on and off, allowing new water to enter the bladder and the cycle is repeated. The separate bladder chamber does not allow the sample to come in contact with the compressed air. Check valves at the top and bottom prevent backwash from the sample tube and bladder. Flow can be readily controlled and low rates of 100 ml/min are easily obtainable. Teflon bladders and Teflon/stainless steel outer shells are readily available and recommended.

Bladder pumps have been used to depths greater than 200 feet and are available in sizes designed for 2-inch wells. The need for a power source and compressed air limits mobility, especially in remote areas. Potential problems include sediment damaging the inner bladder and high suspended solids concentrations causing failure of check valves for some models (Nielsen and Nielsen 2006). Strainers or screens are available that attach below the bladder to filter material. Note that samples collected through a strainer or screens are not considered to be filtered.

Bladder pumps are generally recognized as the best overall sampling device for both inorganic and organic constituents (U.S. EPA, 1992). Muska et al., (1986) found that bladder pumps generate reproducible analytical results. Kasper and Serkowski (1988) concluded that the sampling rate and reliability of the bladder pump outperformed both the gas and mechanically driven piston pumps. Tai et al. (1991) concluded that a bladder pump yielded

representative recoveries of VOCs compared to a control sample. Pohlmann and Hess (1988) determined that bladder pumps are suitable for collecting samples for almost any constituent.

Bladder pumps are recommended for purging and sampling. Whenever possible, the pump should be dedicated to the well. Doing so eliminates the need to transport and decontaminate the pump, thereby reducing the potential for cross contamination as well as saving time and reducing project cost.

Electrical Submersible Pumps

A variety of electrical submersible pumps are available. In the past, electrical submersible pumps were primarily designed for use in water supply wells and could not be used for contaminant monitoring purposes. However, manufacturers have since designed low-flow electrical submersible pumps for 2-inch diameter monitoring wells that are capable of collecting representative samples. Submersible pumps designed for ground water sampling incorporate non-sorptive materials (e.g., stainless steel, Teflon®, etc.) that are appropriate for collecting VOCs and other sensitive parameters. One disadvantage is that the heat generated by the motor could increase sample temperature, resulting in the loss of dissolved gases and VOCs and subsequent precipitation of trace metals (Nielsen and Nielsen, 2006) Therefore, after sampling, it is recommended that a sample be withdrawn and the temperature measured to assess whether the pump has increased the water temperature. Another disadvantage is the number of intricate parts, which may cause decontamination and maintenance to be time-consuming and difficult.

Two types of submersible pumps available are the centrifugal and the progressive cavity (helical-rotor) pumps. Both are positive displacement devices.

Centrifugal Submersible Pump

Centrifugal submersible pumps designed for 2-inch monitoring wells are usually cooled and lubricated with water rather than hydrocarbon-based coolants and lubricants that could contaminate samples. The electric motor spins or rotates an impeller (or series of impellers) that causes water to be accelerated outward and then upward into and through the pump's discharge lines. The higher the pumping rate, the greater the potential for sample alteration by agitation, increased turbulence, and pressure changes. Therefore, a variable-speed centrifugal submersible pump capable of low-flow purging and sampling is essential for collecting a representative sample. Low-flow centrifugal submersible pumps appear to perform similarly to low-flow bladder pumps with respect to preserving sample integrity.

Progressive Cavity (Helical-Rotor) Pumps

Progressive cavity (helical-rotor) pumps are appropriate for collecting sensitive samples if low-flow pumping rates are used. An electric motor at the base turns a corkscrew-like helical rotor near the top. The helical rotor causes an upward movement of water trapped in the vacuities of the rotor and the water moves up and through the discharge line. A check valve at the top ensures that water in the discharge line (sampling tube) does not re-enter the pump. A controller box at the surface allows for variable flow rates.

Gas-Driven Piston Pumps

Although not commonly used, the gas-driven piston pump is acceptable as long as the parts contacting samples are chemically inert (i.e., will not affect sample representativeness). This device utilizes gas pressure to drive a piston between two chambers, one for gas and one for water. Gas is injected through one of two tubes to lower the piston in the gas chamber, allowing water to fill the upper water chamber. Pressure is then applied to a separate tube that pushes the piston upward and propels the sample to the surface. Water and gas remain separated. These pumps can operate at great depths and collect large-volume samples. Disadvantages are that valves and pistons are known to be damaged by fine-grained sediments and mobility is limited by the need for a gas supply. Additionally, the valving mechanism may cause a series of pressure drops that could cause sample degassing and pH changes (U.S. EPA, 1992).

Suction Lift Pumps

Suction lift pumps deliver samples by applying a vacuum at the surface. The negative pressure is applied by a portable pump attached to a tube lowered into the well. Suction pumps are limited by practical suction limits, which restricts their use to wells with water levels less than 25 feet below ground.

Surface centrifugal and ***peristaltic*** are the two major types of suction lift pumps. The peristaltic offers greater advantages over the surface centrifugal. Surface centrifugal pumps must be primed before being operated, and should employ a vacuum flask to prevent contact of the sample with moving parts. Peristaltic pumps are self-priming and create a vacuum by a series of rotating wheels that compress the sample tubing. As the sample only contacts the tubing when using a peristaltic pump, no moving parts need to be decontaminated. Usually, disposable tubing is used. Peristaltic pumps generally cause less agitation then surface centrifugal pumps.

Suction lift pumps are very portable, widely available, and relatively inexpensive. Flow rates are controlled easily, providing adequate rates for sampling. These devices typically can be used in wells of any diameter and plumbness. The major drawback is that the application of strong negative pressures promotes degassing; therefore, these devices are not recommended for collecting samples to be analyzed for volatile, semi-volatile, pH, Eh, dissolved metals, dissolved gasses, and other gas-sensitive parameters. The National Council of Industry for Air and Stream Improvement (NCASI, 1984) found a 10 to 30 percent loss in VOC concentrations from peristaltic/vacuum flask systems compared to results for bailers, bladder pumps, or submersible pumps. Imbrigiotta et al. (1988) also attributed losses of VOCs due to the vacuum created by peristaltic pumps.

Passive Diffusion Samplers

Passive diffusion bag samplers (PDBs) use a low-density polyethylene diffusion membrane filled with deionized water to collect water samples for VOC analysis. The polyethylene acts as a semi-permeable membrane allowing volatile contaminants to diffuse into the deionized water. Once chemical equilibrium is reached, a water sample that is representative of the VOC concentrations may be obtained for the interval at which the sampler is placed. Use of

multiple PDB samplers at different depths within a well screen interval can allow for a vertical profile of the VOC contamination within the well. Advantages of PDB sampling include its low cost, minimal purging and water disposal, and the ability to monitor a variety of VOCs. A disadvantage is that they are not applicable to inorganics and other contaminants that do not readily diffuse across the semi-permeable membrane. PDB sampling may not be applicable for sites where water in the well casing may not be representative of the saturated zone adjacent to the well screen. This may occur when water in the well casing is stagnant, or when there is a vertical flow within the well. In addition, PDB samplers do not provide a discrete time-interval sample, but rather an average of the concentrations in the well over the equilibrium period.

Passive diffusion bag samplers are appropriate for long-term monitoring at well-characterized sites. The target analytes should be limited to chemicals that have been demonstrated to diffuse well through polyethylene (i.e., most VOCs and limited non-VOCs), as listed in Tables 1-1 and 4-1 of ITRC's PDB sampler guidance document (ITRC, 2004). A combined version of these tables is provided below as a reference (Table 10.2). However, as the compound list may change as further tests are conducted, ITRC (http://www.itrcweb.org) should be contacted for the most recent list of chemicals favorable for sampling with PDB. The site sampled should have sufficient ground water flow to provide equilibrium between the water in the well screen and the surrounding ground water zone. ITRC (2004) suggests that care should be given in interpreting PDB results when the hydraulic conductivity is $<10^{-5}$ cm/s, the hydraulic gradient is <0.001, or the ground water velocity is < 0.5 ft/day. Use of PDBs is not appropriate when a vertical flow in the well exists. A deployment time of at least two weeks is recommended to allow for diffusion of the analytes across the membrane (ITRC, 2004, Vroblesky, 2001; Vroblesky and Hyde, 1997; Yeskis and Zavala, 2001; and U.S.G.S , 2002).

Other Devices

The ***gas drive sampler*** operates by applying positive gas pressure into a sample chamber to force the water to the ground surface. Water enters through a valve at the bottom of the sampler into the sample chamber. When pressure is applied, the valve closes and water is forced through a discharge line to the surface. When the pressure is reduced, the valve reopens, allowing water to enter the chamber, and the cycle is repeated.

Gas drive samplers are available with inert components and in a variety of diameters. They can provide continuous flow at acceptable rates for sampling. Their major drawback is that they allow for gas contact with the sample, which can cause the loss of dissolved gasses and VOCs and potentially other chemical alterations. Gas can also mix with the sample, causing further alteration. For these reasons, use of these samplers is generally not recommended. Additionally, mobility is limited by the need to provide compressed gas. When sampling very deep wells, high gas pressures are needed, and the device should be designed to handle this added stress.

Gas lift samplers inject air or gas into the water column to "blow" water to the surface. The gas acts as a carrier fluid; however, the gas (even if inert) causes degassing and volatilization. Additionally, aeration and turbulence can further alter the original water chemistry (Lee and Jones, 1983). Therefore, gas lift systems are unacceptable.

Table 10.2 Compounds tested with PDB in laboratory and field tests.

Favorable laboratory diffusion testing results		
Benzene Bromodichloromethane* Bromobenzene** Bromochloromethane** Bromoform* *n*-Butylbenzene** *sec*-Butylbenzene** *tert*-Butylbenzene** Carbon disulfide** Carbon tetrachloride Chlorobenzene Choroethane Chloroform* Chloromethane 2-Chlorovinylether* Dibromochloromethane Dibromomethane 1,2-Dichlorobenzene	1,3-Dichlorobenzene 1,4-Dichlorobenzene Dichlorodifluoromethane 1,1-Dichchloroethane** 1,2-Dichloroethane 1,1-Dichloroethene *cis*-1,2-Dichloroethene *trans*-1,2-Dichloroethene 1,2-Dichloropropane *cis*-Dichloropropene* 1,2-Dibromoethane* *trans*-1,3-Dichloropropene* Ethyl benzene Hexachlorobutadiene** p-Isopropyltoluene** 1-Methylethylbenzene**	Napthalene* 1,1,2,2-Tetrachloroethane Tetrachloroethene (PCE) Toluene 1,2,3-Thrichlorobenzene** 1,2,4-Trichlorobenzene** 1,1,1-Trichloroethane 1,1,2-Trichloroethane Tricholoroethene (TCE) Trichlorofluoromethane 1,1,2-Trhichloro-1,2,2-trifluoroethane** 1,2,3-Trichloropropane* Vinyl chloride *m,p*-Xylene** *o*-Xylene** Xylenes (total)
Unfavorable diffusion testing results		
Acetone* tert-Amyl methyl ether**# Bromoform**# Methyl *iso*-butyl ketone*	Methyl tert-butyl ether* Naphthalene** n-Propylbenzene**	Styrene* 1,2,4-Trimethylbenzene** 1,3,5-Trimethylbenzene**

* Laboratory results only, (Vroblesky 2001a)
**Results from field tests only, (Parsons 2003)
#The data set for this compound was relatively small (fewer than five instances of comparison), so the power of the classification (i.e., acceptable or unacceptable) is fairly low.

Use of Packers

Packers are inflatable rubber devices used in a well or open borehole to isolate water-bearing intervals for hydraulic testing or ground water sampling. Packers can be used to minimize purge volumes in wells with long intake columns by isolating the sampled zone from stagnant water above the screen. Both single and double packer assemblies are used. For sampling, a pump is typically installed above or below a single packer or within a double packer assembly with a discharge line extending through the upper packer. Packer assemblies may include a drop tube through which water level tapes, transducers, pump control and discharge lines, and other monitoring and sampling equipment may extend to the isolated interval.

Prior to using packer assemblies for sampling, all potential limitations or problems should be carefully evaluated and resolved, and the use of packers should be justified. For example, packer materials selected should not leach or sorb contaminants. In addition, the water level within the packer interval should not be drawn down below the upper packer. The potential for vertical movement of ground water to or from the packer interval outside of the well or borehole should be evaluated, as well as the potential for leakage around the inflated packers. For additional discussion on packers, refer to Oliveros et al.(1988).

Table 10.3 Summary of recommendations for sampling mechanisms[5].

