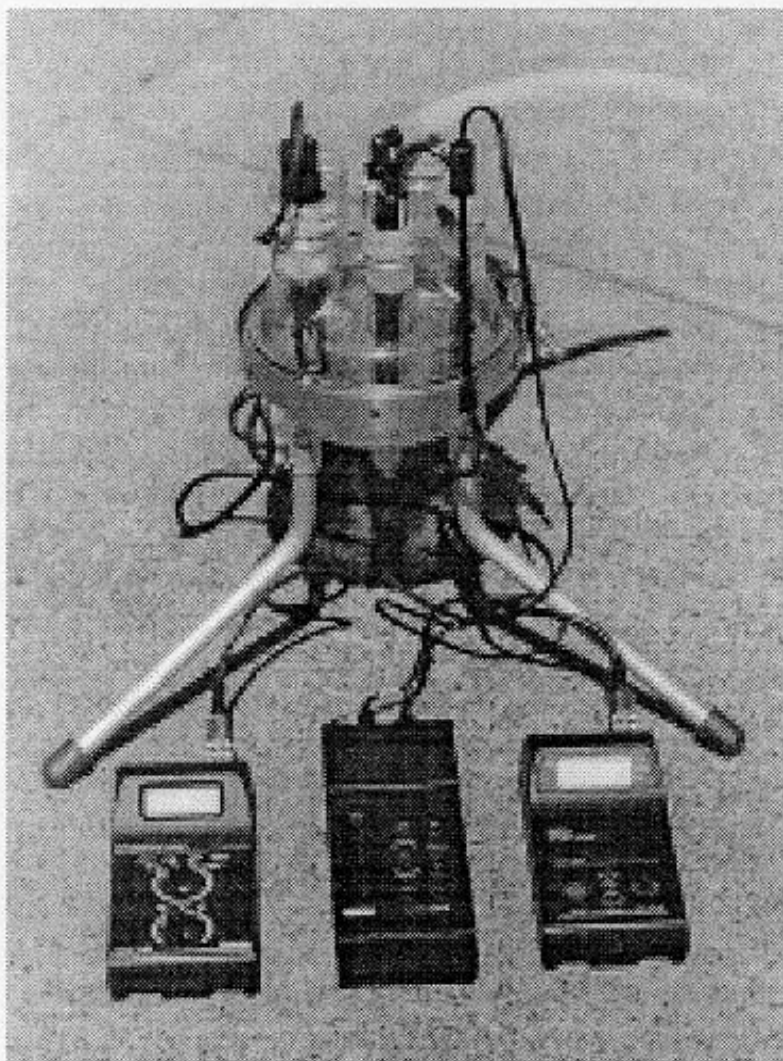# Groundwater Sampling Desk Reference

Groundwater Sampling Desk Reference

PUBL-DG-037 96

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ADDITIONAL COPIES

Additional copies of this document titled **Groundwater Sampling Desk Reference, Stock # 1728,** and the accompanying document titled **Groundwater Sampling Field Manual, Stock # 1729,** may be purchased from Wisconsin Department of Administration, Document Sales Unit. Call Document Sales at (608) 266-3358 or TTY (608) 264-8499 for pricing information (business hours 7:45 am to 4:30 pm).

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CONTENTS

GROUNDWATER SAMPLING DESK REFERENCE

TABLES

FIGURES

COMMONLY USED ACRONYMS

AA	Atomic absorption
ASTM	American Society for Testing and Materials
CERCLA	Comprehensive Environmental Response, Compensation and Liability Act
CLP	Contract Laboratory Program
DNAPL	Dense Non-Aqueous Phase Liquid
DQO	Data quality objectives
DO	Dissolved oxygen
GC	Gas chromatogram
GC/MS	Gas chromatogram/mass spectrometry
gpm	gallons per minute
HSP	Health and safety plan
ICP	Inductively coupled plasma
LNAPL	Light Non-Aqueous Phase Liquid
mg/L	milligrams per liter
mv	millivolts
NTUs	Nephelometric turbidity units
POC	Purgeable organic compounds
PPE	Personal protective equipment
ppb	parts per billion
ppm	parts per million
PRP	Potentially responsible party
PTFE	Polytetrafluoroethylene, commonly available as Teflon®
PVC	Polyvinyl chloride
QA/QC	Quality Assurance/Quality Control
RCRA	Resource Conservation and Recovery Act
SAP	Sampling and analysis plan
SDWA	Safe Drinking Water Act
μg/L	micrograms per liter
μmhos/cm	micromhos per centimeters
VOCs	Volatile organic compounds
WDNR	Wisconsin Department of Natural Resources
WUWN	Wisconsin Unique Well Number

1.0 INTRODUCTION

1.1 PURPOSE AND USE

This desk reference can assist you with collecting data that represents in-situ, unaltered groundwater conditions. It emphasizes the importance of determining data objectives, developing and following site-specific sampling plans, making thorough pre-sampling preparations, following purging, sampling and quality assurance procedures<u>consistently</u>, and documenting the entire sampling event.

Included is a common reference of reliable purging and sampling techniques for a variety of groundwater contaminants and hydrogeologic conditions; however, the Wisconsin Department of Natural Resources (WDNR) recognizes that the recommended procedures may not suit all hydrogeologic and geochemical conditions and contaminants or parameters being collected or measured. Therefore, the WDNR will be flexible in allowing alternative procedures as long as they provide scientifically valid and legally defensible groundwater data.

This document and the accompanying *Groundwater Sampling Field Manual, PUBL-DG-038 96,* include a variety of procedural options for each task (e.g., purging and sampling monitoring wells). For each task, the first option consistently yields the highest level of data quality. Subsequent options may yield lower levels of data quality. A project's sampling plan should include specific procedures for collecting groundwater data.

1.2 GROUNDWATER QUALITY

Groundwater quality reflects the physical, chemical and biological processes and contaminants, whether natural or human caused, that transfer impurities to groundwater. Many human-caused contaminants can affect groundwater quality, such as hazardous spills, fertilizers, pesticides, leaking underground storage tanks and leaking landfills.

Shallow groundwater systems are particularly susceptible to impacts from certain land use practices (e.g., fertilizer and pesticide application), as well as seasonal variations in water quality and composition. Groundwater in shallow systems may also be oxygenated to some extent.

Deeper groundwater systems commonly have a high dissolved mineral content, due to long groundwater/mineral contact time. They also exhibit low dissolved oxygen, less seasonal variation in water quality and composition and are under greater hydraulic pressure than shallow groundwater systems. Deeper groundwater systems commonly contain one or more of the following naturally-occurring constituents: hardness, iron, radon, total dissolved solids, manganese, sulfate and radium.

Because of water's polar nature and hydrogen-bonding abilities, it acts as a nearly universal solvent; it dissolves and mixes with many organic and inorganic substances. A substance's water solubility is

a good indication of the maximum concentration available for dissolution into groundwater. The actual chemical species of a compound or element dissolved in groundwater or attached to a solid's surface largely depends upon the solution's oxidizing-reducing status, the water's acid-base balance and the presence of complexing agents in the water. The following affect a chemical's transport and fate: 1) The nature of the mineral and the organic carbon content of aquifer materials (e.g., the organic content that affects a compound's retardation); 2) biological metabolic processes; 3) its precipitation or coprecipitation out of solution; and 4) the chemical's phase as it moves through an aquifer.

Groundwater may, or as is more likely the case, may not be in equilibrium with the aquifer materials and dissolved gases in the aquifer. The geochemical composition of groundwater typically reflects the geologic material it has flowed through and with which it has reacted (Summers and Gherini 1987).

1.3   COLLECTING PRELIMINARY SITE DATA

A common approach to assessing the degree and extent of groundwater contamination at a site is to install and sample a few monitoring wells. Several additional phases of well installation and sampling may also be required. By the time a project is completed, it is often apparent that some wells weren't necessary and that some wells should have been placed at different locations or screened at different depths.

Proper stratigraphic characterization of a site and the use of discrete-depth groundwater sampling can provide valuable preliminary information about subsurface hydrostratigraphy and the degree and extent of groundwater contamination. This information can prove invaluable for determining the appropriate number, location, screen length and depth of permanent monitoring wells and can save substantial time, money and sampling over a project's life.

1.3.1 Subsurface Stratigraphy

Hollow stem auger and split-spoon (i.e., split-barrel) samplers have been the norm for determining subsurface stratigraphy. Alternative methods may prove less costly and may be more effective under certain circumstances. Most of these alternative methods are described as direct push technologies (e.g., Geoprobe®, Diedrich®, Stratiprobe®, Precision®, etc.,) and can be used for soil sampling and subsurface stratigraphic profiling. Direct push technologies may also be used for soil vapor sampling and preliminary groundwater sampling. Common direct push technologies are hydraulic pushing systems, electric rotary-impact hammers, or hand-held slide hammers.

The main advantages of direct push methods over standard drilling methods (e.g., hollow stem augers) include: little or no generation of soil cuttings; faster soil sampling rate; lower cost; and equipment access into restricted clearance areas (e.g., inside buildings). The main disadvantages of direct push methods include: depth and soil type use limitations; smaller sample volumes; and the inability to collect certain types of soil samples. The sample tube opening of the direct push sampling tools is smaller and more restrictive than that of the standard split-barrel samplers. The presence of significant amounts of materials greater than one inch in diameter and the presence

of dry unconsolidated materials make sample recovery problematic for direct push sampling tools.

Cone penetrometers (another direct push method) are also gaining increased use and acceptance for characterizing site stratigraphy. A hydraulic ram pushes a mechanical or electronic cone penetrometer into the subsurface at approximately 4 feet per minute (1.2 meters per min). The penetrometer is commonly housed in a large truck specifically designed for cone penetration tests (CPTs) (**Figure 1**).