MECHANISM	***RECOMMENDATIONS***	***POTENTIAL FOR CHEMICAL ALTERNATION****	***COMMENTS***
Bailer	Double check valve bailers with bottom emptying device Can be used for sampling organics and inorganics.	slight to moderate	Samples may show statistically lower analytical results. Other techniques ***may*** be more appropriate when low levels of organics exist.
Bladder pump	Highly recommended. Can be used for sampling organics and inorganics	minimum to slight	Provides efficient well purging and representative samples over a range of conditions.
Electric Submersible Pumps	Pumps should be constructed of inert components and capable of sampling at low flow rates. Can be used to sample organics and inorganics.	slight to moderate	Good for purging and sampling deep, high yielding wells. Recommend monitoring temperature, to assure pumping does not increase sample temperature.
Gas Driven Piston Pumps	Acceptable if sample compositions are met. Can be used to sample organics and inorganics.	slight to moderate	Difficult to decontaminate.
Syringe Sampler	Recommended for low volume sampling of discrete zones. Can be used for sampling inorganics and non-volatile organics, not recommended when sampling for volatiles.	minimum to slight	Cannot be used for purging.
Suction Lift Pumps (Peristaltic/ Centrifugal)	Not recommended for sampling for volatiles and semi-volatiles	moderate to high	Can cause significantly lower recoveries of purgeable organic compounds and gases.
Passive Diffusion Bag Samplers (PDB samplers)	Long-term monitoring of VOCs at sites with sufficient ground water flow. Cannot be used for inorganics or most non-VOCs	slight	Sampler does not provide a discrete time-interval sample, but instead an average concentration over the equilibration period Not appropriate if chemicals of concern are transported on suspended particles Not acceptable for inorganics or phthalates.

[5]Table does not address gas drive and gas lift samplers. These devices generally are not recommended.

FIELD PROCEDURES

As appropriate, the health and safety plan should be reviewed prior to initiating field procedures. Sampling personnel should not use perfume, hand lotion etc. when collecting a ground water sample. If insect repellent is necessary, then care should be taken not to allow the repellent to come into contact with the sampling equipment and it should be recorded that insect repellent was used (Wilson, 1995). Activities that may affect sampling, such as fueling a vehicle, should be avoided.

Prior to sampling, several tasks should be completed and documented to ensure that representative samples can be obtained. These tasks include, but are not limited to: observation of field conditions, well inspection and preparation, well measurements, and immiscible layer detection. (Documentation guidance is provided in subsequent parts of this chapter).

FIELD CONDITIONS

Weather and site-specific conditions that could affect sample representativeness should be documented. The approximate ambient air temperature, precipitation, and wind and other field conditions should be noted in a field notebook or field sampling form. In addition, any site-specific conditions or situations that could potentially alter the ground water samples or water level measurements should be recorded. Examples include, but should not be limited to: excavation or construction activities, accidental spills, and presence of smoke, vapors, or air contaminants from anthropogenic activities.

WELL INSPECTION AND PREPARATION

Upon arrival, the well protective casing, cap, and lock should be carefully inspected and observations recorded to document whether damage or tampering has occurred.[6] Cracks in the casing and/or surface cement seal should be noted, as well as soil washouts and depressions around the casing.

Before taking any measurements, all weeds and debris should be cleaned from the well area. All equipment should be covered and stored off the ground to avoid potential cross-contamination. A clean plastic sheet can be placed on the ground to help prevent contamination of equipment if there is a concern that sample equipment may come into contact with the ground. The plastic should be disposed properly following completion of sampling at each well. A portable field table covered with a new plastic sheet at each well is convenient for preparing equipment and performing field measurements (Wilson, 1995).

[6] See Chapter 8 (Well Development, Maintenance, and Redevelopment) for additional information on periodic well maintenance checks and well-integrity tests).

WELL MEASUREMENTS

Appropriate measurements should be made before any water is purged and sampled. These include measuring of static water levels and total well depth, and depending on site-specific conditions or circumstances, detection of gases, organic vapors and immiscible liquids.

Detection of Organic Vapors and Gases

Because VOCs often present health and safety concerns, it may be prudent to use field screening instruments if VOCs are suspected. Two field screening instruments that may be useful are the photoionization detector (PID) and an organic vapor analyzer (OVA).[7] PIDs and OVAs are typically used to provide an estimate of the total volatile organic vapor concentration (e.g., benzene, vinyl chloride, tetrachloroethane), rather than a quantitative result for individual compounds. OVAs are capable of detecting methane, while PIDs are not. The selection of the correct lamp is important when using a PID meter. Field meters are available for detecting methane, carbon dioxide, and hydrogen sulfide, including combination meters that can be used to screen for two or more of these gases. Vapor measurements can give useful information about potential ground water quality and allow for sampling personnel to take appropriate safety precautions. It also may be useful to determine the potential for the presence of immiscible layers, which necessitate additional sampling procedures and concerns.

Gases that typically may be of concern include methane, carbon dioxide, and hydrogen sulfide. Generally, methane and carbon dioxide may occur in monitoring wells at solid waste landfill facilities. Methane may also be present as natural gas in bedrock formations. The presence of methane is significant because it may include trace amounts of VOCs that are too low to be detected with a PID or OVA. Additionally, methane is a health and safety concern because it can cause a potentially explosive atmosphere. Carbon dioxide may affect ground water chemistry by altering pH or alkalinity. Hydrogen sulfide, which is typically associated with sewage or decaying vegetation, may affect pH meter performance. Hydrogen sulfide gas can also be naturally occurring in carbonate bedrock aquifers.

Water Level

In addition to providing hydrogeologic information on a continuing basis, measurement of the water level in a well enables determination of the volume of water contained, which may be useful for purging determinations. Measurements should be taken from the entire well network before any water removal to obtain a single "snapshot" of current hydraulic head conditions and to avoid potential effects on the water levels in nearby wells. The measurements should be made within a period of time short enough to avoid temporal variations in ground water flow that could preclude an accurate determination of ground water flow rate and direction. The period of time should not exceed 24 hours.

Measurements can be taken manually or automatically. Table 10.4 summarizes the manual methods. Automatic, continuous recording devices may be useful for collection of long-term

[7]For further information on types and uses of these instruments, see Anastas and Belknap (1980), Brown et al. (1980) and DuBose et al. (1981).

data and in pumping tests. Water level measurements are described in more detail by Dalton et al. (1991), Aller et al. (1991), and ASTM Method D4750-87. An electronic probe is recommended for taking water level measurements.

Measurements should generally be to within ±0.01 ft. There may be instances where this level of accuracy is not necessary (e.g., steep water table, wells are far apart); however, rules may require this level of accuracy. All wells should have accurate surveyed reference points[8] for water level determination. Typically, a marked point on the top of the inner riser pipe is used.

Equipment should be properly decontaminated before use in each well to ensure sample integrity and prevent cross-contamination. Techniques are discussed later in this chapter.

Light non-aqueous phase liquid (LNAPL) (see below) may affect the water level measurements in a well. It is important to know the density of the free product because water level measurements in monitoring wells that also contain free product should be corrected to account for the different densities of water and product and the thickness of the product layer. See U.S. EPA (1996a) for procedure to correct for an LNAPL layer.

Well Depth

Measuring the depth of a well indicates the amount of siltation that has occurred. Natural siltation can block water from entering, which could lead to erroneous water level measurements and bias analytical results by increasing sample turbidity. Checking depth also provides a check on casing integrity. Corrosion can cause collapse of the well casing.

Depth can be determined with a weighted tape measure or marked cable, each of which should be composed of inert materials. Often, the same device that is used to measure water levels can be used. Heavier weights are necessary as depth increases to effectively "feel" the well bottom. The measurement should be recorded on the field log.

It generally is not necessary to measure depth every time water levels or samples are obtained. It may not be possible to obtain depth from a well with a dedicated pump unless the pump is removed. In addition, the logistics of decontaminating the entire length of the measuring tape in contact with contaminated ground water may cause depth measurements to be impractical. At minimum, depth measurements should be taken once a year in wells that do not have dedicated pumps. Measurements in wells with pumps should be taken whenever the pump is removed for maintenance. If siltation is suspected to be a problem (e.g., noted increase in sample turbidity, or decrease in pump efficiency), the pump should be removed and the well depth checked

[8]It is recommended, the reference point be based on the National Geodetic Vertical Daturm or local common datum. However, an arbitrary datum common to all wells in the monitoring network may be acceptable if necessary.

Table 10.4 Summary of methods for manual measurement of water levels (based on Dalton et al., 2006, ASTM D4750 and U.S.EPA, 2001).

MEASUREMENT METHOD	MEASUREMENT ACCURACY (in feet)	DESCRIPTION & ADVANTAGES	MAJOR INTERFERENCES OR DISADVANTAGES
NON-FLOWING WELLS			
Weighted steel tape with chalk	0.01	The water level is determined by lowering a weighted steel tape with bottom 2-3 feet coated with carpenters chalk into the well. The water level is calculated by subtracting the submerged distance, as indicated by the lack of chalk color, from the reference point at the top of the well. More accurate than other methods. Recommended when gradient is less than 0.05 ft/ft (Yeskis and Zavala, 2002).	• Water on the side of the casing or cascading water may wet the tape above the actual water level and result in measurement error. • Addition of foreign material to well (chalk). • Approximate depth to water may be unknown, thus too short or too long a length of chalked tape may be lowered into the well. • Submergence of a weight and tape may temporarily cause a rise of liquid in a small diameter well. • Not recommended if obtaining ground water samples for water quality purposes
Air-line	0.25	A small straight tube (usually #0.375 inches in diameter), of accurately known length is installed in the well along with a pressure gauge and a fitting for an air source. A water level measurement is made when air is pumped into the tube and the pressure monitored.	• Less precise • Air-line or fittings can leak
Electrical method	0.01 to 0.1	An electronic probe is lowered into the well. When the probe comes into contact with water, a potential between the two dissimilar metals in the probe is measured at the surface on a millivolt meter.	• Errors result from changes in cable length as a function of use, temperature and depth • Reliable contact may be difficult if LNAPLs are present

MEASUREMENT METHOD	MEASUREMENT ACCURACY (in feet)	DESCRIPTION & ADVANTAGES	MAJOR INTERFERENCES OR DISADVANTAGES
Transducer	0.01 to 0.1	A transducer is lowered a known distance into the well and allowed to equilibrate with fluid temperature. Distance of submergence of the transducer is read on the signal conditioning unit and is subtracted from the cable length referenced at the top of the well.	• Accuracy is dependent upon range and sensitivity of the device.
Float	0.02 to 0.5	A float is attached to the end of a steel tape and suspended over a pulley and lowered into the well. A counter weight is attached to the opposite end. Depth to water is read directly from the steel tape at a known reference point from top of casing.	• Error can be caused by float or cable drag, line shift, submergence of counter-weight, and temperature and humidity.
Popper	0.1	A metal cylinder with a concave bottom is attached to steel tape and lowered into the well. A distinct "pop" can be heard when the cylinder is dropped onto the water surface	• Accuracy is dependent upon skill of measurer and depth to water. • Potential to agitate water. • Contact cannot be made reliably when LNAPLS are on the water surface.
Acoustic Probe	0.02	Adaptation of the popper and electrical method [Schrale and Brandywyk (1979)]. An electric device is lowered into the well until an audible sound is emitted.	• Cascading water can cause false measurements. • Contact cannot be made reliably when LNAPLs are on the water surface.
Ultrasonic	0.02 to 0.1	Water level measurements are determined by an instrument that measures the arrival time of a reflected transmitted sonic or ultrasonic wave pulse.	• Accuracy can be limited by the change of temperature in the path of the sound wave and other reflective surfaces in the well (i.e., casing, pumps, etc.). Greater depth, the less accurate.
Radar	0.02	Unit provides a pulsed or continuous high frequency wave that reflects of the water surface in the well.	• Requires a plumb well, obstacles can prevent a clean line of site down the well. • Generally limited to larger wells and water levels less than 100 feet.

MEASUREMENT METHOD	MEASUREMENT ACCURACY (in feet)	DESCRIPTION & ADVANTAGES	MAJOR INTERFERENCES OR DISADVANTAGES
Laser	0.01	Battery operated units potentially capable of obtaining water level information from monitoring wells.	• Further development is needed for adopting it to ground water monitoring programs • Requires a plumb well, obstacles can prevent a clean line of site down the well. • Beams can sometimes penetrate the water and not reflect back
FLOWING WELLS			
Casing Extension	0.1	A simple extension is attached to the well casing to allow water level to be measured directly.	• The device is only practical when additional height requirement is only several feet. • Accuracy low because water level in flowing wells tends to fluctuate.
Manometer/ Pressure Gauge	0.1 to 0.5	The pressure of water within a sealed or "shut-in" well is measured.	• Gauge inaccuracies. • Calibration is required.
Pressure Transducers	0.02	Procedures are the same as described above for transducers. The range of a pressure transducer should be carefully matched with shut-in well pressure.	• Changes in temperature in the transducers cause errors.

Depth measurements should be to the nearest 0.1 foot (U.S. EPA, 2001). Depth to bottom can be obtained when collecting the round of depth-to-water measurements. Care should be taken to avoid stirring up any accumulated sediments, thus increasing turbidity of the water column. If a well has historically had silting problems, consider taking the depth measurement after sampling.