The basic electronic cone penetrometer used in CPTs consists of two separate soil shear resistance sensors – cone resistance and frictional resistance. These sensors acquire soil strength and stratigraphy data (refer to ASTM Method D-3441-86). Electronic cone penetrometers can also determine soil density, shear strength, and compressibility; and can relate resistance and friction to specific soil classifications (Ehrenzeller et al., 1991). Information obtained from CPT data can provide basic subsurface stratigraphic correlation and mapping data similar to that obtained from borings without human bias. Cone penetrometers can discern different soil types, aquifers and confining layers. If a pressure transducer is added to the electronic cone penetrometer, hydrostratigraphic information (e.g., soil saturation, water table, potentiometric surface and permeability in both aquifers and aquitards) can also be evaluated (Strutynsky and Sainey, 1992).

Cone penetrometers are best suited for sand, silt and clay deposits. Depths of 300+ feet (90+ meters) can be achieved in very soft unconsolidated materials; however, gravel, cobbles and dense or cemented layers reduce a cone penetrometer's effectiveness or may impede it altogether. Depending on the rig and site conditions, anywhere from 300 to 900 feet (90 to 275 meters) of geotechnical readings can be performed in a day. Site disturbance is minimal and there are no drill cuttings.

> **Important note:** All boreholes, including boreholes created by direct push methods, greater than 10 feet (3 meters) deep and all boreholes that intersect a water table must be abandoned in accordance with s. NR 141.25, Wis. Adm. Code. Specifically, the borehole should be grouted from the bottom to the top. With direct push methods, this may require changing the tool on the drive rod.

1.3.2 Discrete-depth Groundwater Sampling

Discrete-depth groundwater samplers are used during initial site investigations to provide preliminary information on the degree and extent of groundwater contamination. This information, along with subsurface stratigraphic data, can assist with determining the appropriate number, location and screening of permanent monitoring wells.

Discrete-depth groundwater samplers have been developed for use with conventional drill rigs (BAT Enviroprobe®, MK2 probe®, QED Hydropunch®, etc), cone penetrometer rigs, or with rigs designed to hydraulically hammer or vibrate the tools or probes to desired depths (Geoprobe®, Deidrich®, Stratiprobe®, etc.,). Some of these devices require that a groundwater sample be collected with a bailer or with a vacuum/suction pump. Other devices have a retrievable sampling chamber or vessel within the drill rod.

20 TON PUSHING FORCE

WATER TANK AND
STEAM CLEANER

HYDRAULIC
RAM

COMPUTER
DATA
ACQUISITION
SYSTEM

STRATOGRAPHICS

GROUT PUMP

ROD WASH CHAMBER

PORE FLUID SAMPLER

SAMPLE
CHAMBER

(Sampler
opened)

PENETROMETER

FRICTION
RESISTANCE

ELECTRICAL
CONDUCTIVITY

PIEZOMETER

CONE END BEARING
RESISTANCE

100+ FT DEPTH CAPABILITY
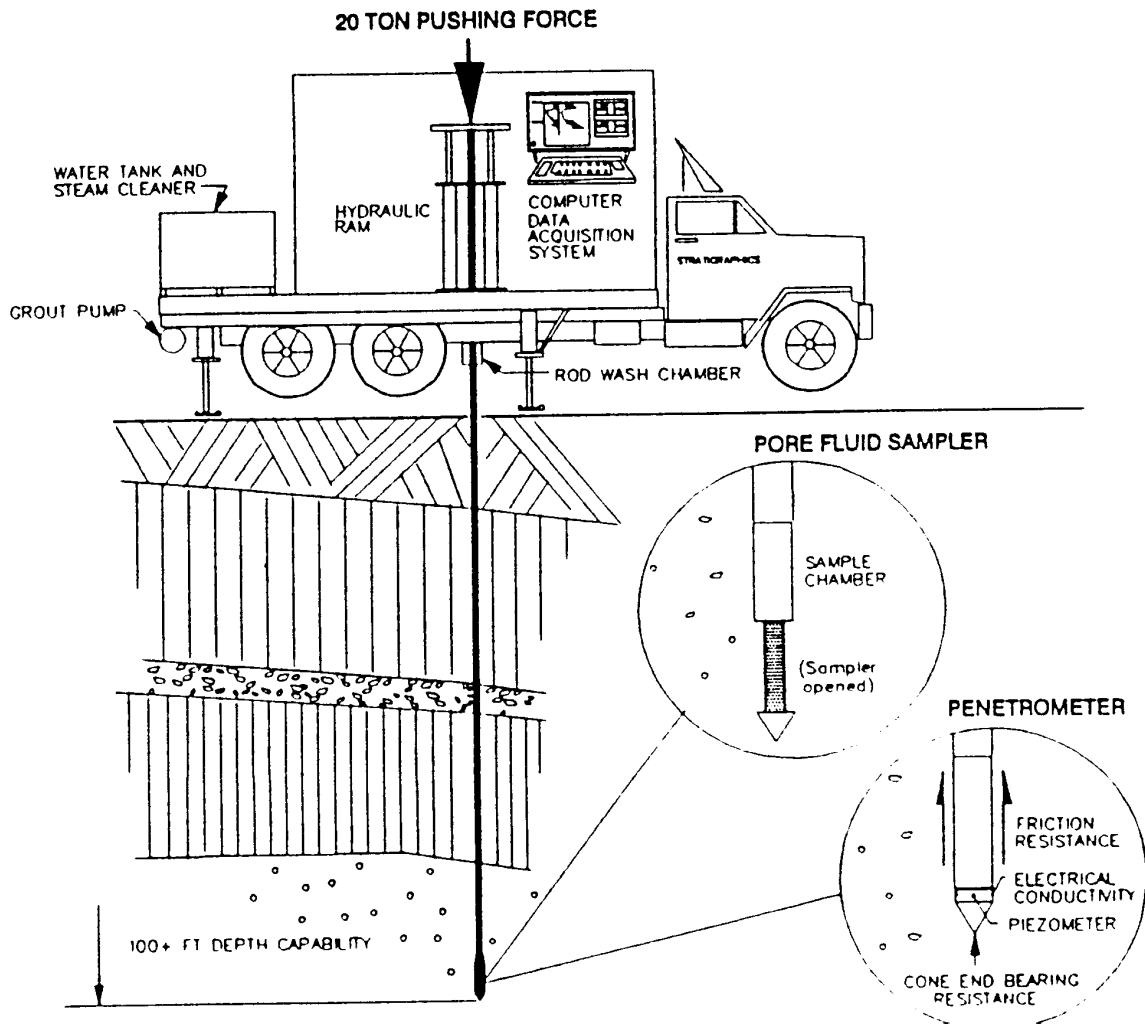
These devices are good preliminary screening tools and are very good at collecting discrete-depth groundwater data. They can accurately characterize variations in the distribution and concentration of contaminants that exist in discrete zones in groundwater. However, discrete-depth groundwater samplers cannot replace properly-constructed monitoring wells for collecting representative, high-quality groundwater samples.

Potential limitations of discrete-depth groundwater sampling devices include the following:

- Some designs are incapable of collecting groundwater samples at the water table surface.
- Some devices have excessively long collection times when obtaining groundwater samples from silt or clay formations.
- Most devices have relatively short screen lengths (<1 to 4 feet or 0.3 to 1.2 meters) that may miss contamination.
- Some devices have limited sample volume capabilities.
- The screens of these devices may allow appreciable quantities of fines to enter the sample chamber.
- It may be difficult, if not impossible, to properly develop the borehole to collect sediment-free samples or samples representative of the surrounding groundwater quality.
- These devices have soil type and depth limitations and are generally not capable of penetrating gravel, cobble, hard or cemented layers and certain sands.
- Boreholes created by these devices may be difficult to properly abandon in accordance with s. NR 141.25 Wis. Adm. Code.

Case studies

Clausen and Solomon (1994) used three different methods for defining the degree and extent of trichloroethene (TCE) and technetium (^{99}Tc), a man-made radionuclide, at a Department of Energy Facility located in western Kentucky. The authors used a van-mounted GeoProbe® which employs a hydraulic hammer to drive a 2.5 cm outer diameter (OD) rod, a Rhino® which employs an air operated hammer and vibrator to drive a 4.8 cm OD rod and a Mr. Missile® which employs a hydraulic hammer to drive a 4.8 cm OD rod. During groundwater sampling, a 1.3 cm OD polyethylene tube outfitted with a check valve at the bottom was inserted down the rod assembly of each tool. The top of the rod was capped and air pressure was applied to bring samples to the surface by air-displacement. A comparison of analytical results for TCE/^{99}Tc ratios for samples collected with the driven discrete-depth system and monitoring wells was comparable and yielded similar regression lines. The driven discrete-depth sample results strongly suggested a vertical distribution of residual dense nonaqueous phase liquid (DNAPL) in the groundwater and a DNAPL pool underlying the site. These were not previously detected by the permanent monitoring wells installed at the facility.

Strutynsky and Sainey (1992) used a cone penetrometer to determine a site's hydrostratigraphy in real-time and collected groundwater samples from a Hydropunch® to preliminarily define the degree and extent of a volatile organic compound (VOC) plume. The results were used to determine subsequent monitoring well locations. The Hydropunch® was successful in obtaining 22 groundwater samples out of 27 attempts. While the Hydropunch® worked well, there were some disadvantages: 1) It was not always clear if the well screen shield had opened; 2) minor seizing of the sampler parts occurred; and 3) there was slight bending of the sample barrel at forces > 10 tons. Use of the cone penetrometer, Hydropunch® and an on-site gas

chromatograph allowed for minimal site disturbance and waste generation, the collection of high quality/high resolution hydrostratigraphic data, the optimal placement of monitoring wells, and meeting deadlines at a minimal cost.