Detection of Immiscible Liquids

Non-aqueous phase liquids (NAPLs) are organic liquids that exist as a separate phase, immiscible phase when in contact with water and/or air. If the presence of NAPLs is suspected, the sampling program should include devices and protocols to detect them. Dense non-aqueous phase liquids (DNAPL) are referred to as "sinkers" because their density (greater than water) causes them to sink. Light non-aqueous phase liquids (LNAPL) are referred to as "floaters" because their density (less than water) causes them to float on the water table surface. If floaters are of concern, it is important that, upon opening the well cap, the air in the casing is monitored with a photoionization detector (PID) or an organic vapor analyzer (OVA). In addition to providing information on worker health risks, air monitoring can serve as a first indication of the presence of volatile floaters.

Protocol to detect immiscible liquids should always include visual inspection of purged water and any equipment that is removed from the well after use. Additionally, probes and reactive pastes have been developed to determine air/immiscible and water/immiscible interfaces. Indicator pastes are used to coat an interface probe or a weighted tape. An observed reaction indicates the presence of an immiscible liquid. Probes and pastes can be utilized for detecting both floaters and sinkers (U.S. EPA, 1992). Transparent bailers also can be used.

SAMPLING IMMISCIBLE LIQUIDS

If an LNAPL is found to be present, a bailer or submersible pump can be used to remove it, if necessary (U.S. EPA, 1992). Any LNAPL greater than 2 feet in thickness can be evacuated using a bottom-valved bailer. The bailer should be lowered slowly to a depth less than the product/water interface. A modified, top-filling bailer (bottom valve sealed off with a fluorocarbon resin sheet between the ball and ball seat) can be used to remove immiscible layers less than 2 feet in thickness. A stainless steel weight can be added to the retrieval line above the bailer to counter its buoyancy. In either case, a peristaltic pump also can be utilized if depth to product is less than 25 feet. Any LNAPL less than 2 inches thick can be collected from the top of the water column using a bailer (U.S. EPA, 1992). Samples collected in this manner consist of both an aqueous and non-aqueous phase.

To the extent possible, the sampling and purging method should prevent the disturbance of DNAPL. A sample of the DNAPL should be obtained after the ground water sample has been obtained. Double -check valve bailers, Kemmerer devices and syringe samplers often are used. Submersible pumps can be used if the dense phase is sufficiently thick (U.S. EPA, 1992).

When an immiscible layer is to be analyzed, additional sampling equipment (i.e., containers) may be needed to have sufficient volume for laboratory analysis. It is important that appropriate QA/QC procedures be followed when collecting samples of any immiscible liquids. If any immiscible layer is removed, it should be properly collected, containerized, characterized, and managed. The Division of Hazardous Waste Management, Ohio EPA, can be contacted for guidance on these issues.

SAMPLING AND PURGING PROCEDURES

Upon completion of the preliminary procedures, purging and sampling of ground water can generally be accomplished by volumetric or low flow rate methods. However, volumetric purging and low flow rate purging/sampling may not be feasible for wells that produce less than 100 ml/min. Therefore other approaches should be considered, including minimum/no purge sampling as well as purging to dryness and sampling as soon as the well has recharged sufficiently. These approaches are discussed below, along with methods to determine when purging is complete by measuring indicator parameters. Where dedicated equipment is not used, sampling should progress from wells least likely to be contaminated to those most likely to be contaminated to minimize the potential for cross-contamination. Care needs to be taken to avoid agitation and temperature increases in the sample during sample collection and shipment to the laboratory.

Field Measurements of Ground Water Indicator Parameters

Indicator parameters are measured in the field to evaluate well stabilization during purging, provide information on general ground water quality, help evaluate well construction, or indicate when well maintenance is needed. Indicator parameter data may be helpful in evaluating the presence of ground water contamination. Indicator parameters measured during well purging and sampling activities may include specific conductance, pH, dissolved oxygen, oxidation-reduction potential, temperature, and turbidity (Garner, 1988). Due to the unstable nature of these parameters, laboratory determinations will likely not be representative of field conditions, and consequently are of limited value.

Specific conductance measures the ability of water to conduct an electric current. For ground water, it is generally reported in micromhos (□ mhos/cm), as natural waters commonly exhibit specific conductances well below 1 □ mhos/cm (Hem, 1992). Specific conductance is a relative measure of the amount of ions present in ground water, as the magnitude of the current conducted by a ground water sample is directly proportional to its ionic concentration. Based on this relationship, total dissolved solid concentrations may be approximated from specific conductance data (Hem, 1992). For most circumstances, specific conductance has been demonstrated to be a reliable indicator of the chemical stabilization of purge water (e.g., Barcelona et. al., 1994).[9] High readings may indicate contamination, especially if the readings are elevated compared to background. Alternatively, elevated specific conductance may indicate grout contamination in a well or an inadequate grout seal, that is allowing infiltration of surface water or ground water from overlying saturated zones. Elevated specific conductance readings may also indicate inadequate well development (Garner, 1988).

pH is a measure of the effective concentration (or activity) of hydrogen ions and is expressed as the negative base-10 logarithm of the hydrogen-ion activity in moles per liter. Uncontaminated ground water typically exhibits a pH ranging from 5 to 9 (Brownlow, 1979;

[9]Specific conductance should not be used by itself to determine whether adequate purging has been completed. Ohio EPA recommends using multiple indicator parameters to determine when to terminate purging and begin sampling regardless of the assumed reliability of the data.

Ohio EPA, 2003). While pH has commonly been used as a purge water stabilization indicator, it is not particularly sensitive in distinguishing stagnant casing water from formation water. However, pH measurements are important for the interpretation of ground water quality data (Puls and Barcelona, 1996), as pH indicates the relative solubility of metals and speciation of many other chemicals (Garner, 1988). First, pH measurements reflect chemical reactions that produce or consume hydrogen ions (Hem, 1992), and therefore, changes in pH from background may indicate the presence of ground water contamination or that existing contamination has spread. Second, pH can be very useful in identifying well construction or maintenance problems. For example, pH readings that consistently increase in (7.8, 8.3, 8.8, 9.4...) during purging may indicate grout contamination in the sand pack and screened interval.

Dissolved oxygen **(DO**) has been demonstrated to be a reliable indicator of the chemical stabilization of purge water under most ground water purging and sampling circumstances (e.g., Barcelona et. al., 1994).[1] DO is a good indicator when sampling for volatile organic compounds (VOCs), because erratic or elevated DO readings may reflect procedures that are causing excessive agitation and aeration of the ground water being drawn from the well and subsequent loss of VOCs (Pennino, 1988). Artificially aerated ground water may also adversely affect dissolved metals analyses. Concentrations of DO in ground water (1 to 4 mg/l, Testa and Winegardner, 1991) tend to be lower than surface water concentrations (7 to 14 mg/l, Deutsch, 1997), but are generally measurable using field probes, even in deep aquifers (Hem, 1992; Rose and Long, 1988). Atmospheric oxygen is the principal electron sink for redox processes in the hydrosphere (Hem, 1992), and DO in ground water is depleted by reactions involving both inorganic and organic constituents. Accordingly, relatively low DO concentrations (< 1 mg/l) in ground water may indicate the biodegradation of organic contaminants, including VOCs (U.S. EPA, 1997). For example, low DO concentration may indicate the presence of petroleum products, industrial solvents, or a solid waste leachate plume.

Oxidation-reduction potential (ORP), also referred to as redox potential or Eh, is a numerical index of the intensity of the oxidizing or reducing conditions within an aqueous solution such as ground water. Oxidizing conditions are indicated by positive potentials and reducing conditions are indicated by negative potentials. ORP measurements are generally expressed in millivolts (mV). The ORP of natural (uncontaminated) ground water typically ranges from +500 to -100 mV (Brownlow, 1979). Ground water contaminated with organic compounds generally exhibits depressed ORP values compared to background conditions and may exhibit ORP values as low as -400 mV (Wiedemeier et. al., 1997). ORP may not be an appropriate stabilization parameter for some ground water conditions (Yeskis and Zavala, 2002). ORP data is useful for evaluating the expected oxidation state of dissolved metals and other chemical species in a general sense, especially when collected with pH data. Such information may be helpful for fate-and-transport modeling. However, aquifers and other saturated zones are open systems that are effected by many variables, and therefore, the actual chemical species present in ground water will not necessarily correspond to measured ORP and pH data (Hem, 1992; Rose and Long, 1988). In addition, ORP values cannot be used to derive or infer dissolved oxygen values, and vice versa (Rose and Long, 1988).

Temperature is not necessarily an indicator of ground water chemical stabilization, and is generally not very sensitive in distinguishing between stagnant casing water and formation water (Puls and Barcelona, 1996). Nevertheless, temperature is important for data interpretation. For example, stabilized temperature readings that are representative of typical ground water conditions help demonstrate that the sample was collected in a manner that minimized exposure to elevated temperature variations, e.g., heating from the electric motor of a submersible pump. Elevating the temperature of a sample may result in loss of VOCs or the progression of chemical reactions that may alter the sample quality in an undesirable manner. Ground water temperatures in Ohio typically range from 9 to 13 C (Heath, 1987).

Turbidity, which is the visible presence of suspended mineral and organic particles in a ground water sample, also is not an indicator of ground water chemical stabilization and does not distinguish between stagnant casing water and formation water. However, turbidity can be useful to measure during purging. Relatively high or erratic measurements may indicate inadequate well construction, development or improper sampling procedures, such as purging at an excessive rate that exceeds the well yield (Puls and Powell, 1992; Paul *et. al.*, 1988). Purging and sampling in a manner that produces low-turbidity water is particularly important when analyzing for total metals, which may exhibit artificially elevated concentrations in high-turbidity samples (Gibbons and Sara, 1993). Generally, the turbidity of *in-situ* ground water is very low (Nightingale and Bianchi, 1977). When sampling for contaminants or parameters that may be biased by turbidity, Ohio EPA recommends stabilizing the turbidity readings at or below 10 NTUs (Yeskis and Zavala, 2002). It is recognized that some ground water zones may have natural turbidity higher than 10 NTUs. If turbidity is being used as a stabilization parameter, it may be necessary to evaluate the stabilization criteria on a site-by-site basis. The stabilization criteria would be 10 percent.

Table 10.5 provides stabilization criteria for each parameter discussed above. It is recommended that specific conductance plus two additional parameters be selected. A parameter can be considered stable when at least three consecutive readings have stabilized. The interval between measurements is discussed in the particular purging/sampling methodology section.

Field measurements performed to fulfill regulatory requirements, beyond those used to measure for stabilization, should be obtained after purging and before samples are collected for laboratory analysis. Portable field instruments should be used. Probes enabling down-hole measurement can be used and may increase data representativeness. All in-well instruments and probes should be appropriately decontaminated before use to prevent contamination of the well water. Flow-through cells can be used when sampling with pumps.

Calibration of instruments should occur in the field, as close to the time of use as possible and, at least, be at the frequency suggested by the manufacturer. A pH meter should be periodically calibrated with a two-point calibration by using two buffer solutions that bracket the expected pH range of the ground water. If field measurements fall outside the calibrated range, then the meter may need to be recalibrated with appropriate solutions. Calibration of dissolved oxygen meters should be done at least once a day and possibly more if changes in elevation or atmospheric pressure occur. Checking and documenting the performance of an electronic dissolved oxygen meter against a titration method at least once per day is

recommended. A conductivity meter should be checked with standard solutions prior to going out in the field. If it is out of the prescribed tolerances, it may need servicing prior to use. Checking and documenting the performance of the conductivity meter may be done in the field with two audit solutions. All calibration and recalibration checks should be recorded in a field notebook or on field forms (Wilson, 1995).

Table 10.5. Stabilization Criteria with References for Water-Quality Indicator Parameters (Yeskis and Zavala, 2002).

Parameter	Stabilization Criteria	Reference
pH	± 0.1 standard units*	Puls and Barcelona, 1996 Wilde et al. 1998
specific conductance	± 3%	Puls and Barcelona, 1996
oxidation-reduction potential (ORP)	± 10 millivolts	Puls and Barcelona, 1996
turbidity	± 10% (when > 10 NTUs) maintained at < 10 NTUs, consider stabilized	Puls and Barcelona, 1996 Wilde et al. 1998
dissolved oxygen (DO)	± 0.3 milligrams per liter	Wilde et al. 1998
temperature	± 0.5 º Celsius	

* The ± 0.1 may not always be obtainable, especially if purging and sampling with bailers. Therefore, professional judgement may be needed.

Volumetric Purging & Sampling

Traditionally, a sample has been collected after purging of a specified volume of water. The various types of sampling and purging equipment, their pros and cons, and recommended uses are described in detail in the section on types of equipment (page 10-10). It is recommended that sampling equipment be dedicated to specific wells to eliminate the need for decontamination. This is most important when pumps are used because their intricate design can often make adequate cleaning difficult.

The amount of water purged is usually three to five well volumes. Some have suggested the number of bore volumes should range from less than 1 to more than 20 (Gibb et. al., 1981).

One well volume can be calculated as follows:

$$V = H \times F$$

where:

V = one well volume.
H = difference between depth of well and depth to water (ft).
F = factor for volume of 1-foot section of casing (gallons).

Table 10.6 provides F for various casing diameters. Multiplying the computed volume (V) times the number of desired volumes to be purged will give the volume of water in gallons to be evacuated.

Table 10.6 Volume of water in one-foot section of well casing.

Diameter (Inches)	F[1] (Gallons)
1.5	0.09
2	0.16
3	0.37
4	0.65
6	1.47

[1] F is the volume (in gallons) in a 1-foot section of the well and is computed using:

$$F = 3.14 \left[\frac{D}{2}\right]^2 \cdot 7.48 \frac{gal}{ft^3}$$

Where: D=the inside diameter of the well casing (ft).

Field stabilization parameters, as discussed above, should be monitored for stability to determine if additional purging is necessary.

For volumetric purging, it is suggested that stabilization parameters be collected every ½ well/screen volume after an initial 1 to 1½ well volumes are purged (U.S. EPA, 2002). The volume removed between readings can be adjusted as well-specific information is developed. Field meters or flow through cells that allow continuous monitoring of stabilization parameters can be used. When using a flow meter, the capacity of the cell should be such that the flow of water in the cell is replaced between measurements of the stabilization parameters.

Purging should be at or below rates used for development and those observed for well recovery. Excessive rates may result in the introduction of ground water from zones above or below the well screen, which could dilute or increase contaminant concentration in samples. Overpurging also may cause formation water to cascade down the screen, enhance the loss of VOCs, and introduce oxygen into the subsurface, which may alter water geochemistry and affect chemical analysis. As indicated by Puls and Powell (1992), excessive rates may also lead to increased sample turbidity and the exposure of fresh surfaces capable of adsorbing dissolved metals. If bailers are used for purging, entry and withdrawal to and from the water column should be as slow as possible. Water entrance velocities into bailers can correspond to unacceptably high purging rates (Puls and Powell, 1992).

Monitoring wells should be sampled immediately after purging, unless site-specific conditions preclude it (e.g., if some wells are too low-yielding). This minimizes the time for physical and

chemical alteration of water in the well casing. Where immediate resampling is precluded, sample collection should begin no later than 24 hours after purging.

Low-Flow Purging/Sampling

Low-flow purging, also referred to as low-stress purging, low-impact purging, minimal drawdown purging, or Micropurging®, is a method of well purging/sampling that does not require large volumes of water to be withdrawn. The term low-flow refers to the fact that water enters the pump intake with a low velocity. The objective is to minimize drawdown of the water column in the well, avoid disturbance of the stagnant water above the well screen, and draw fresh water through the screen at a rate that minimizes sample disturbance. Usually, this will be a rate less than 500 ml/min and may be as low as 100 ml/min. Once drawdown stabilizes, the sampled water is isolated from the stagnant water in the well casing, thus eliminating the need for its removal (Powell and Puls, 1993).

The method is based on the principle that water within the screened zone passes through continuously and does not mix with water above the screen. After drawdown has stabilized and indicator parameters have stabilized, water in the screen can be considered representative of water in the formation. Given this, purging of multiple well volumes is not necessary (Kearl et al., 1994; Powell and Puls, 1992; Nielsen and Nielsen, 2002, ASTM Method D6771-02). A packer assembly may be necessary in fractured bedrock.

Low-flow sampling offers several advantages. It lessens the volume of water to be purged and disposed, reduces aeration or degassing, maintains the integrity of the filter pack, and minimizes disturbance within the well water column and surrounding materials, thus reducing turbidity. Accordingly, filtering of samples may be avoided, and low-flow sampling may allow for the quantification of the total mobile dissolved phase and the contaminants sorbed to mobile particles. Disadvantages include higher initial setup costs, need for greater setup time in the field, and increased training needs. In addition, this procedure does not address sampling from wells with LNAPL or DNAPL.

When performing low-flow purging and sampling, it is recommended that the pump be set in the center of the well screen interval to help prevent disturbance of any sediments at the bottom of the well. If known, the pump can be placed adjacent to the areas with the highest hydraulic conductivity or highest level of contaminants. The use of dedicated pumps is preferred to minimize disturbance of the water column. If a portable pump is used, the placement of the pump can increase turbidity and displace water into the formation. Therefore, the pump must be placed far enough ahead of the time of sampling so that the effect of the pump installation has completely dissipated. The time between pump placement and sampling may vary from site to site, but may be in excess of 48 hours (Kearl, et al., 1992; Puls and Barcelona, 1996; Nielsen and Nielsen, 2002). Use a submersible pump with an adjustable rate, such as a low-flow centrifugal or bladder pump. The pumping rate should be adjusted to less than 1 L/min; pumping rates as low as 500 mL/min to 100 mL/min may be needed. If using a bladder pump, follow the manufacturer's recommendations for adjusting the emptying/filling cycle to minimize the potential for turbid flow. During subsequent sampling events, try to duplicate as closely as possible the intake depth and the stabilized extraction rate from the previous events.

Because the object during low-flow purging and sampling is to minimize drawdown, it is important to measure the water level in the well before pumping. To begin purging, the pump should be started at the lowest speed setting and then the speed can be slowly increased until water begins discharging. Check the water level and slowly adjust the pump speed until there is little or no drawdown or drawdown has stabilized. The stabilization should be documented. Water level should be monitored frequently during purging; every three to five minutes is recommended. In practical terms, to avoid drawing stagnant water into the pump, the water level should not exceed the distance between the top of the well screen and the pump intake (Nielsen and Nielsen, 2006). The water level should not be allowed to fall to the pump intake level. If the static water level is above the well screen, the water level should not be allowed to fall below the top of the screen. To minimize disturbance, pumping rate adjustments are best made within the first fifteen minutes of purging.

A sample can be considered representative when both drawdown and water quality indicators have stabilized. In general, at least one screen volume will typically need to be purged; however, stabilization can occur before or after one screen volume. Stabilization measurements should begin after drawdown of the water level has stabilized. Indicator parameters (such as pH, temperature, specific conductance, dissolved oxygen, turbidity, and oxidation/reduction potential) should be monitored frequently. The measurements should be with a hand-held meter or a flow-through-cell and be at least three to five minutes apart. When using a flow meter, the capacity of the cell should be such that the flow of water in the cell is replaced between measurements.

An indicator parameter can be considered stable when at least three consecutive readings have stabilized (See Table 10.5). When all parameters have stabilized, the well may be considered purged and sampling may commence. A turbidity level of less than10 NTUs is desirable. If the recharge rate of the well is less than the lowest achievable pumping rate, and the well is essentially dewatered during purging, a sample should be taken as soon as the water level has recovered sufficiently to collect the sample, even if the parameters have not stabilized.

When conducting low flow sampling at new wells or established wells being sampled for the first time by low flow procedure, it is recommended the purging process be verified by continuing to purge 9 to 15 minutes, then retaking the stabilization parameters. If the parameters remained stable, then the purging procedure can be established for that well based on pump location, rate of purging, and frequency of obtaining the three sets of stabilization parameters. This will help support whether an appropriate amount of water has been purged from the system.

Minimum/No Purge Sampling[10]

Minimum/no purge sampling is best suited for wells that have a tendency to go dry when using other purging and sampling techniques. Minimum/no purge sampling should only be conducted when volumetric or low-flow sampling is not feasible (e.g., well yields less than 100 ml/min) and where there is sufficient water to ensure submergence of the pump intake

[10]Referred to in some literature as passive sampling.

during purging and sampling (Nielsen, 2002). It is considered less disruptive then well evacuation.

This method obtains the sample from within the well screen above the pump intake and removes the least possible volume of water prior to sample collection, which is generally limited to the volume of the sampling system, i.e., pump and discharge tubing. A sample is collected immediately after this volume is withdrawn, and is presumed to represent formation water. Very low flow rates are used for minimum/no purge sampling, generally 100 mL/min or less. With minimum/no purge sampling, indicator parameters for chemical stabilization are not monitored. However, indicator measurements may still be needed for other purposes (.e.g. regulatory requirements, evaluation of general quality of the ground water). Where the volume of water available is limited, a low-volume flow-through cell can be used to measure indicator parameters.

The volume of water available for sampling within t he well screen located above the pump intake should be determined before purging and sampling to avoid drawing down stagnant water from the overlying water column into the well screen interval and compromising the sample. Because of the low hydraulic conductivity and flow rates, the yield may not be sufficient to meet the demands of the pump; thus drawdown is unavoidable. Drawdown should be measured during pumping to ensure that the water above the screened interval is not drawn into the pump. The amount of drawdown should be no more than the distance from the top of the screen and the position of the pump intake within the screen, minus a 2-foot safety margin (Figure 10.1) (Nielsen and Nielsen, 2002).

If available water is insufficient to meet the sample volume requirements, it may be necessary to discontinue the sampling once allowable drawdown is reached. Sample collection should proceed when the well has recharged sufficiently to meet the remaining sampling requirements.

Bladder and low-flow submersible pumps are recommended for minimum/no purge sampling. Bailers, inertial lift samplers, and peristaltic pumps should not be used (ASTM D4448-01, Powell and Puls, no date). Pumps should be placed within the well screen, but not too close to the bottom to avoid drawing in any sediments that may have settled, or too close to the top to avoid incorporating stagnant water that is above the well screen. One to two feet above the bottom is generally sufficient. As with low-flow purging and sampling, lowering a pump into the well can increase turbidity and displace water into the formation. Therefore, the pump must be placed far enough ahead of the time of sampling so that the effect of the pump installation has completely dissipated. Though the time between placement and sampling can vary from well to well, it may be in excess of 48 hours (Kearl, et al., 1992; Puls and Barcelona, 1996; Nielsen and Nielsen, 2002).

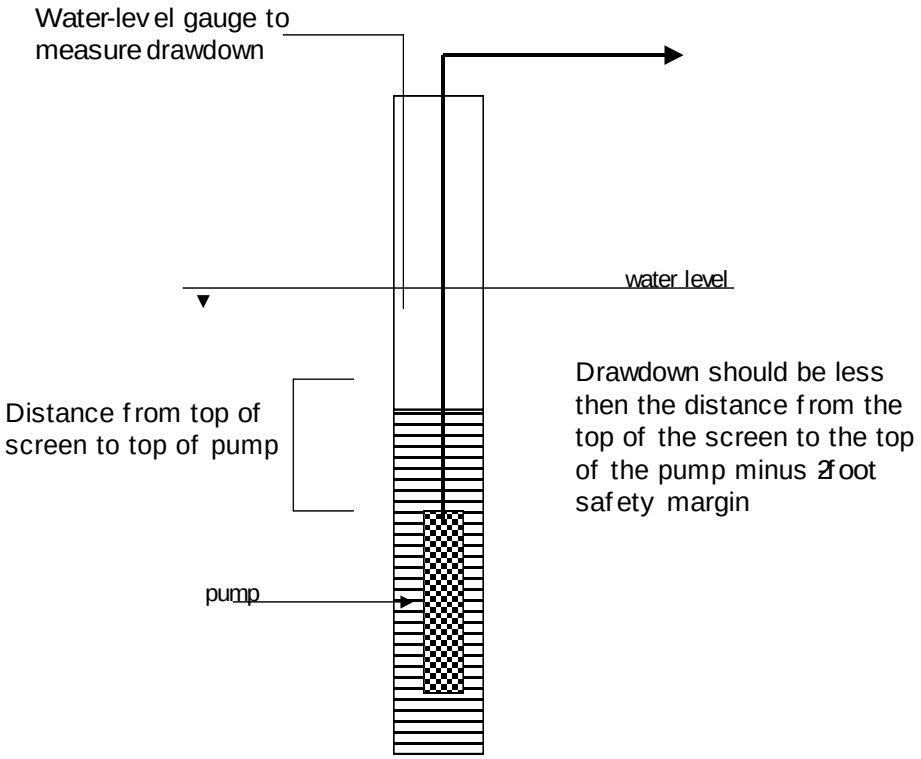

Figure 10.1. Maximum drawdown for minimum/no purge sampling and purging procedure.

Purge to Dryness & Sampling

Traditionally, low-yielding wells have been sampled by purging a well dry and obtaining a sample upon sufficient recovery of the well. However, there are concerns when a well is purged dry, including (Nielsen and Nielsen, 2002: U.S. EPA 2001):

- Cascading water as the well recovers may result in a change of dissolved gases and redox state, thus affecting the concentration of the analytes of interest through oxidation of dissolved metals. In addition, the cascading water can strip volatile organic constituents that may be present;

- Stressing the formation may increase sample turbidity by inducing soil fines into the well or stirring up any sediments that may have accumulated at the bottom of the well;

- Draining the water from the filter pack may result in air being trapped in the pore spaces, with lingering effects on dissolved gas levels and redox states; and

- The time required for sufficient recovery of the well may be excessive, affecting sample chemistry through prolonged exposure to atmospheric conditions.