Kaback et al., (1990) compared the ability of a Hydropunch® and four adjacent monitoring wells to collect similar groundwater sample data. Results for two of the wells showed excellent correlation with Hydropunch® analytical data. However, results for the other two wells showed variation. These other two wells were screened in the most concentrated part of the plume, which existed as a very thin lens close to the water table surface. However, the Hydropunch® design required that it be placed at least 5 feet (1.5 meters) below the water table to allow hydrostatic forces to fill it, and the Hydropunch® was unable to sample the plume near the water table surface. The study concluded that the Hydropunch® was an excellent screening tool for trace metals, pH and major cations and anions; however, contamination near the water table may be missed.

A similar study conducted by Bergen et al., (1990) looked at the Hydropunch's® ability to reproduce VOC data collected from five adjacent monitoring wells. The study found that the analytical results for the Hydropunch® and well samples were statistically similar and that the Hydropunch® served as a good initial screening tool. Hydropunch® difficulties included: 1) Missing contaminants near the water table surface; 2) physical deformation of the sampler when hammered through well-sorted coarse sand layers; 3) sample collection times of up to two hours in silt and clay zones; and 4) the unit's filter mesh allowing significant intake of fines into the sample chamber.

2.0 SAMPLING PROCEDURES FOR MONITORING WELLS

2.1 OBJECTIVES, PLANS, PREPARATIONS AND DOCUMENTATION

Primary components of a successful groundwater monitoring and sampling program include: determining data objectives; developing and following an effective site-specific sampling plan; preparing carefully before sampling; and meticulously documenting each sampling event.

2.1.1 Data Objectives

Before monitoring, it is critical to identify and understand the purpose for monitoring and how the resultant data will be used. Groundwater quality data are collected to meet a variety of objectives, including, but not limited to, protection of public health and the environment, facility performance evaluations and assessment of groundwater contamination remediation efforts.

Establishing Data Quality Objectives

The data quality objective (DQO) process is a systematic planning process for determining the type, quantity, and quality of data and information necessary to make well-informed, valid and defensible decisions. DQOs clarify a project's goals and objectives. They explain what data and information will be used, and how and why it will be collected. DQOs also specify acceptable levels of uncertainty or errors in data, and the risks of making wrong decisions.

The following DQO process steps, presented in various USEPA guidance documents, describe project design optimization and can be used in varying degrees for large and small monitoring projects:

1) **State the Problem:** Concisely state the problem to be studied.
2) **Identify the Decision:** Identify what questions the study will attempt to answer and what actions may result.
3) **Identify Inputs to the Decision:** Identify the data and measurements necessary to resolve the decision. Consider any factors influencing the decision such as cost or public perception of risk.
4) **Define the Study Boundaries:** Specify the time periods and spatial area to which the decision will apply and when and where to collect data.
5) **Develop a Decision Rule:** Consider the parameters of interest, the action or cleanup levels and alternative actions. Choose among the alternative actions.
6) **Specify Limits on Decision Errors:** Determine tolerable limits on decision errors based on consideration of the consequences of making an incorrect decision.
7) **Optimize the Design:** Generate alternative data collection designs and choose the most resource-effective design that meets all DQOs.

For projects that collect groundwater data and measurements, or are responding to a groundwater

quality standards exceedance, the following considerations should ensure that the data collected meets data quality objectives (DQOs):

■ Regulatory objectives and requirements.
■ Contaminant considerations.
■ Sampling considerations.
■ Data quality and quantity.
■ Laboratory constraints: methods, limits of detection and analytical data quality.

Regulatory Objectives and Requirements

Chapter NR 140, Wis. Adm. Code, requires that all facilities, practices and activities that may affect groundwater quality and that are regulated by a state agency protect, monitor and remediate groundwater quality when necessary [see s. NR 140.03]. State agencies that regulate facilities, practices and activities include the Wisconsin Department of Natural Resources (WDNR), the Department of Agriculture, Trade and Consumer Protection (DATCP), the Department of Transportation (DOT), and the Department of Industry, Labor and Human Relations (DILHR). Each state agency that requires groundwater monitoring has specific statutes, administrative codes and guidance documents that describe their regulatory objectives and requirements.

Chapter NR 140 requires that groundwater samples must be collected using procedures specified by WDNR (i.e., this document and the accompanying *Field Manual*). Where no procedures are specified (e.g., procedures for collecting groundwater samples containing radioactive substances), other published sampling procedures may be used [see s. NR 140.16(1)]. Chapter NR 712.05 describes minimum qualifications for those people collecting environmental samples, including groundwater samples. Chapter NR 140 requires that groundwater quality samples be analyzed by a laboratory certified and registered under ch. NR 149. Chapter NR 149 establishes the minimum requirements for laboratories; however, if a project's objectives necessitate a higher level of quality, the laboratory may need to validate the analytical data to ensure it meets the project's DQOs.

Chapter NR 140 and the NR 700 series already include many of the important aspects of the DQO decision process. Chapter NR 140 specifies groundwater quality standards for substances detected in groundwater; these are action or cleanup levels. The NR 700 rule series includes the complete process that responsible parties must follow to report, investigate and clean up soil and groundwater contamination. This incorporates several aspects of the DQO process including identifying what data are needed, the study boundaries and investigation requirements, the response alternatives evaluation and decision process and action levels for soil. These aspects of the DQO process strongly encourage the most effective means to meet all project DQOs.

WDNR and other state agencies that monitor or require the monitoring of groundwater quality do so to meet one or more of the following regulatory objectives or requirements:

■ Define the nature and extent of groundwater problems in Wisconsin.
■ Reduce groundwater pollution and prevent contamination of groundwater.
■ Provide a basis for facility or practice design, construction and operation.
■ Evaluate a facility's or site's performance and environmental impacts.
■ Comply with ch. NR 140, Wis. Adm. Code, groundwater quality standards.

- Protect public health, welfare and the environment.
- Define and sample potable wells at risk from groundwater contamination.
- Evaluate the need for a change or revision of a facility's or site's monitoring, design, construction, operation, waste treatment or disposal practices.
- Evaluate the need for prohibition or closure and abandonment of a facility or site.
- Meet Wisconsin Pollution Discharge Elimination System (WPDES) permits.
- Evaluate the degree, extent and environmental fate of groundwater contamination.
- Evaluate and verify the remediation of groundwater contamination.

Contaminant Considerations

Determining and evaluating the type, concentration and stability of contaminants and parameters collected or measured is important. The susceptibility of contaminants to extraneous contamination or loss during purging, sampling and handling will help define the rigor and stringency of chosen procedures and protocols.

During monitoring of contaminants that are unstable, subject to alteration during collection, or may be present at concentrations near the analytical detection limit, rigorous purging, sampling, handling and decontamination procedures are necessary. Sensitive substances such as volatile organic compounds (VOCs) and dissolved metals, usually analyzed and regulated at the micrograms per liter (µg/l) or parts per billion (ppb) levels, fall into this category. Strict and rigorous sampling procedures, QA/QC procedures and careful documentation of the sampling event are necessary.

On the other hand, routine compliance monitoring for major, stable ions (e.g., monitoring chloride ions at a wastewater spray irrigation site) that are not subject to alteration during sampling or handling can have less stringent and less rigorous sampling and handling procedures. QA/QC and documentation procedures used depend on project objectives.

Sampling Considerations

The larger and more complex a site's hydrogeology and contamination plume are, the more rigorous and detailed the sampling plan should be. The site's stratigraphy, hydrogeology and complexity in relation to the fate and transport of contaminants should be determined and evaluated. Any restraints or considerations these factors may place on establishing sampling procedures, QA/QC procedures and documentation procedures should be noted.

Timing and frequency of data collection are also important considerations. For example, pesticide concentrations in groundwater are most likely to be highest right after a recent rain and soon after application. Consequently, variations of pesticide concentrations in groundwater will likely be greatest in spring and summer. Another example is a site with residual petroleum contamination in soil directly above the water table. Concentrations of petroleum in groundwater may be highest soon after rains because water infiltrating through the soil will dissolve petroleum and, as the water table rises, residual petroleum in the soil will dissolve into the groundwater.

A common monitoring goal is to determine the actual concentrations of contaminants present in groundwater. Due to the nature of collecting groundwater samples, the true levels present in the groundwater may be underestimated. Ignoring analytical error and bias, how closely contaminant concentrations approach the actual concentrations present in the groundwater depends on how sampling and handling errors are controlled. Ultimately, sample integrity drives the quality of analytical results.

Overall Data Quality and Quantity Needs

The quality of a data set relates to the level of uncertainty or error inherent in a data set, usually expressed as the precision, accuracy, bias, representativeness, comparability and completeness of a data set. Unfortunately, determinations of data quality often focus solely on the laboratory component, overlooking or avoiding the significant contribution of sampling and handling.

Data quality for a specific project or site specifies the level of uncertainty that will be tolerated in a set of environmental data. The higher the data quality, the more confidence an individual will have in the accuracy and representativeness of a data set. The quality of a data set is expressed:

> 1) qualitatively as a specified set of procedures and protocols used for collecting the data (i.e., purging and sampling procedures) and
>
> 2) quantitatively as the amount of acceptable variation and error (precision, accuracy and bias) inherent in the data set attributable to sampling equipment, sampling procedures, analytical methods and the concentration of the contaminant in relationship to method detection limits.

Analytical laboratories are required to follow approved methods, specify quality control/quality assurance procedures, and keep detailed records. However, field sampling activities and procedures typically are not as defined or stringent as the analytical procedures. Because of this, the level of uncertainty inherent in a data set attributable to field sampling procedures and protocols is often difficult to quantify or is unknown. Therefore, identifying project data quality needs, creating and following a site-specific sampling and analysis plan and quality assurance/quality control plan and carefully documenting each sampling event will go a long way in controlling the uncertainty in the measurements and minimizing the risks to decision-making.