Attempts should be made to avoid purging to dryness; however, in some situations it may be the only feasible method (e.g., low yielding wells, insufficient water column to use minimum/no purge). If an operating facility monitoring program has been historically

established on purging to dryness, then for consistency, it may be necessary to continue this practice.

If purging to dryness is unavoidable or inadvertent, then samples should be taken as soon as there is a sufficient amount of water. Extended recovery times after purging (hours) allow the ground water to equilibrate with atmospheric conditions. In the case of a well with very slow recharge, sample collection may continue for several days. However, sample collection should be attempted at least every 24 hours. Herzog et al. (1988) concluded that the common practice of next day sampling for low yield, slow recovery wells is adequate. The intervening time should be consistent from event to event. In addition, it is important to evaluate all data from slowly recovering wells based on the possibility that it may be unrepresentative of actual conditions.

Passive Diffusion Sampling

Passive diffusion samplers are a simple and inexpensive way to sample monitoring wells for a variety of VOCs. As described in the previous section (Types of Equipment), the passive diffusion bag is suspended in the well at the target horizon by a weighted line and allowed to equilibrate with the surrounding water (typically 2 weeks). The sampler bags are retrieved from the well after the equilibration period and the enclosed water is immediately transferred to the sample container. Passive diffusion sampling is recommended only for long term ground water monitoring of VOCs at well-characterized sites (ITRC, 2004). PDS is not applicable for inorganics, were there is vertical flow, or when discrete interval samples are needed. See pages 10-15 for more description of the applicability of PDS.

FILTRATION

Ground water samples collected from monitoring wells may contain noticeable amounts of sediment. This sample “turbidity” is an important field concern for samples to be analyzed for metals (e.g., cadmium, nickel, zinc) or metalloids (e.g., arsenic, selenium). If large, immobile particles to which metals are bound are allowed to remain in field-acidified samples, laboratory "total" analyses will overestimate the true concentration of mobile species because acidification dissolves precipitates or causes adsorbed metals to desorb. Additionally, changes in the relative degree of sedimentation over time (due to changes in well performance, sampling device, or sampling personnel) and space (due to natural hydrogeologic variations) can result in data interpretation difficulties.

Removal of sediment by filtration prior to containerization and acidification also presents problems. The potential for filter clogging, variable particle size retention, filter media leaching, and aeration is well documented (Puls and Powell, 1992). Also, filtration has the potential to remove particles that may be mobile in certain hydrogeologic environments. As described by McCarthy and Zachara (1989) and Puls et al. (1990), colloidal material (particles less than 10 micron) may be transported large distances. Because of these difficulties, some investigators (Puls and Barcelona, 1989a & b; Kearl et al., 1992; Puls and Powell, 1992) have recommended against field-filtering. Further, federal regulations [40 CFR 258.53(b)] for ground water monitoring at municipal solid waste landfills specify that analyses for metals be performed on unfiltered samples.

For sampling at sites that are not municipal solid waste landfills, filtration may be appropriate in some instances, provided it is done properly. Significant turbidity is sometimes unavoidable, and filtration may be necessary to remove immobile particles. For example, reducing turbidity may be difficult when a clay-rich glacial deposit is monitored. Clay and natural organic matter can attract contaminants and physically retard particle movement. Therefore, particles in ground water may be presumed to be immobile in formations primarily containing natural organic material and clays. Additionally, while unfiltered data generally would be preferred for a risk assessment of the drinking water pathway, filtered data may be used if there is an obvious discrepancy between filtered and unfiltered data or if secondary MCLs are exceeded (U.S. EPA, 1991). In this case, unfiltered samples might be too turbid to represent drinking water. It is recommended that entities work closely with the Agency to define project requirements. The following sections provide Ohio EPA's general recommendations on whether and how to filter.

Deciding When to Filter

Ohio EPA recommends a general framework (Figure 10.2) for making decisions as to whether filtering is appropriate. As the framework indicates, adequate monitoring wells and sampling techniques that minimize disturbance should be confirmed before any decision is made. Filtration generally should occur only when <u>all</u> of the following conditions are present:

- ***The samples have been collected from monitoring wells that are properly designed, installed, and developed.*** Adequate wells are essential to minimizing turbidity and obtaining representative samples. When turbidity is an issue at an existing well, the well should be redeveloped using appropriate well development techniques outlined in Chapter 8 prior to sampling.

- ***The samples have been collected using procedures that minimize disturbance.*** Low-flow purging and sampling procedures are recommended to minimize agitation of the water column and minimize turbidity. Achieve stabilization of indicator parameters prior to sampling to ensure that the sample is representative of natural ground water conditions. Indicator parameters can include temperature, pH, and conductivity.

- ***Turbidity has been demonstrated to stabilize above 10 NTU***. (See the Sampling and Purging Procedure Section.)

- ***Professional judgement indicates that the formation sampled does <u>not</u> exhibit a high degree of particle mobility, making it reasonable to assume that a portion of the sediment in the samples may be attributable to immobile particles.*** In general, this judgment can be based on the geology of the ground water zone. For example, clays, because the size of the pores, would prevent particle mobility. Examples of formations that <u>do</u> show significant particle mobility include, but are not limited to, karst; bedrock with open, interconnected fracture, and clean, highly porous gravel-to-boulder sized deposits.

Note that one should exercise professional judgement when applying this approach. Deviations may be necessary if the practices would cause undesirable problems in data

interpretation. For example, if a site is underlain by karst bedrock and the historical data for metals has been based on analyses of filtered samples, filtration could be continued to ensure data consistency and comparability. If a single zone is monitored both by wells that are capable of providing samples that meet the turbidity criterion and wells that are not capable of meeting it, it may be prudent to filter all of the samples to ensure spatial consistency and valid statistical comparisons.

Some entities may wish to collect both filtered and unfiltered samples. The advantage of having both types of data is that a comparison can help determine the form in which a chemical exists (e.g., primarily adsorbed to particulate matter or primarily dissolved) (U.S.EPA, 1989)[11]**.** The comparative data may help justify which data set is more appropriate.

Recommended Procedure/Equipment When Filtering is Necessary

If filtration is necessary, the following are recommended:

- ***Use "in-line" filtering whenever possible.*** In-line methods use positive pressure provided by a sampling pump to force the sample through an attached filter. The advantage is that samples remain isolated prior to atmospheric exposure. Stolzenburg and Nichols (1986) compared different filtering methods and found in-line to provide the best results. If bailers are used for sampling, in-line filters cannot be used unless a pressure or vacuum hand pump (i.e., peristaltic) is utilized to force the sample through.

- If it is not possible to filter in-line, "open system" techniques may be used. These techniques require a transfer of the sample before filtration, thus allowing for additional exposure and agitation. Open system filtration should be conducted immediately in the field, at the wellhead, and prior to sample acidification and containerization. If filtration does not occur immediately, metals can begin to precipitate and, upon filtration, be removed, causing laboratories to underestimate actual concentrations. Agitation should be kept to a minimum, and the use of "double" filtration is not recommended. "Double" refers to filtering a sample twice using filters with progressively smaller pore sizes. This has been used to speed up filtration; however, it can cause excessive agitation.

- Open system techniques offer varying degrees of portability and ease of decontamination. In addition, changes in pressure and aeration/oxygenation can alter sample representativeness. Open system filtration is primarily driven by either pressure or vacuum mechanisms. For pressure, only pure, inert gas should be used (i.e., nitrogen). If a pump is used, the peristaltic is commonly employed. Whereas pressure "pushes" the sample using compressed gas or a pump, vacuum "pulls" the sample through the filter. Vacuum can cause extensive degassing, which can seriously alter metals concentrations (U.S. EPA, 1986a; EPRI, 1987; and Barcelona et al., 1985); therefore, vacuum is not recommended. The extensive alteration is due to an

[11]For example, if the concentration of a chemical is much greater in unfiltered samples compared to filtered samples, it is likely that the majority of the chemical is sorbed onto particulate matter and not dissolved in the ground water.

exacerbation of the pressure decrease inherent with bringing a sample to the surface.

- ***Filter samples using a polycarbonate or cellulose acetate filter.*** Filtration media should be inert and selected to minimize bias. Polycarbonate membrane filters are recommended. Puls and Barcelona (1989b) have stated that this material should be used due to its more uniform pore size, ease of cleaning, and minimization of adsorptive losses. The NCASI (1982) also found polycarbonate to be most appropriate. Cellulose membranes and glass microfiber filters have been used commonly.

- ***Prepare the filter prior to collecting the sample.*** Filters must be pre-rinsed following manufacturer's recommendations to remove the residue from the manufacturing, packing, or handling. In-line filters should be flushed with sample water before collection to create a uniform wetting front.

- ***Use of a 5 micron filter is recommended to ensure that the mobile fraction of turbidity is sampled.*** While a 5 micron size filter is recommended, a filter with a different pore size may be used based upon site conditions. Theoretically, the filter pore size should equal the size of the largest mobile particles in the formation, although differences in particles passing different sizes may be lessened significantly by clogging. Traditionally, 0.45 micron filters have been used; however, different pore sizes can be used in specific instances if justified. Puls and Powell (1992) suggested a coarse filter size such as 5 micron. If estimates of dissolved metal concentrations are desired, use of 0.1 micron filters is recommended (Puls and Powell, 1992). Samples filtered with a medium with a small pore size (e.g., 0.1 micron for dissolved concentrations) may be appropriate for geochemical modeling (Puls and Powell, 1992).

- ***The filtration medium should be disposed between wells***

- ***If the ground water is highly turbid, periodic filter changes may be necessary (e.g., between samples)***

- ***The filtration device, tubing, etc. should be appropriately decontaminated as sample-contacting equipment (see Decontamination Section)***

SAMPLE HANDLING, PRESERVATION, CONTAINERS, AND SHIPPING

Once a sample has been removed from a well, appropriate procedures should be utilized to containerize, preserve, and transport it to the laboratory. This ensures that an in-situ state is maintained as much as possible prior to analysis. Issues that should be considered include preservation, containers and labels, holding times, and shipping. Examples of containers, preservatives, and holding times for some chemicals are listed in Table 10.7. Deviating from Table 10.7 does not necessitate that a sample is invalid. Deviations should be recorded on the data reports and should be evaluated on a case-by-case basis. Appropriate preservation and handling should be coordinated with the laboratory prior to a particular sampling event.

Sample Acquisition and Transfer

Transfer to a container or filtration device should be conducted in a way that minimizes agitation and aeration. Samples should be transferred directly to the final container for laboratory submittal and not collected in a larger container with subsequent transfer to smaller containers. (Exceptions for filtration are allowable.) Care should be taken to prevent overfilling so that the preservative, if used, is not overly diluted. If no preservative is used, the containers should be rinsed with sample water prior to collecting the sample. After sealing, containers should not be opened in the field for any reason.

Special considerations are needed when sampling for VOCs. Samples should be placed in 40 ml glass vials until a meniscus is formed. Flow rate into the vials should be between 100 and 500 ml/min. The vials should be sealed with a fluorocarbon-lined cap. It is very important that no air bubbles or headspace remain to prevent the loss of VOCs. Check for air by inverting the vial and tapping. If any bubbles are present, the vial should be discarded and a new sample taken (U.S.EPA, 1996b; Yeskis and Zavala, 2002). The presence of air bubbles in a vial generally indicates either improper sampling technique or a source of gas evolution with the sample. If a sample cannot be obtained without air bubbles due to off-gassing, then the presence of air bubbles should be noted on the field log or field data sheet. Also, air bubbles may form during shipment to the laboratory. These bubbles do not necessarily invalidate the sample[12]**.** The container should not be opened and "topped-off" to fill the additional head space (U.S. EPA, 1992). When sampling for VOCs, collection, handling, and containerization *should not* take place near a running motor or any type of exhaust system.

[12]Studies conducted by U.S. EPA indicate that “pea-sized” bubbles (1/4 inch or less in diameter) did not adversely affect data. These bubbles were generally encountered in wastewater samples.