In addition to quality considerations, the quantity of data available is an important consideration, particularly during application of statistics to the data set. Data quantity is the number of samples needed to support the decision at the specified level of uncertainty. The question "How many data points do you need to make a decision?" is deceptively simple. Answering it may be considerably more difficult, particularly when you assess the risks of making the wrong decision. Anyone who has worked with a statistician to design a monitoring project realizes that it is frequently not practical or feasible to collect enough samples to achieve the desired level of certainty. The risks to decision-making must be weighed against physical, regulatory and fiscal constraints.

Quality assurance and quality control (QA/QC) requirements and procedures should match the level of data quality required and the DQOs derived for a site or project. Refer to Section 2.10.1

for further discussion of QA/QC requirements, procedures and development of a QA/QC plan. Brynes (1994) and EPA (1995 and QA/G-4 Interim final) provide detailed discussion of the overall data quality objectives process.

Laboratory Constraints: Methods, Limits of Detection and Analytical Data Quality

How close the laboratory's limit of detection for a contaminant is to the suspected concentration and regulatory limit (e.g., ES or PAL) for the project should indicate the level of care needed in sampling for a given contaminant or parameter. For example, if contaminants may be present near the analytical limit of detection, then particular attention should be paid to sampling procedures to avoid contaminating the sample or losing the contaminant.

The U.S. Environmental Protection Agency (EPA) has identified five separate analytical quality levels (EPA 1987) that may be appropriate for a site or project**Table 1** summarizes the levels and their appropriateness in relation to data uses, type of analysis, limitations, and the data quality for which each level should provide. For most groundwater monitoring and contamination investigation/remediation projects regulated under s. 144.76 or 144.442, Wis. Stats., and not subject to CERCLA or RCRA requirements, the I, II and III analytical levels will meet data quality needs. Levels IV and V may be appropriate for special needs such as Superfund sites and obtaining strong, legally defensible results.

■   Level I data are collected with portable field screening instruments such as an organic vapor instrument (e.g., PID, FID). Results are not compound specific, detection limits are high (e.g., ±mg/L) and results are in real time (i.e., seconds to minutes).

■   Level II data are collected with more sophisticated portable analytical instruments (e.g., mobile laboratory equipped with a gas chromatograph). Level II data quality depends on the calibration standards used, reference materials, sample preparation equipment and training and skill of the instrument's operator. Results are available within minutes or several hours. Level I and II data are used in site characterization and defining the degree and extent of contamination.

■   Level III data are analyzed at a non-portable laboratory and are commonly analyzed using SW-846. In Wisconsin, this data must be analyzed by a laboratory certified under ch. NR 149, Wis. Adm. Code. The laboratory does not have to be CLP-certified and the data is not subject to special validation and documentation procedures.

■   Level IV data are analyzed by a Contract Lab Program (CLP) analytical laboratory following CLP procedures. Level IV data analysis is characterized by rigorous QA/QC protocols and documentation. In Wisconsin, certain projects may require CLP protocols and data packages but allow a non-CLP laboratory to perform the analysis. In such cases, ch. NR 149 requirements are no longer applicable. However, analyses not subject to CLP protocols must follow Ch. NR 149 requirements and any additional QA/QC and reporting specified in the project plan and data validation.

■   Level V data are analyzed by non-standard analytical methods. Analysis may or may not be performed by a CLP laboratory (CLP special analytical services are level V). Analytical method development or modification of an existing method may be required for a specific constituent or to meet required detection limits.

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TABLE 1: SUMMARY OF ANALYTICAL LEVELS APPROPRIATE TO DATA USES

ANALYTICAL LEVEL	DATA USES	TYPE OF ANALYSIS	LIMITATIONS
LEVEL I	• Site characterization • Monitoring	• Total organic/inorganic field instruments • Field test kits	• Results are not compound specific • High detection limits • Naturally-occurring interferences
LEVEL II	• Site characterization • Remedial alternatives evaluation • Engineering design • Monitoring	• Variety of organics by GC; inorganics by AA • Tentative identification; analyte specific • Detection limits vary from low ppm to low ppb	• Tentative identification • Techniques and instruments limited mostly to volatiles and metals
LEVEL III	• Site characterization • Remedial alternatives evaluation • Engineering design • Monitoring • PRP determination • Risk evaluation	• Organics/inorganics using SW-846 • In WI, laboratory must be ch. NR 149 certified • RCRA characteristics tests	• Tentative identification in some cases • Data is not subject to validation and documentation as CLP
LEVEL IV	• Remedial alternatives evaluation • Engineering design • PRP determination • Risk evaluation	• CLP laboratory following CLP procedures • Organics/inorganics by GC/MS; AA; ICP • Low ppb detection limits	• Rigorous QA/QC procedures may cause long turn-around time for results
LEVEL V	• PRP determination • Risk evaluation	• Non-conventional parameters/methods • Method-specific detection limits • Modification of existing method	• May require method development/modification • Mechanism to obtain services requires special lead time • May or may not be a CLP laboratory

Maintaining Data Quality Objectives

Meeting and maintaining an established level of data quality can be accomplished by:

1.   Following a sampling and analysis plan (SAP) and quality assurance/quality control (QA/QC) plan specifically tailored to a site or project.

2.   Documenting the samples collected, measurements taken and procedures followed during each sampling and monitoring event. The SAP and QA/QC procedures can serve as documentation of equipment and procedures used; however, any deviations from the established procedures and protocols must be documented.

3.   Strictly adhering to the DQOs and quality assurance/quality cotrol (QA/QC) procedures established for the project.

2.1.2 Developing Site-specific Plans

Sampling and Analysis Plan (SAP)

A sampling and analysis plan (SAP) should be site-specific and should bring the sampling and monitoring procedures and protocols, data quality objectives (DQOs) and other project requirements into one clear plan. The sampling plan should document the equipment and procedures used during a sampling event. The procedures and protocols specified in the SAP should be consistently followed throughout the life of a project. Any deviations, including reasons for the deviations, should always be clearly documented.

Depending on a project's complexity and any regulatory requirements, a SAP may be fairly short and simple (e.g., small seepage lagoon, 3 monitoring wells, sampled quarterly for indicator parameters), to long and complex (e.g., CERCLA, RCRA, or Superfund sites). Chapter NR 716 specifies site investigation work plans, field investigations and sampling and analysis requirements for responsible parties investigating a hazardous substance discharge (e.g., underground storage tank discharge) subject to regulation under s. 144.76 or 144.442, Wis. Stats.

If a SAP is modified during the life of a project, the modifications must be considered when evaluating the data generated from the project. Refer to Section 2.5, "important note," related to the validity, representativeness and comparability of a project's groundwater data.

All the following items may not be necessary for a project's SAP. Include those items applicable to the specific project, established data quality objectives and as required by applicable state and federal rules and regulations:

1.   The project or site name and location (include maps).
2.   A brief history of the site including chemical use inventory/history, land use, known and suspected spills, environmental media affected, etc,.
3.   Regulatory objectives and data quality objectives (DQOs).
4.   Type, concentration and form (e.g., free product, dissolved) of contaminants and parameters to be measured and sampled.

5. Transportation to the site and site access arrangements (e.g., meeting times, keys, permission).
6. Sampling team personnel and their duties.
7. The location of all wells (include map), well names or numbers (e.g., Wisconsin Unique Well Numbers), well diameters, screen lengths and well depths.
8. Order in which wells are sampled, prior site sampling history and problems/constraints.
9. Which documentation sheets and forms (e.g., well specific field sheet, chain of custody form, etc.,) should be completed for each sampling/monitoring event.
10. Equipment, procedures and protocols for:
    a. measuring static water level,
    b. measuring and sampling immiscible layers,
    c. purging and sampling wells,
    d. filling sample containers and preserving samples,
    e. taking water quality measurements and
    f. filtering samples.
11. Laboratory analytical methods and limits of detection for each contaminant being sampled.
12. Laboratory analytical data submittal form (e.g., electronic, tables, forms) and regulatory data submittal deadlines (e.g., 10 days).
13. The QA/QC plan and procedures including the handling, storing, transporting and shipping samples and the collection of quality assurance samples. The QA/QC plan and procedures should be incorporated into the SAP, or less preferably, can be created as its own separate plan (see Section 2.10.1).

Health and Safety Plan (HSP)

The Code of Federal Register 29 CFR Section 1910.120 and Occupational Safety and Health Association (OSHA) includes many of the requirements for individuals performing hazardous waste operations and emergency response and should be referenced. While specific health and safety concerns and regulatory requirements are beyond this document's scope, some health and safety considerations common to groundwater contamination and monitoring activities include:

1. A hazard analysis for each site task (including a list of contaminants, concentrations and associated health hazards).
2. List of sampling personnel, site safety and health supervisor, hazardous waste training, and personnel medical monitoring received.
3. Level and type of personal protective equipment required (e.g., level A, B, C, or D). Check the compatibility of the personal protective equipment with the types and concentrations of known or suspected contaminants at the site. Manufacturers of personal protective equipment often have charts and tables for choosing appropriate types and materials of protective wear applicable to a variety of contaminants.
4. Frequency and type of air monitoring, personnel monitoring, environmental sampling and instrumentation to be used.
5. Site control (access) measures.
6. Personal hygiene and decontamination procedures.
7. An emergency response and contingency plan (including emergency phone numbers and map to nearest medical facility).
8. Work limits for inclement weather, confined space entry, etc.
9. A spill containment plan.

Another potentially useful resource related to health and safety includes the NIOSH*Pocket Guide to Chemical Hazards*, DHHS (NIOSH) Publication No. 90-117. Copies of this and other NIOSH documents are available by calling (513) 533-8287.

2.1.3 Other Preparations

Careful planning, and advanced checking and preparing of equipment before heading into the field will save time, money and problems.

Pre-field Work Procedures Checklist - Monitoring Wells

The following checklist should help you conduct a smooth, effectively-prepared groundwater sampling program for your project. This checklist, in abbreviated form, is also included in Appendix A of the *Groundwater Sampling Field Manual, PUBL-DG-038 96*

All the following procedures may not be necessary for each sampling event. Use those procedures applicable to your sampling plan or customize this list as appropriate.

Logistics

1. Arrange for site access with the land/home/facility owner and tenants. Besides avoiding site access delays, pre-arranging site access will help maintain good relations with the site's owner. This will also provide a good opportunity to update the owner on progress at his/her site and answer any questions he/she may have.

2. Locate the nearest post office, UPS office, or Fedex drop off spot if you will be mailing the samples from the field. (UPS has a 70 pound weight restriction per container.) Make sure you have the proper materials for shipping samples (e.g., sufficient coolers and ice).

3. Determine how the purge water and wastewater will be stored and discarded. If the purge water and wastewater will be disposed of into a sanitary sewer, contact the water utility department and receiving wastewater treatment facility to obtain permission and establish where, when and how much wastewater will be disposed of into the sanitary sewer system.

Laboratory Arrangements

1. Select a laboratory to perform the sample analysis. Pay careful attention to the laboratory selection process. Selection based on price and turn-around alone may doom the project. Evaluate quality objectives for the project and laboratory analyses. Evaluate reporting requirements and other considerations specific to the project. Check that the laboratory (and subcontracted laboratory) is certified or registered under ch. NR 149 to perform the required sample analysis. Check that the laboratory will follow the proper analytical methods and can meet required limits of detection.

2. Discuss with the laboratory who will supply what sample containers. If the laboratory will supply some or all of the containers, make arrangements for delivery of the number and type needed - **get extras!** Don't forget QA/QC sample containers and trip blanks if VOC samples will be collected. Appendix C of the *Groundwater Sampling Field Manual,* specifies container types and provides recommendations on the <u>minimum</u> sample volumes for a variety of analytical parameters.

3. Discuss sample preservation, holding time and shipping requirements with the laboratory. Some laboratories provide preservative already in sample containers, or in other containers (e.g., ampules) that you can later dispense into the sample containers. Discuss QA/QC expectations and the type of information that should accompany analytical results (e.g., LOD and LOQ data).

4. Inform the laboratory of when and how many samples will be sent. This will help the laboratory prepare for analyzing your samples and meet sample holding times.

5. Familiarize yourself with chain of custody and other sample tracking procedures.

6. Discuss any other procedures required by the laboratory (e.g., noting gross sample contamination, field turbidity readings if metal samples are to be analyzed). Some laboratories request previous analytical results for each well to help determine appropriate sample dilutions up front.

7. Include in the contract quality objectives (QA/QC, MDLs, etc), project-specific requirements (e.g. providing raw package with the report) and any special agreements made with the laboratory. This helps avoid misunderstandings about expectations and may provide additional tools to deal with data that falls far short of quality objectives.

<u>Site History</u>

1. Review the sampling and analysis plan (SAP) and past water quality and sapling data.

<u>Equipment and Field Preparation</u>

1. Review the SAP and QA/QC plan or equivalent. Refer to Section 2.1.2 for developing a SAP and Section 2.10 for developing a QA/QC plan.

2. Organize groundwater monitoring and sampling equipment. Do this at least one day ahead of the scheduled sampling day. Refer to Appendix A of the *Groundwater Sampling Field Manual a*nd use the "Equipment Checklist - Monitoring Well Sampling" or customize your own equipment checklist.

3. Check that sampling equipment is in good working condition:

   ✓ Test and recharge/replace batteries as necessary.
   ✓ Test the equipment with tap water or calibration standards when possible.
   ✓ Inspect the equipment for defects, loose bolts, frayed wiring, etc.

    ✓   Check the instruments' ability to calibrate and function properly. Check its ability to operate in very cold, hot or wet weather.

4.   Check that all the equipment is properly decontaminated and stored for transport.

5.   Complete the well-specific field sheet (WSFS), data logs or other field data sheets as much as possible before going to the field.

<u>Health and Safety Equipment and Preparation</u>

1.   If applicable, review the health and safety plan (HSP). Refer to Section 2.1.2 and applicable federal, state and local laws, codes and requirements related to health and safety requirements.

Equipment Checklist - Monitoring Well Sampling

A complete monitoring well sampling equipment checklist is included in Appendix A of the *Groundwater Sampling Field Manual, PUBL-DG-038 96* All of the items included in the checklist may not be necessary for each sampling event. Modify and customize this list as necessary and appropriate.

2.1.4 Documentation

Meticulous documentation of monitoring and sampling data and collection/measurement procedures is essential. Documentation provides a permanent record of data collected, equipment and procedures used, sampling personnel, and problems that occur at a site. This information will help ensure that data are collected consistently and that deviations in protocols are noted for later evaluation. Careful documentation also helps prepare a project's data for legal scrutiny.

Clearly document the methods, procedures and equipment you use to collect groundwater data in the data reports you generate for a site or project. Also, clearly document any deviations from the standard sampling and monitoring protocol, along with a discussion of potential effects on the data.

Documentation of the Sampling Event

1.   **Site-specific Sampling and Analysis Plan (SAP) or Equivalent.** A SAP or other sampling plan should act as documentation of the sampling event. All sampling personnel should read it before heading out to the field and should bring it to each sampling event. Document any <u>deviations</u> from the sampling plan; you can use the "Field Procedures Documentation" sheet included in Appendix A of the *Groundwater Sampling Field Manual* to document any deviations.

2.   **Well Specific Field Sheet - Monitoring Wells** Document well-specific purging, sampling and field water quality measurement data on this sheet (included in Appendix A of the *Groundwater Sampling Field Manual*). Or, customize your own data sheet. Hand-held data loggers are becoming popular because they provide a permanent record of well data that can be easily down-

loaded to a computer.

3. **Field Procedures Documentation.** A SAP or other sampling plan should act as documentation of sampling procedures; however, if a sampling plan is not available, use the "Field Procedures Documentation" sheet included in Appendix A of the *Groundwater Sampling Field Manual.* You can customize this sheet to meet specific needs.

4. **Chain of Custody Form (Appendix A).** Document the possession of groundwater samples by filling out chain of custody or other sample tracking forms. Complete this form for every sampling event no matter the size of the sample set. If a project is later subjected to legal action, chain of custody procedures and whether they were followed will likely be an important part of the case.

2.2 MEASURING STATIC WATER LEVEL

The measurement and interpretation of hydraulic head data are important components of any groundwater monitoring project. A basic understanding of hydraulic head is necessary before interpreting such data. A water level measurement collected from a well represents hydraulic head. Hydraulic head is the sum of the fluid velocity, elevation head and pressure head in a well. Groundwater flow velocities in porous media are extremely low and therefore, groundwater flow velocities are commonly ignored when calculating hydraulic head. Therefore, hydraulic head is the sum of the elevation head (feet or meters) and pressure head (fluid pressure divided by fluid density times acceleration of gravity) as expressed by:

$$h = z + h_p$$

h = hydraulic head

z = elevation head

h_p = pressure head

Technical note: Technically, all hydraulic head measurements are obtained using piezometers. Classically, a piezometer is defined as a pipe open at the top and bottom that measures hydraulic head at a discrete point (i.e., the bottom open portion of the pipe) in groundwater. However, groundwater professionals in Wisconsin today typically refer to piezometers as only those wells that are sealed below the water table. This is technically incorrect as water table wells (i.e., monitoring wells screened to intercept the water table) are piezometers where the pressure head equals zero (atmospheric pressure). To avoid confusion, this document refers to piezometers as those wells sealed below the water table.

As long as the water table surface intersects a well's screen, water level measurements collected from such a well represent the water table surface elevation (i.e., elevation head only: pressure head = 0 and is therefore ignored). This type of well is referred to as a "water table well." If a well is sealed below the water table surface, water level measurements collected from such a well represent the potentiometric surface (i.e., elevation head + pressure head) as measured in the well (i.e., the center or average of the well screen and filter pack area). This type of well is referred to as a "piezometer." A piezometer must be sealed below the water table (i.e., the well screen, filter pack and fine sand sealed below the water table) if it is to measure both the elevation head and pressure head in the groundwater system. The term "monitoring well" is used to refer to both water table wells and piezometers.

Figure 2 illustrates the concepts of the water table surface and respective water table well, potentiometric surface and respective piezometer, unconfined and confined aquifers, a perched water

table and springs.

Dalton et al., (1991) provide a good discussion on collecting and interpreting hydraulic head data. Fetter (1988) and Freeze and Cherry (1979) provide detailed information regarding hydraulic head data and their relation to the aquifer system.

2.2.1 Technical Considerations

Important technical considerations for collecting accurate water level measurements include:

1. **Measure the static water level for a well before purging, sampling or inserting any instrument or device into a well.** If a well is purged, sampled, or a device is inserted into a well before measuring the static water level in the well, the measurement will not represent the static "undisturbed" water level or hydraulic head existing in the well.

2. **Collect measurements from all wells on the site as quickly as possible.** The best method is to collect measurements from all of the site's wells before doing any other tasks on the wells. This may be impractical and too time consuming for some sites. Typically, you take a water level measurement, sample the well, measure the next well's water level, sample that well, and so on. This method is acceptable if you collect all water level measurements at a site on the same day and the barometric pressure for that day does not change significantly (e.g., changing high or low pressure, advancing storm, etc.,). If the barometric pressure does change significantly during collection, a second round of measurements may be appropriate.

3. **Collect measurements in the order of least-to-most contaminated wells.** Furthermore, decontaminate the measuring device between each well to prevent cross-contamination. Do not let any parts of the instrument or tape touch the ground or any contaminated surface.