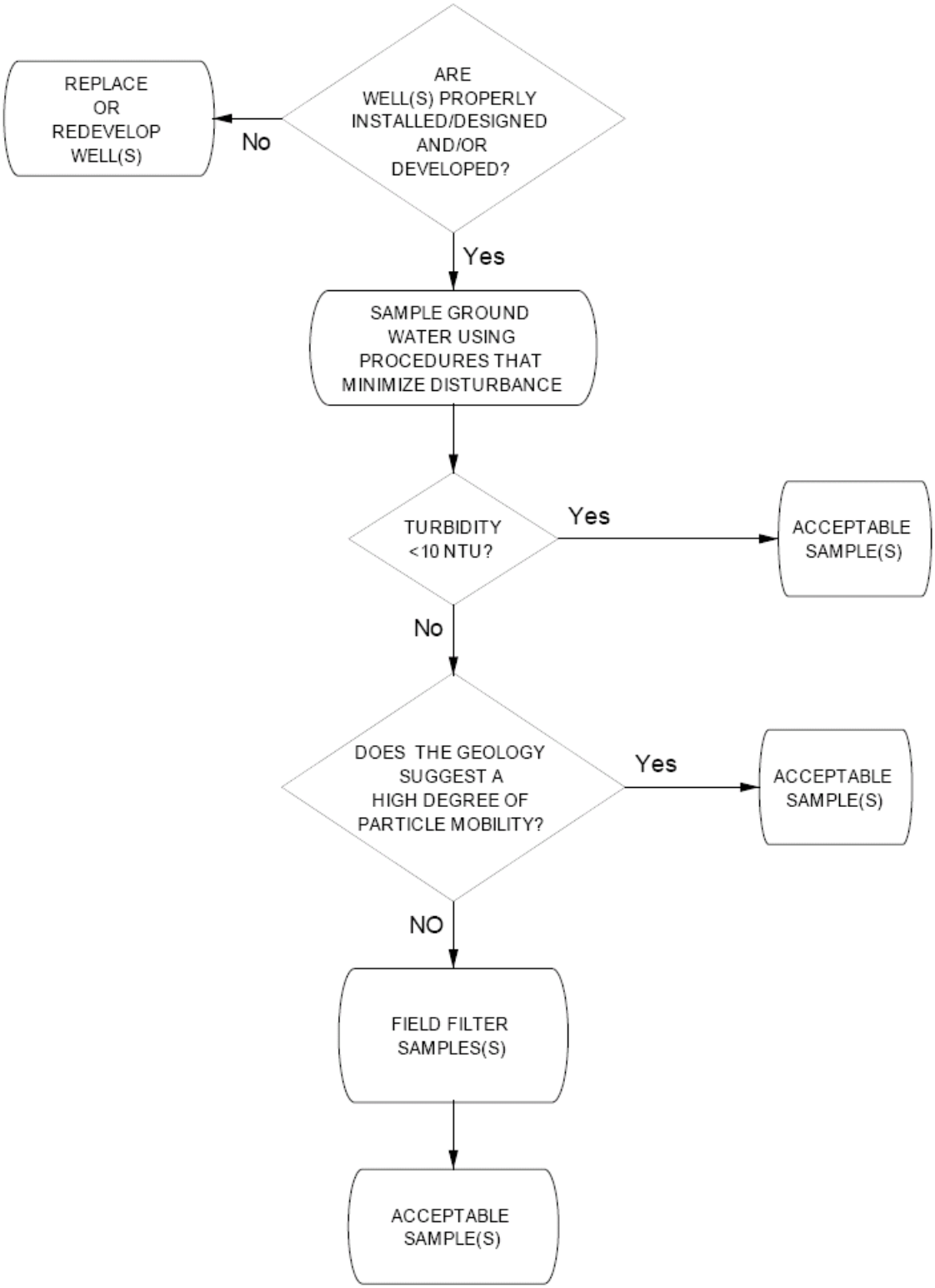

Figure 10.2 Ground water field filtration decision tree.

Samples should be collected and containerized in the following order of volatilization sensitivity (U.S. EPA, 1986a):

- Volatile organic compounds (VOCs).
- Purgeable organic carbon.
- Purgeable organic halogens.
- Total organic halogens (TOX).
- Total organic carbon (TOC).
- Extractable organics.
- Total metals.
- Dissolved metals.
- Phenols.
- Cyanide.
- Sulfate and chloride.
- Nitrate and ammonia.
- Radionuclides.

In addition to the sensitivity, the relative importance of each parameter should be evaluated on a site-by-site basis to establish sampling order protocol. Therefore, when a low-yielding well is being sampled, it may be necessary to change the order of sampling to ensure that a representative sample is collected for the most important constituents for a particular site.

Sample Splitting

Samples are often split into two separate portions and submitted to different laboratories to determine the accuracy of lab results. The proper procedure is to fill the two containers alternately until both are filled. However, if samples for VOC analysis are being collected, the first container should be completely filled, followed by filling of the split container.

Sample Preservation

Preservation is an important step that should be conducted to stabilize the collected sample and prevent physical and chemical changes from occurring during transport to the laboratory and storage before analysis. Preservation is intended to retard biological action, prevent hydrolysis of chemical compounds and complexes, and reduce volatility of constituents (U.S. EPA, 1982). Preservation methods generally are generally limited to pH control, chemical addition, refrigeration, and protection from light. Appropriate techniques(see Table 10.7), generally should be implemented immediately upon collection (and after filtration) to minimize changes that begin when a sample is exposed to the atmosphere. Any preservation used should be reported to the appropriate regulatory agency when submitting analytical results.

Sample preservation usually involves reducing or increasing the pH by adding an acid or a base. For example, acids are added to samples submitted for dissolved metals analysis because most metals exist in the dissolved state at low pH. If not preserved, most metals will oxidize and precipitate, which prevents representative analysis. If preserved in the field, the chemical preservative should be obtained from the laboratory contracted to analyze the sample and the appropriate aliquot placed in the sample container, preferably before entering the field. Many laboratories will provide sample bottles containing the appropriate amount

and type of preservative. Sampling personnel may want to carry limited amounts of some preservatives in the event that additional preservation is needed for a particular sample. However, if previous samples indicate that a sample may be acidic or alkaline, the amount of preservative should be discussed with the laboratory prior to sample collection.

Samples for temperature-sensitive parameters should be thermally preserved immediately after collection by placement into an insulated cooler maintained at a temperature of approximately 4°. 2° C[13] with ice or an ice substitute. Any deviation in temperature should be noted and assessed as to its impact on sample quality. Care should be taken to ensure that the paperwork and samples are not damaged by ice water. The laboratory should record whether or not the cooler contains any amount of visible ice. The presence of ice is sufficient to demonstrate that the samples are adequately preserved. If no ice is present, the laboratory should obtain a measure or estimate of the sample temperature upon receipt of the samples.[14] This can be accomplished by either a temperature blank, or measuring the internal temperature of the cooler.

Containers and Sample Labels

Upon collection, samples should be contained properly to maintain integrity. Specifications on container design, including shape, volume, gas tightness, material construction, and use of cap liners, are defined for specific parameters or suites of parameters. For example, various fluorocarbons (i.e., Teflon), polyethylene plastic, or glass bottles with Teflon-lined lids are recommended for metals analysis. Samples to be analyzed for VOCs should be containerized in 40 ml glass vials. Specifications on containers are documented in parameter-specific analytical methods (e.g., SW-846). Clean containers can usually be obtained from the contracted laboratory. Note that analytical laboratories may not accept samples for analysis if the bottles have not been cleaned by their own laboratory. If cleaning is necessary, decontamination should be performed and appropriate blanks collected to verify cleanliness.

Samples should be properly identified with labels. The labels should be permanent and remain legible when wet. When sampling for VOCs the pen's ink may cause false positives, so labels should be completed and the ink allowed to dry before being affixed to the bottles (Wilson, 1995). The following information should be included:

- Sample field identification number (e.g., well location).
- Name or initials of collector.
- Date and time of collection.
- Place of collection.
- Parameters and method requested for analysis.
- Chemical preservatives used.

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[13]The Environmental Laboratory Accreditation Program (NELAP) has adopted a standard temperature of 4∀2EC and has asked U.S. EPA to adopt this standard. U.S. EPA is proposing # 6EC (unfrozen)

[14]Some regulatory programs may require that the temperature of the cooler/sample be recorded regardless of whether there is visible ice.

Table 10.7 Common Examples of Containers, preservation, and holding times.
(Note: The preservative and holding times may vary with sampling procedures and method analysis. The table is partially based on U.S. EPA, Federal Register, Volume 69, No.66, April 6, 2004)

PARAMETER	CONTAINER	PRESERVATIVE[3]	MAXIMUM HOLDING TIME
INORGANIC TESTS			
Acidity	P,G	Cool, 4∀2°C	14 days
Alkalinity	P,G	Cool, 4∀2°C	14 days
Ammonia	P,G	None	7days
		Cool, 4∀2°C; H_2SO_4 to pH<2	28 days
Bromide	P,G	None required	28 days
Chloride	PG,	None required	28 days
Chlorine, residual	P,G	None required	Analyze immediately (within 15 minutes)
Cyanide, total	P,G	Cool 4∀2°C; NaOH to pH<12 ascorbic acid if oxidants (e.g., Chlorine) is present.)	14 days
Hardness	P.G	HNO3 to pH<2; H_2SO_4 to pH<2	6 months
Kjeldahl and organic nitrogen	P.G	none	7 days
		Cool, 4∀2°C; H_2SO_4 to pH<2	28 days
Nitrate	P,G	Cool, 4∀2°C	48 hours
Nitrate-nitrite	P,G	Cool, 4∀2°C; H_2SO_4 to pH<2	28 days
Sulfate	P,G	Cool, 4∀2°C	28 days
Sulfide	P,G	Cool, 4∀2°C, add zinc acetate plus sodium hydroxide to pH > 9	7 days
Sulfite	P,G	None required	Analyze within 15 minutes
Metals, except Cr(VI) & Hg	P,G	HNO_3 to pH<2 at least 24 hours prior to analysis	6 months
Chromium (Cr) VI	P,G	Cool , 4∀2°C	24 hours
Chromium (Cr) VI	P,G	use sodium hydroxide and ammonium sulfate buffer solution to pH 9.3 to 9.7 to extend holding time to 28 days	28 days
Mercury (Hg)	P,G	HNO_3 to pH<2	28 days
ORGANIC TESTS			
Volatiles	G, Teflon-lined cap	Cool, 4∀2°C; 0.008% $Na_2S_2O_3$[3] ; HCl to pH<2 No head space	14 days

PARAMETER	CONTAINER	PRESERVATIVE[3]	MAXIMUM HOLDING TIME
(Acrolein and acrylonitrile	G, Teflon-lined septum	Cool, 4∀2°C; 0.008% $Na_2S_2O_3$[3], adjust pH to 4-5	14 days
Dioxins and Furans	G, Teflon-lined cap	Cool, 4∀2°C	30 days until extraction, 45 days after extraction
Oil and grease	G	Cool, 4∀2°C; H_2SO_4 or HCl to pH<2	28 days
Phenols	G, Teflon-lined cap	$Na_2S_2O_3$	7 days until extraction, 40 days after extraction
PCBs	G, Teflon-lined cap	Cool, 4∀2°C	1 year
Pesticides	G, Teflon-lined cap	Cool, 4∀2°C; pH 5-9	1 year
RADIOLOGICAL Alpha, beta, and radium	P,G	HNO_3 to pH<2	6 months

1 Polyethylene (P), Glass (G)
3 For some constituents free Chlorine must be removed by the appropriate addition of $Na_2S_2O_3$.

Shipping

When samples are to be shipped to a laboratory, an appropriate container should be used to protect and preserve them. Chests with ice or manufactured blue ice packets are commonly used. However, blue ice packets may not stand up to the rigors of shipping during warm weather. This routinely results in samples being received at the laboratory out of range for temperature. During warm weather, copious amounts of ice are generally recommended.

Forms such as a sampling request sheet and/or chain-of-custody containing pertinent information should be included (See page 10-48). Evidence tape also should be placed around the shipping container (and around each container, if desired), to guard against disturbance or tampering. It is important that, if samples are hazardous or potentially hazardous, they meet all federal and state transportation laws. At the state level, contact the Ohio Department of Transportation (ODOT) and the Public Utilities Commission of Ohio (PUCO) for additional information.

Not all samples will maintain complete stability, regardless of the preservation technique. Therefore, a limit on when analysis should take place has been set for most parameters (see Table 10.7). These "holding times" specify the maximum allowable time between sample collection and laboratory analysis. Depending on the specific circumstances, if one is exceeded, the sample may need to be discarded and a new sample obtained. Therefore, it is important that the time of sampling and transportation to the lab be documented to ensure that the limits are met. Be aware of analytical holding times and minimize the time between sampling and delivery to the laboratory.