4. **Read measurements from the top of the casing or a reference elevation on the well.** This is usually a permanently and clearly-marked or notched spot located at the highest point on the top of the well casing. All top-of-casing or reference elevations must be surveyed to a common point of known elevation so that the water level measurements can be converted to groundwater level elevations, usually expressed as feet above mean sea level (MSL) or as USGS datum. Water level measurements must be accurate and precise to ±0.01 foot (± 0.25 cm.).

5. **Whenever possible, use one measuring device and one person operating it for all wells at a site during each sampling event.** Better yet, use the same measuring device and same person for all wells at a site over the life of a project. This will help ensure that water level data are accurate and comparable. If more than one measuring device is used, check both instruments against a calibrated standard, the same well, and against each other to ensure that they provide the same water level measurements. If necessary, use a correction factor to equalize the readings. Do this after checking each device to determine which tape length is correct.
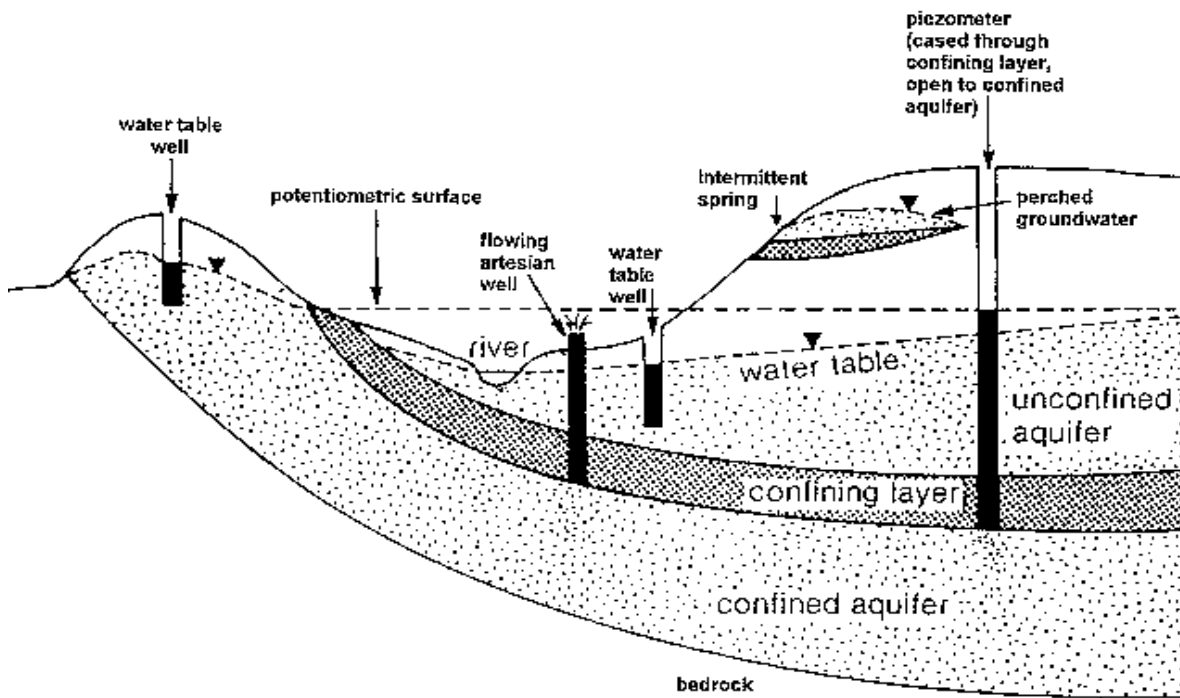
Modified from Brassington, 1990

6.   **After removing a water/air-tight well cap (e.g., flush mount piezometer), allow the pressure within the well to stabilize.** This is necessary because water/air-tight well caps do not allow the water level in the well to equalize with the ground surface atmospheric pressure as long as the well cap is in place. This is especially important for wells screened in silt and clay (low permeability) formations. Take several measurements spaced several minutes apart to confirm that the water level in the well has stabilized.

2.2.2 Equipment and Procedures

Equipment and procedures used for taking water level measurements vary substantially. Choose water level measuring devices based on their accuracy, precision, ease of use, reliability, durability, ease of decontamination and cost. Under most circumstances, WDNR requires that water level measurements be read to the nearest 0.01 foot (0.25 cm).

Water level measuring devices typically are either manual, non-recording devices or continuous measuring devices that provide a paper or electronic record of changing water levels over time. Although not exhaustive, the following discussion describes equipment and methods most frequently used by groundwater professionals. You can find specific procedures for collecting water level measurements with the first three devices in the *Groundwater Sampling Field Manual*, Section 2.2.

Table 2: Manual methods of water level measurements in groundwater monitoring wells (modified from Dalton et al., 1991).

Method	Accuracy (Feet)	Major Interference or Disadvantages
Electronic	0.01 to 0.1	Cable wear or kinks; hydrocarbons on water surface.
Popper	0.01 to 0.1	Well depth; well and ambient noise; operator skill; well pipes and pumps; tape clinging to well casing.
Indicator substance	0.01	Casing condensation; depth to water unknown; **indicator substance may affect the chemical characteristics of groundwater samples**.
Transducers	0.01 to 0.1	Temperature changes; electronic drift; blocked capillary.
Air-lines	≥0.25	Air line or fitting leaks; gauge inaccuracies; operator error **(not acceptable for monitoring well water level measurements)**.
Floats	0.02 to 0.5	Float or cable drag and stretch; float size and lag.
Ultrasonics	0.02 to 0.1	Well's temperature gradient; well pipes and pumps; well depth; casing joints.

2.2.3 Electronic Methods

These devices commonly operate by completing a circuit between two electrodes housed in a probe. When the electric probe contacts a water surface, a light, amperage gauge, or buzzer signals the operator that the probe has intersected a water surface. Most of these devices are manually-operated, non-recording devices. The operation of other electrical methods relies on such physical characteristics as resistance, capacitance or self-potential to produce a signal (Dalton et al., 1991).

Probably the most commonly-used electrical method is the electronic water level indicator. **Figure 3** illustrates the use of an electronic water level indicator. This device may be subject to measurement errors due to the probe contacting condensation on the inside wall of a well's casing or electrical problems with the device. Other potential sources of measurement errors include kinks in the cable, inaccurate gradation, or the banded measuring marks on the cable becoming loose and sliding. Check the measuring cable for proper length and gradation at least quarterly against a steel tape or some other accurate means of length calibration. Also, regularly check batteries and electrical connections. You may want to bring along another device (e.g., popper) as backup in case the electric method malfunctions.

If there is a substantial layer of floating hydrocarbons (i.e., immiscible layer) in a well, you <u>cannot</u> reliably make a water level measurement. Refer to Section 2.3 for precautions related to the effect an immiscible layer may have on water table elevation measurements.

Electronic water level indicators can provide fast and accurate water level measurements during baildown tests, slug tests and aquifer pumping tests. These devices are best suited for piezometers during these tests; cascading of water in a water table well's screen may provide false water level readings. When conducting baildown, slug or aquifer pumping tests on monitoring wells, transducers provide the simplest and most accurate water level measurements.

2.2.4 Poppers

A simple device known as a "popper" is a quick, inexpensive and commonly-used method for measuring the water level in a well. This device is also a manually-operated, non-recording method. **Figure 4** illustrates a common design for the popping device consisting of a metal cylinder 1 to 1.5 inches in diameter, 2 to 3 inches long and including a hollow bottom. The metal cylinder (i.e., popper) is attached to a non-stretching flexible tape or steel measuring tape.

To take water level measurements with this device, you lower the popper into the well until you hear a "pop" sound. This indicates that you've reached the water surface. By repeatedly raising and lowering the popper onto the water surface and listening for the "pop" sound, you determine the depth to water. Some practice is required to determine at what point the popper contacts the water surface. The precision and accuracy of this technique <u>highly depend</u> on the user's skill and the well's depth (more accurate for shallow wells). You may also use the popper for measuring well depth by lowering it through the water column until the tape slackens. Slowly pull the tape up until it just becomes taut again; this is the well depth.

REEL AND
INDICATOR GAUGE

WELL CASING

ELECTRICAL
CABLE

CONTACT
ELECTRODE

WATER LEVEL

1 INCH
APPROX.
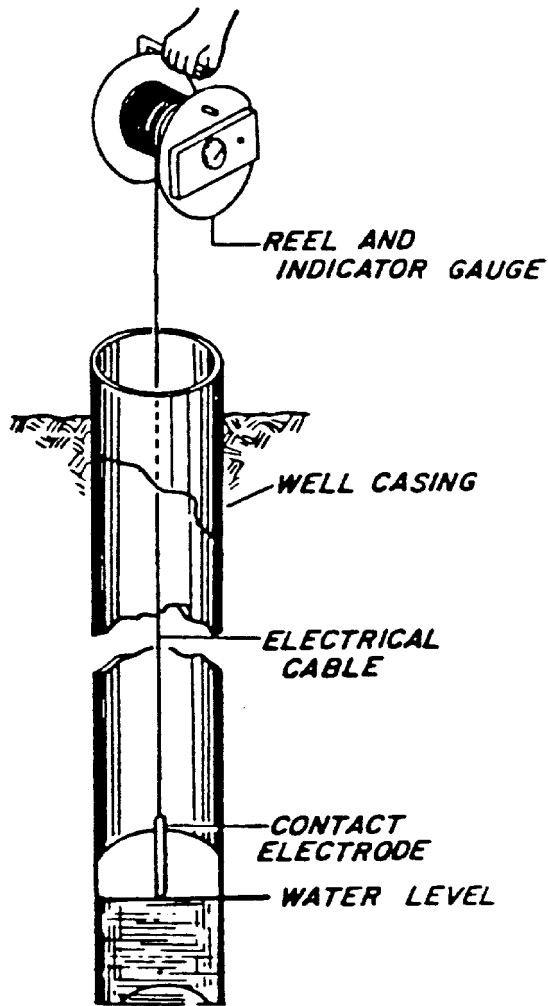
Figure 3: Electronic water level indicator
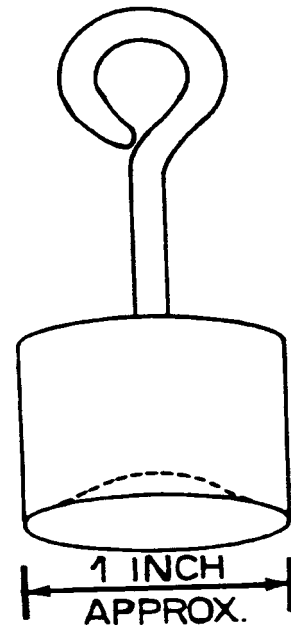
Figure 4: Common "popper" design

When a popper is connected to a tape, no length corrections should be necessary (i.e., depth to water measurements can be measured directly without adding or subtracting the length of the popper). Steel tape is recommended over flexible tape. Flexible tape can stretch and therefore should be calibrated quarterly against a known length standard. A high-quality steel tape or metallic monuments anchored in concrete are acceptable calibration methods.

Although simple and inexpensive, the popper method is prone to errors and measurement difficulties. If the water table intersects the well screen, if the well has a high gas content, or if the well is near a noisy area, the "pop" may be difficult to hear. Wet tape, especially wet flexible (non-steel) tape, may stick to the well casing making it difficult, if not impossible, to collect accurate measurements. Floating hydrocarbons in a well may also interfere with collecting accurate measurements. Be prepared with an alternate method for measuring water level when leaving for the field.

2.2.5 Indicator Substance

> **Important Note:** The indicator substance used to coat a measuring tape may contaminate the groundwater in a well and subsequent samples collected from that well. If an indicator substance is used, the user **must ensure** that the indicator substance will not contaminate the well or subsequent samples. If there is any doubt, choose another water level measurement method.

According to Dalton et al., (1991), and others, the coated tape (wetted tape) is one of the most accurate techniques for measuring water level. Equipment used for this technique commonly includes flexible or steel tape (recommended), carpenter's chalk or another indicator substance, and a slender metallic weight, typically a lead weight. Substances that change appearance are recommended over substances that wash away into the well. Steel tapes and hand reels are commercially available for lengths up to 1,000 feet (305 meters); however, shorter lengths are recommended due to their lighter weight and lower cost (Dalton et al., 1991). Check the length of the measuring tape, especially flexible tape, quarterly against an acceptable standard.

To collect a water level measurement using this method, coat the bottom 3 feet (1 meter) or so of the tape with the indicator substance and lower the tape slowly 1 or 2 feet (< 1 meter) into the water column. When the coated portion of the tape is lowered, the water either changes the appearance of the indicator substance or washes it away. The depth to water equals the tape reading at the top of the casing or reference elevation minus the wetted length of the tape. With a steel tape and sufficient operator skill, the precision and accuracy of this method is ±0.01 foot (± 0.25 cm).

Condensation on the well's casing wall may wet the tape as it is lowered, thus causing measurement errors. In addition, if the approximate depth to water is unknown, too little or too much of the tape may be lowered, thereby requiring a number of attempts.

2.2.6 Transducers

A transducer can act as a discrete or continuous measuring device. These devices lend themselves well to recording time vs. drawdown/recovery data typical of bail down, slug and aquifer pumping tests. They are also useful for determining long-term changes in water elevations when evaluating changing groundwater flow directions and fluctuating groundwater elevations.

Pressure transducers commonly consist of a silicon-based strain gauge pressure sensor with a 4-20 milliampere (mA) current transmitter. Other transducers on the market include the vibrating wire pluck (VWP) pressure transducer and the vibrating strip pluck (VSP) force transducer coupled with buoyancy cylinders (**Figure 5** - Dalton). The VSP force transducer is recommended over the VWP pressure transducer for obtaining precise measurements of water level changes.

Pressure transducers are available for pressures ranging from 5 to 500 pounds per square inch (psi), but typically transducers of 5 to 25 psi are used for monitoring groundwater levels. Transducers are rated in terms of their precision over their full psi range. A 0-5 psi transducer will provide measurements that are twice as precise as a 0-10 psi transducer of equal precision (Durham and Bumala, 1992). For example, a 0-5 psi transducer rated at 0.01 percent will provide measurements accurate to the nearest 0.01 foot while a 0-25 psi transducer rated at 0.01 percent will provide measurements to the nearest 0.05 foot (Dalton et al., 1991).

Pressure transducers commonly have a small capillary tube vented to the atmosphere that allows the transducer to automatically compensate for barometric (atmospheric) pressure. Pressure transducers measure the pressure head (water column) above the transducer. Pressure transducers are usually connected to a data logger that contains microprocessors to convert pressure information to feet or meters of water column above the transducer or depth to water from the top of the well casing. The data can easily be downloaded to a computer and subsequently used to calculate an aquifer's hydrogeologic properties.

The precision, accuracy, calibration, reliability and operating procedures for pressure transducers and their accompanying data controller units vary throughout the industry. Various transducer systems offered on the market should be carefully researched to ensure that the chosen system meets the data collection needs and required accuracy for a particular project.

2.2.7 Air-line or Bubble Tubes

Air-line and bubble tubes are commonly used on water supply wells where the well's static and pumping water levels must be frequently observed and recorded. While air-line and bubble tube measurements may provide acceptable water-level data for water supply wells, they do not provide water level data accurate enough for monitoring wells.

To collect water level measurements, you install a small-diameter (typ. <0.4 inches) hollow rigid tube of known length into the well. The tube may be made of copper, plastic or steel and must not have any bends or kinks. The air-line and fittings must be air tight and the tube end submerged several feet below the lowest expected water level. The pressure gauge and air or

Hanger

Hanger

Suspension
Cable

Support Tube
with Hanger
VWP
Data Collector
Inside

Well
Casing

VWP
Data
Collector

Well
Casing

Suspension
Cable

Signal
Cable

VWP
Force
Transducer

Signal
Cable

Buoyancy
Cylinder

VWP
Pressure
Transducer
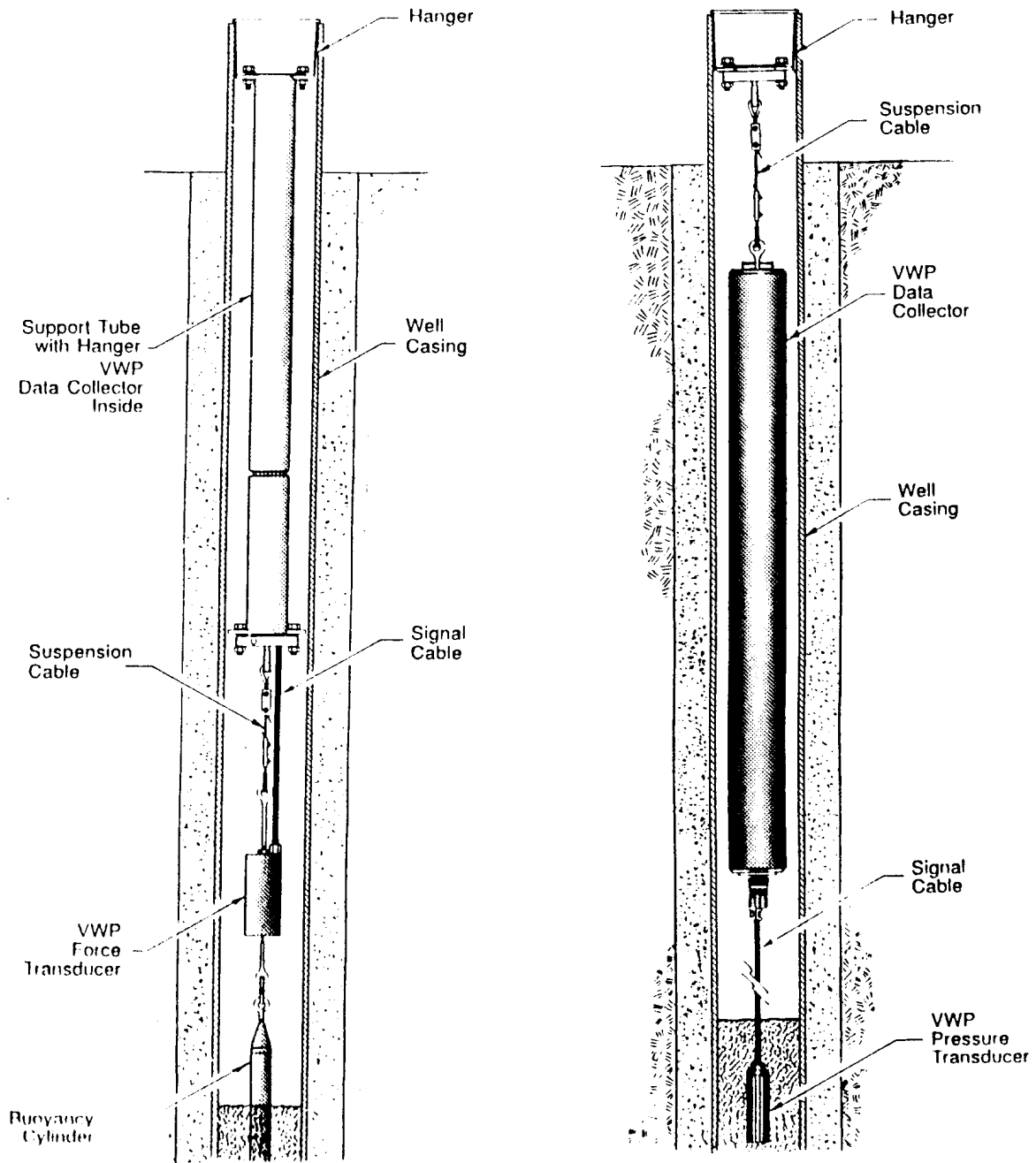
other gas source is attached to the air-line. Measurements taken on deep wells usually employ a small air compressor while measurements on shallow wells may use a hand pump.