DISPOSAL OF PURGED WATER

Though it is not the intent of this document to define/determine Ohio EPA's policy on disposal of purged water, the following guidance is provided. In general, purged water should be containerized until the ground water samples are analyzed. If the samples are free from contaminants (e.g., constituent concentrations are not above ambient/natural levels), then it may be acceptable to discharge the purged water onto the ground away from the wellhead but within the limits of the site/facility.[15] Purged ground water that exhibits constituent concentrations above ambient/natural quality may need to be managed as wastewater or hazardous waste. If the water has been contaminated by a listed hazardous waste constituent or exhibits, a characteristic of hazardous waste as specified in 3745-51 of the Ohio Administrative Code, it will need to be managed as a hazardous waste. However, if the ground water is treated such that it no longer contains hazardous waste, the ground water would no longer be subject to regulation. Information on this subject can be found at: http://www.epa.gov/correctiveaction/resource/guidance/remwaste/refrnces/12cntdin.pdf

If the ground water is known or suspected to contain VOCs, the purged water should be screened with air-monitoring equipment, as well as water-quality field instruments. If these parameters and/or the facility background data suggest that the water is hazardous, it should be contained and disposed of properly as determined on a site-specific basis.

DECONTAMINATION PROCEDURES

If non-dedicated sampling equipment is used, it should be cleaned between wells to prevent cross-contamination. This includes all non-dedicated equipment that is submerged in a monitoring well or otherwise contacts a ground water sample. The level of decontamination is dependant on the level and type of suspected or known contaminants. A sampling event where high levels of contaminants are known or suspected would require the most stringent decontamination procedure, which may involve the use of solvent rinses. In general, solvent rinses should only be used when high levels of organic contaminants are known or suspected to be present. Care should be taken to avoid the any decontamination product (or breakdown products) from being introduced into the sample.

The decontamination area should be upwind of activities that may contribute dust or other contaminants to the solutions used. The process should occur on a layer of polyethylene sheeting to prevent surface soils from coming into contact with the equipment. The effects of cross-contamination can also be minimized by sampling the least contaminated wells first and then progressing to the more contaminated wells.

Table 10.8 outlines sequences and procedures that should be used (modified from ASTM D5088-02 and Yeskis and Zavala, 2002). The procedures are based on equipment contact with collected samples. Sample-contacting equipment includes non-dedicated bailers and pumps (i.e., devices used for purging and sampling), sample containers, tubing, downhole field parameter probes, water level probes, non-dedicated filtration equipment, etc. In most

[15] Under detection monitoring, it may be possible to discharge the purged water without containerizing if historical ground water records indicate that ground water quality beneath the site is similar to the ambient quality. The Division with authority over the site/facility should be contacted for approval of this disposal method.

instances, a distilled water rinse should be sufficient for field parameter measurement probes that are not lowered into wells. Many items are inexpensive and disposable (i.e., gloves, rope, tubing). Items dedicated to a well or disposed of between wells (i.e., gloves, cord, plastic sheet, bailer) would not need to be decontaminated. These items should be properly discarded[16] and new materials provided for the next well.

Table 10.8 Decontamination procedure for ground water sampling equipment.

- Wash with non-phosphate detergent and potable water. Recommend using pressure spray filled with soapy water. Use bristle brush made from inert material to help remove visible dirt.
- Rinse with potable water.
- If analyzing samples for metals, may* need to rinse with 10% hydrochloric or nitric acid (note: dilute HNO_3 may oxidize stainless steel). This rinse is only effective on non-metallic surfaces.
- Rinse liberally with deionized/distilled water.
- If analyzing for organics, may* need to rinse with solvent-pesticide grade isopropanol, acetone, or methanol, alone or if required, in some combination. This solvent rinse should not be an analyte of interest. This rinse is important when a hydrophobic contaminant is present (such as LNAPL or DNAPL, high levels of PCB's etc.)
- Rinse liberally with deionized/distilled water.
- Air-dry thoroughly before using.
- Wrap with inert material if equipment is not to be used promptly.

*In most cases, solvent rinses will not be needed. Solvent/acid rinses may only be needed when high levels of contaminants are known to be present.

DOCUMENTATION

Field Sampling Logbook

A field logbook or field sampling forms should be completed and maintained for all sampling events. It should document the following for each well sampled[17].

- Identification of well.
- Well depth.
- Static water level depth and measurement technique.
- Presence of immiscible layers and detection method.

[16]As discussed in the applicable sampling and analysis plan or equivalent protocol, e.g., a standard operation procedure.

[17]Items documented on the chain-of-custody do not need to be repeated in the field log.

- Thickness of immiscible layers, if applicable.
- Well yield - high or low.
- Purging device, purge volume and pumping rate.
- Time well purged.
- Measured field parameters.
- Collection method for immiscible layers (if applicable) and identification numbers.
- Sampling device used.
- Well sampling sequence.
- Sample appearance.
- Types of sample containers and sample identification numbers.
- Preservative(s) used.
- Parameters requested for analysis.
- Field analysis data and method(s).
- Sample distribution and transporter.
- Field observations on sampling event.
- Name of collector(s).
- Climatic conditions (e.g., air temperature, precipitation, and wind conditions
- Problems encountered and any deviations made from the established sampling protocol.

Chain-Of-Custody

A chain-of-custody record should be established to provide the documentation necessary to trace sample possession from time of collection to final laboratory analysis. The record (Figure 10.3) should account for each sample and provide the following information: (U.S. EPA, 1992).

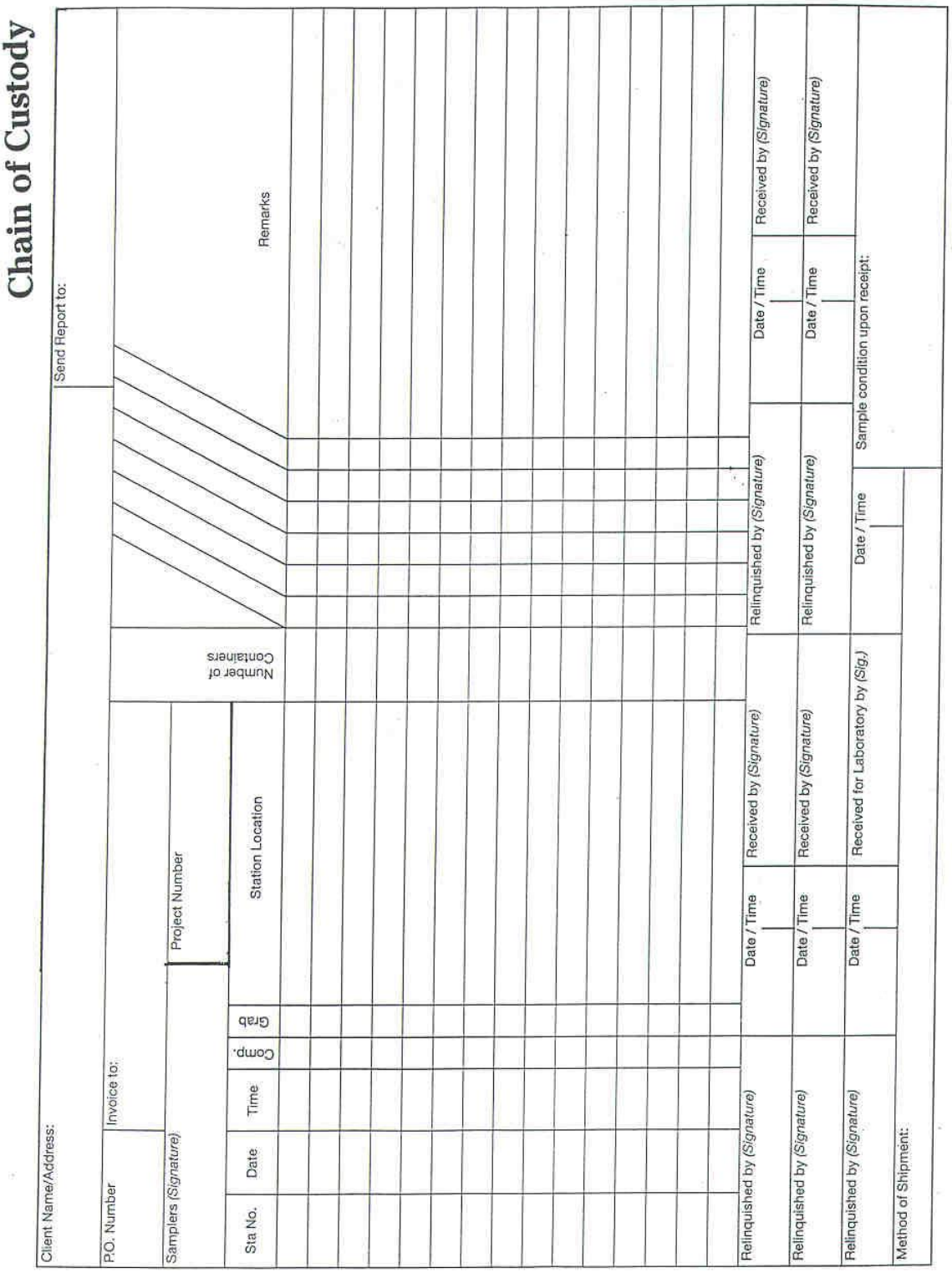
- Sample identification number.
- Printed name and signature of collector.
- Date and time of collection.
- Sample type (i.e., ground water).
- Identification of well.
- Number and types of containers.
- Parameters requested for analyses.
- Preservatives used.
- Carrier used.
- Printed name and signature of person(s) involved in the chain of possession[18].
- Date/time samples were relinquished by sampler and received by the laboratory
- Internal temperature of shipping container upon opening at laboratory, if applicable.
- Special handling instructions (if any).

[18]Including all persons relinquishing the samples and all persons receiving the samples, but excluding the U.S. Postal Service, courier services, or commercial shipping companies.

Sample Analysis Request Sheet

A request sheet may also accompany samples on delivery to the laboratory. However, the chain-of-custody may be used as the sampling analysis request sheet if it contains the following information. Figure 10.4 is an example of a typical sheet.

- Sample type (e.g., ground water).
- Sample identification number.
- Name of person receiving the sample.
- Date and time of sample collection.
- Date of sample receipt.
- Analyses to be performed.
- Analysis method requested (if needed).
- Name of sampler.
- Internal temperature of shipping container upon opening at the laboratory.



Chain of Custody

Client Name/Address:

Send Report to:

P.O. Number

Invoice to:

Samplers (*Signature*)

Project Number

Sta. No.	Date	Time	Comp.	Grab	Station Location	Number of Containers	Remarks

Relinquished by (*Signature*) Date / Time Received by (*Signature*) Relinquished by (*Signature*) Date / Time Received by (*Signature*)

Relinquished by (*Signature*) Date / Time Received by (*Signature*) Relinquished by (*Signature*) Date / Time Received by (*Signature*)

Relinquished by (*Signature*) Date / Time Received for Laboratory by (*Sig.*) Date / Time Sample condition upon receipt:

Method of Shipment:

Figure 10.3 Example Change of Custody Form

OhioEPA Division of Environmental Services — Conventional Parameters Analysis

WATER QUALITY LABORATORY CHEMICAL REPORT FORM

Station ID# _____

Date Received ___/___/___ Date Approved ___/___/___ Approved by: _____ Lab Number _____

Station _____

Sample Use: ☐ Monthly ☐ Litigation ☐ DERR ☐ Complaint ☐ WQ Survey ☐ Compliance

Sample Type: ☐ Grab ☐ Composite ☐ Sediment ☐ Tissue

Sample Collected by _____

Report Analysis to _____

Bill to: _____

Division: _____

☐ CO ☐ NEDO ☐ NWDO ☐ SEDO ☐ SWDO ☐ CDO ☐ WQM

Date & Time of Sample Begin (Y Y M M D D H H M M) ☐☐☐☐☐☐ ☐☐☐☐

End ☐☐☐☐☐☐ ☐☐☐☐

Frequency & Duration of Composite Sample _____

	PARAMETER	STORET CODE	RESULTS	DATE ANALYZED	ANALYST	SEDIMENT mg/kg
FIELD MEASUREMENTS	☐ Chlorine, Total Resd., mg/l	P50060,	.			
	☐ Conductivity, umhos/cm	P94,	.			
	☐ Dissolved Oxygen, mg/l	P299,	.			
	☐ Flow, CFS	P61,	.			
	☐ pH, SU	P400,	.			
	☐ Temperature, Water, °C	P10,	.			
	☐ Gage Height, ft.	P65,	.			
	☐					
LABORATORY MEASUREMENTS	☐ Arsenic, Total As, ug/l	P1002,	.			
	☐ Barium, ug/l	P1007,	.			
	☐ Cadmium, Total Cd, ug/l	P1027,	.			
	☐ Calcium, Total Ca, mg/l	P916,	.			
	☐ Chromium, Diss, Hex Cr, ug/l	P1220,	.			
	☐ Chromium, Total Cr, ug/l	P1034,	.			
	☐ Copper, Total Cu, ug/l	P1042,	.			
	☐ Iron, Total Fe, ug/l	P1045,	.			
	☐ Lead, Total Pb, ug/l	P1051,	.			
	☐ Magnesium, Total Mg, mg/l	P927,	.			
	☐ Manganese, Total Mn, ug/l	P1055,	.			
	☐ Mercury, Total Hg, ug/l	P71900,	.			
	☐ Nickel, Total Ni, ug/l	P1067,	.			
	☐ Potassium, Total K, mg/l	P937	.			
	☐ Selenium, Total Se, ug/l	P1147,	.			
	☐ Sodium, Total Na, mg/l	P929,	.			
	☐ Zinc, Total, ug/l	P1092,	.			
	☐ Hardness, Total $CaCO_3$, mg/l	P900,	.			
	☐					
	☐					

	PARAMETER	STORET CODE	RESULTS	DATE ANALYZED	ANALYST	SEDIMENT mg/kg
LABORATORY MEASUREMENTS	☐ Acidity, Total $CaCO_3$ mg/l	P70508,	.			
	☐ Alkalinity, Total $CaCO_3$ mg/l	P410,	.			
	☐ BOD, 5-day, mg/l	P310,	.			
	☐ cBOD, 5-day, mg/l	P80082,	.			
	☐ BOD, 20-day, mg/l	P324,	.			
	☐ cBOD, 20-day, mg/l	P80087,	.			
	☐ BOD, ultimate, mg/l	P319,	.			
	☐ Carbon, Total Org, mg/l	P680,	.			
	☐ COD, mg/l	P335,	.			
	☐ Chloride, Cl, mg/l	P940,	.			
	☐ Conductivity at 25°C, umhos/cm	P95,	.			
	☐ Cyanide, Total, ug/l	P720,	.			
	☐ Nitrate-Nitrite, as N, mg/l	P630,	.			
	☐ Nitrite, as N, mg/l	P615,	.			
	☐ Nitrogen, Ammonia as N, mg/l	P610,	.			
	☐ Nitrogen, Total Kjeldahl, mg/l	P625,	.			
	☐ Oil and Grease, mg/l	P556,	.			
	☐ pH, SU	P403,	.			
	☐ Phenolics, ug/l	P32730,	.			
	☐ Phosphorus, Total, mg/l	P665,	.			
	☐ Residue, Total, mg/l	P500,	.			
	☐ Residue, Total Flt, mg/l	P70330,	.			
	☐ Residue, Total Nflt, mg/l	P530,	.			
	☐ Sulfate, SO_4 mg/l	P945,	.			
	☐ Fecal Coliform, MF, #/100 ml	P31616,	.			
	☐ Total Coliform, MF, #/100 ml	P31501,	.			
	☐ Fecal Strept					
	☐					
	☐					

PRESERVATIVES

☐ NaOH ☐ HNO_3 ☐ N/P

☐ H_2SO_4, nutrients ☐ H_2SO_4, phenolics ☐ H_2SO_4, oil and grease

☐ Other ☐ Filtered

DISTRIBUTION:
WHITE-LAB
GREEN-STORET
CANARY-DISTRICTS
PINK-DISTRICT
EPA 4700

COMMENTS:

Figure 10.4 Example Analysis Request Form

FIELD QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

To assure adequate QA/QC in the field, the sampling plan should be followed consistently. To verify if procedures are contaminating ground water samples, a variety of samples and blanks need to be collected and analyzed. The following are typical checks:

- **Field Duplicates** - Field duplicates are samples collected as close to each other in time and space as practical at a specific location. Ultimately, upon analysis, both should yield the same results within an acceptable range. Excessive variation could indicate problems with the sampling procedures or problems with the analysis. If strict protocols are followed, variability as a result of the field procedures should be minimal. At minium, duplicates should be collected at a frequency of one per twenty samples (Yeskis and Zavala, 2002), one per week, and one per sampling event.

- **Trip Blanks** - Trip blanks are generally prepared by the laboratory before entering the field. Containers are filled with analyte-free, distilled, deionized water and sealed. These blanks are taken to the field and handled along with the collected samples, thereby acting as a control sample to determine potential VOC contamination from the containers themselves. Trip blanks should be included in each cooler containing VOC samples. At, minimum, at least one trip blank should accompany each sampling event. Trip blanks are never opened in the field.

- **Equipment Blanks** - Whenever non-dedicated sampling equipment is used, equipment/field blanks should be collected. An equipment/field blank is obtained by passing analyte-free, distilled, deionized water through a cleaned sampling apparatus (pump, bailer, filtration gear, etc.) and collecting it in a clean container. This blank is used to assess the effectiveness of the decontamination procedures implemented between sampling locations. Ideally, equipment blanks should be collected after sampling the well(s) that historically show(s) highest levels of contamination. They should be collected at a frequency of one blank per 20 samples (Yeskis and Zavala, 2002), one per week, and one per sampling event.

- **Field Blanks -** Field blanks (also known as ambient blanks) are containers containing de-ionized water, which are opened and remain open during field operations. They are used to assess whether there is a potential for sample contamination from air sources in the surrounding area. Analysis from field blanks cannot be used to adjust sample results. Field blanks are rarely collected as a control measure.

- **Temperature Blank** - A temperature blank may be used to estimate the sample temperature at the time the sample is received by the laboratory (ASTM, D6517-00).

Trip blanks and equipment blanks may not be necessary if it is assumed that any chemical of concern detected is present in the ground water or confirmation sampling and analysis is conducted.

All duplicates and blanks should be subjected to the same analysis as the ground water samples. The results are used to determine if proper procedures were followed. Blank

contamination can result from improper decontamination of sampling equipment, poor sampling and handling procedures, contaminated rinse water or preservatives, or the interaction between sample and container. The concentration levels of any contaminants found should ***not*** be used to correct the ground water data. Blank contamination should trigger a re-evaluation of procedures to determine the source of the problem.

GROUND WATER SAMPLE ANALYSIS

SELECTION OF ANALYTICAL METHOD

The selection of the method for ground water analysis is determined by the parameters of interest and the purpose of the investigation. Several methods may exist for the same parameter. The selected analytical method should be capable of accurately measuring the constituent of concern in the sample. Some regulatory programs may mandate that the analytical method be U.S. EPA-approved or may suggest a preferred method. Therefore, it is recommended that one check with the regulatory program prior to specifying an analytical method.

There are different methods that are approved by U.S. EPA. The following web sites may be helpful in choosing an appropriate method:

http://www.epa.gov/epahome/standards.html (U.S. EPA tests methods and guidance),
http://www.epa.gov/epaoswer/hazwaste/test/main.htm (U.S. EPA, SW-846 manual), and
http://www.epa.gov/SW-846/info.htm (U.S. EPA Web site that provides links to other sites).

The most important analytical requirement generally is the detection limit. For example, claims that no contamination is present in ground water samples are correct only to the quantitative extent that the analysis is capable of detecting the contaminant (Vitale et al., 1991). This level is known as the method detection limit (MDL). The MDL is the minimum concentration of a substance that can be measured and reported with a 99% confidence that the analyte concentration is greater than zero. Useless data may result if the detection limits are not low enough for the purpose of the investigation. For example, the primary objective often is to determine the risk to human health and the environment. In this case, the MDLs should be at or below human health-based criteria and environmental-based criteria.

Due to matrix interference and irregularities in instruments, the MDL may not always be obtained. In addition, the actual detection limit will be higher for samples that require dilution or reduced size to avoid saturation of the detector. The actual limit attained during the analysis should be reported with the data.

LABORATORY QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

It is not the intent of this document to discuss laboratory QA/QC procedures. Procedures, methods, and levels of quality control are discussed in various U.S. EPA publications (1979a, 1979b, and 1986b). Laboratory QA/QC may include, but may not be limited to, qualifications, performance, matrix effects (e.g., blanks and matrix spikes), documentation, and record reporting. For sites under the CERCLA process, Ohio EPA-DERR (1990) has established set guidelines and specifications for preparing quality assurance project plans.

For additional information on QA/QC plans the reader is referred to the Ohio EPA, Division of Hazardous Waste Data Validation Guidance.

To obtain reliable results, appropriate laboratory procedures and methods should be followed. An extensive laboratory QA/QC program ensures the production of scientifically sound, defensible results that can be documented and verified. Whether Ohio EPA review is required depends on the regulatory program involved. For example, submittal of a laboratory QA/QC plan is not required for sites undergoing RCRA closure (Ohio EPA, DHWM Program); however, the owner/operator should demonstrate that the laboratory has a plan that contains the elements listed by U.S. EPA (1986b). A laboratory QA/QC plan should be approved for sites remediated under the CERCLA process (Ohio EPA, DERR program).

An appropriate level of laboratory QA/QC data should be submitted with sample results to allow verification that the samples were properly handled and analyzed. A particular regulatory program may dictate the amount and type of data. All QA/QC data should be kept and made available upon request.

This data may be valuable for explaining outliers and questionable results. However, the laboratory QC results should not be used to alter the sample analytical data. A report on analytical data is incomplete without some verification of laboratory QA/QC.

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APPENDIX A
ADDITIONAL INFORMATION FOR SAMPLING WATER SUPPLY WELLS

Water supply wells are often sampled as part of characterizing a potential pollutant source. This information is helpful for characterizing the extent of a plume and to ensure that the public has a safe source of water. The name(s), address, and phone numbers of the resident or water supply owner/operator, should be obtained, so that they can be informed of the results.

Many of the same techniques and protocol for sampling monitoring wells also apply to collecting a representative sample from a water supply. This includes: planning and preparation; sample preservation, sample containers, handling and shipping; and documentation. These are discussed in other sections of this document. However, there are additional conditions/procedures that must be considered when selecting the sampling point and the actual sample. These additional considerations are summarized below.

Selecting the Sampling Point

The following should be considered when choosing the location to collect a water sample:

- Prior to sampling, existing information such as well construction, yield and depth should be obtained. The Ohio Department of Natural Resources, Division of Water keeps records of all well logs. Well log records can be searched on-line at http://www.dnr.state.oh.us/water/. If a well log record does not exist, then the local heath department should be contacted to see if they have any records. Also if no log exists, the depth of the well should be measured, if possible, and compared to the ODNR Ground Water Resource maps. These maps can be obtained at the above cited web link.

- The intake of the water supply well should be screened/opened to the targeted ground water zone of interest.

- The tap selected for sample collection should be the closest to the water source and prior to any treatment system. Also, if possible, the sampling point should be prior to entering the residence, office, building, or holding tanks etc. It is noted that for some small systems the first tap down stream from the pressure tank and upstream from any water treatment may be the best tap available.

- The sampling tap should be protected from exterior contamination associated with being to close to a sink bottom or to the ground. Contaminated water or soil from the faucet exterior may enter the bottle during the collection procedure since it is difficult to place a bottle under a low tap without grazing the neck interior against the outside faucet surface. If the tap is too close to the ground for direct collection into the appropriate container, it is acceptable to use a smaller (clean) container to transfer the sample to a larger container. The smaller container should be made of glass or stainless steel, or of the same composition of the sample bottles. Also, if samples are

to be collected for bacteria, then the tap needs to be disinfected prior to sampling. The laboratory should provide you with their tap disinfection procedures.

- Leaking taps that allow water to discharge from around the valve stem handle and down the outside of the faucet, or taps in which water tends to run up on the outside of the lip, should be avoided as sampling locations.

- Disconnect any hoses, filters, or aerators attached to the tap before sampling. These devices can harbor a bacterial population if they are not routinely cleaned or replaced when worn or cracked. If disconnection from an aerator, or treatment system, is required, permission should be obtained from the well owner.

- Taps where the water flow is not constant should be avoided because temporary fluctuation in line pressure may cause clumps of microbial growth that are lodged in a pipe section or faucet connection to break loose. A smooth flowing water stream at moderate pressure without splashing should be used. The sample should be collected without changing the water flow. It may be appropriate to reduce the flow for the volatile organic compounds aliquot to minimize sample agitation.

- When sampling for bacterial content, the sample container should not be rinsed before use due to possible contamination of the sample container or removal of the thiosulphate dechlorinating agent (if used). When filling any sample container, care should be taken that no splashing drops of water from the ground or sink enter into either the bottle or cap.

Sampling Technique

The following procedures should be followed when collecting samples from water supplies:

1. Ideally, the sample should be collected from a tap or spigot located at or near the well head or pump house and before the water supply is introduced into any storage tanks or treatment units. If the sample must be collected at a point in the water line beyond a pressurization or holding tank, a sufficient volume of water should be purged to provide a complete exchange of fresh water into the tank and at the location where the sample is collected. If the sample is collected from a tap or spigot located just before a storage tank, spigots located inside the building or structure should be turned on to prevent any backflow from the storage tank to the sample tap or spigot. It is generally advisable to open several taps during the purge to ensure a rapid and complete exchange of water in the tanks.

2. If the water system is not actively running, purge the system for at least 15 minutes. Systems that are actively pumped may require less purging (e.g., 3-5 minutes). After purging for several minutes, measure the stabilization parameters (See page 10-27). Continue to monitor these parameters until three consistent readings are obtained.

3. After three consistent readings have been obtained, samples may be collected. Samples collected from potable water supplies should not be filtered.

A detailed operation/procedural process for sampling water supplies can be found in the following references:

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