After the tube is completely filled with air (when the air pressure measured by the gauge stops rising and stabilizes), it is ready to collect water level measurements. Air pressure changes measured by the

gauge are used to calculate water level changes in the well. A pressure gauge calibrated in feet of water is preferred to gauges calibrated in psi. For gauges calibrated in psi, convert these measurements to feet by multiplying psi by 2.31.

2.2.8 Float Method

For this method, you attach a float or buoyant cylinder to a length of steel tape or wire and suspend it via a pulley assembly into the water column. You attach a counter weight to the steel tape or wire opposite the float. Simple devices of this type employ a chart recorder, typically a marking pen and graph, which records water level changes for many months, if desired. These float-operated devices are subject to many errors including float lag, line shift, submergence of counter weight, temperature and humidity affecting measurements, and tape or wire stretch (Dalton et al., 1991). Typically, the smaller the float used, the greater the error potential. Most float devices were not designed to be used in small diameter wells (2-inches or less) and therefore are not often used in monitoring wells.

The buoyancy cylinder vibrating strip force transducer is also suited for measuring water-level changes in standard 2-inch monitoring wells. A vibrating strip force transducer system equipped with a 1.5-inch diameter buoyancy cylinder provides a precision of ±0.045 inches and can measure water level changes of 15 feet or less.

2.2.9 Ultrasonic Method

Ultrasonic devices measure the amount of time it takes for a sound wave to travel down a well casing, reflect off the water surface and return to the device. These devices use a microprocessor to transmit and receive multiple signals per second. This allows for rapid verification of readings. Models are available that can be placed on top of the well without ever lowering anything into it. This allows for rapid water level determination even in deep wells and reduces the potential of cross-contamination between wells.

Depending on the sophistication of the instrument, accuracy varies from ±0.02 to 0.1 foot. Well temperature gradients, joints, pumps, and other obstructions in a well can impede accuracy. An immiscible layer in a well may affect water level measurements. (Refer to Section 2.3.)

2.3   MEASURING AND SAMPLING IMMISCIBLE LAYERS

An immiscible layer may exist in a monitoring well either as a light non-aqueous phase liquid (LNAPL) or as a dense non-aqueous phase liquid (DNAPL). LNAPLs, also known as "floaters" or "floating free product," are relatively water-insoluble organic liquids (e.g., gasoline), are less dense than water (i.e., they have a specific gravity <1.0) and they typically spread on top of the capillary fringe and water table. **Figure 6** illustrates a LNAPL spill of diesel fuel and its distribution in an aquifer. Notice that the LNAPL tends to depress the capillary fringe and the water table.

DNAPLs, also known as "sinkers" or "sinking free product," are also relatively water- insoluble organic liquids (e.g., trichloroethylene), are more dense than water (i.e., the have a specific gravity >1.0) and typically migrate downward in an aquifer **Figure 7** illustrates a trichloroethylene (TCE)

DNAPL spill and its distribution in an aquifer. Notice that the mobile DNAPL in the bottom of the aquifer can actually travel in the opposite direction of groundwater flow if the right conditions exist. DNAPLs also tend to accumulate in low pockets on top of impervious layers existing in the aquifer.

2.3.1 Measuring Immiscible Layers

To measure the thickness of a LNAPL in a well, you typically use either a NAPL/water interface probe that distinguishes between water and NAPLs or a weighted tape coated with a water and non-water indicator substance. Interface probes are also available that can measure the thickness of DNAPLs.

Determining the difference between the LNAPL's "true" thickness in the aquifer and its "apparent" thickness in a water table well can be difficult **Figure 8** illustrates how different they can be. The apparent thickness is actually a sum of the LNAPL thickness in the capillary fringe, the true product thickness and the thickness of the LNAPL that is depressing the water table. Because of the difficulty in measuring the true product thickness, most investigators do not focus on it (Domenico and Schwartz, 1990). Investigators use apparent product thickness in a well as a relative measurement.

2.3.2 Sampling Immiscible Layers

If you are collecting a LNAPL or a DNAPL sample from a well, do it before purging the well. Because a LNAPL or DNAPL usually exist in a well at a minimal thickness, a bailer is commonly used rather than a pump for collecting an immiscible layer sample.

Refer to Section 2.3 of the *Groundwater Sampling Field Manual, PUBL-DG-038 96,* for specific procedures for measuring and sampling immiscible layers in water table wells and piezometers.

2.4 PURGING AND SAMPLING DEVICES

2.4.1 Technical Considerations

Table 3 provides operational and performance characteristics for a variety of commonly-used purging and sampling devices. This table can assist you with choosing appropriate purging and sampling equipment for a specific project. However, be cautioned that the operation and performance of a particular model of a device may vary from what is listed in this table. Reference the manufacturer's equipment and materials specifications and published literature on the performance of a specific model when evaluating its use, operation and performance.

Hydrocarbon
spill

Diesel
fuel

Residual hydrocarbon
hold up in soil

Mobile hydrocarbon

Water table

Vadose zone

Capillary fringe

Hydrocarbon
dissolved in groundwater

Saturated zone

Groundwater flow ———▶

Chlorinated hydrocarbon spill

TCE

Vadose zone

Water table

Saturated zone

Ground-water flow

Residual DNAPL

DNAPL dissolved in
the ground water

Flow of mobile DNAPL

Mobile DNAPL

Confining Layer

TABLE 3: Generalized Characteristics of Common Purging and Sampling Devices

	Device	Maximum Sample Depth	Minimum Well Diameter	Range of Flow Rate or Volume	Ability to Control Flow Rate	Sensitive Sample Alteration	Eas Transp Se
P O S I T I V E D I S P L A C E M E N T	**Centrifugal submersible pump (low-flow)**	~ 90 meters ~ 300 feet	4.45 cm. 1.75 in.	0.1- 30 L/min 0.03 - 8 gpm	Good if flow controller used	Low	Requir generat set
	Bladder pump (low-flow)	305 meters 1000 feet	3.8 cm. 1.5 in.	0 - 11 L/min 0 - 3 gpm	Good if flow controller used	Low	Bul transp set

Device	Maximum Sample Depth	Minimum Well Diameter	Range of Flow Rate or Volume	Ability to Control Flow Rate	Sensitive Sample Alteration	Eas... Transp... Se...
Progressive cavity (helical-rotor) pump (low-flow)	50 meters 160 feet	5 cm. 2 in.	0.1 - 6 L/min 0.03 - 1.5 gpm	Good with rheostat	Low to moderate	Bulky... set
Gear-drive pump (low-flow)	60 meters 200 feet	5 cm. 2 in.	0 - 6 L/min 0 - 1.5 gpm	No	Probably low to moderate	E...
Piston pump (gas-drive)	275 meters 900 feet	3.8 cm. 1.5 in.	0 - 6 L/min 0 - 1.5 gpm	Highly variable	Variable	Eas... diff...
Gas-displacement or air-displacement pump	90 meters 300 feet	2.5 cm. 1 in.	0.5-38 L/min 0.1-10 gpm	Variable	Moderate to high	Mod...
Piston pump (manual)	Variable	2.5 cm. 1 in.	Variable	Variable	Moderate to high	Eas... diff...

TABLE 3 (continued)

Device		Maximum Sample Depth	Minimum Well Diameter	Range of Flow Rate or Volume	Ability to Control Flow Rate	Sensitive Sample Alteration	Eas... Transp... Se...
G R A B	**Open bailer**	No limit	1.3 cm. 0.5 in.	Variable but typ. < 8 L/min typ. < 2 gpm	Use bottom emptying device	Low to high	V... ea...
	Point-source		1.3 cm.	Variable but typ. < 8 L/min	Use bottom emptying	Low to	V...

	bailer	No limit	0.5 in.	typ. < 2 gpm	device	high	ea
	Syringe sampler	No limit	3.8 cm. 1.5 in.	0.04-0.8 L/min 0.01-0.2 gpm	Variable	Moderate to high	Mod
S U C TI O N	**Peristaltic pump**	8 meters 25 feet	1.3 cm. 0.5 in.	0.04-30 L/min 0.01 - 8 gpm	Good	Variable	E:
	Surface centrifugal pump	8 meters 25 feet	2.5 cm. 1 in.	4 - 95 L/min 1 - 25 gpm	Highly variable	Very high	Mod
O T H E R S	**Inertial lift pump**	60 meters 200 feet	2.5 cm. 1 in.	0 - 8 L/min 0 - 2 gpm	Variable	Moderate	Mod
	Gas-lift or air lift pump	Variable	2.5 cm. 1 in.	Variable	Variable	Very high	Mod

Sources: Parker (1994), Pohlmann and Hess (1988), U.S. Environmental Protection Agency (1993), U.S. Environmental
            et al. (1991).

Operation, Service, Reliability and Durability

Easy operation and servicing, plus the reliability and durability of a piece of equipment are important considerations for choosing purging and sampling equipment. The equipment should be easy to operate, decontaminate and service in the field. The more mechanically simple the device and its accessories, the less chance it will malfunction and the easier it will be to operate and service in the field. If a well is located in a remote area not accessible by a vehicle, the equipment's portability can be very important.

Proper training on equipment operation, maintenance and service is essential to ensure top quality samples. If the equipment is not operated and maintained properly, sample quality will suffer.

Time and Cost

Consider the time it takes to operate, decontaminate and transport a piece of equipment during selection. Initial capital cost, and operation and maintenance costs are also important considerations; however, *do not compromise data quality to save time and cost* Choose equipment that meets data quality objectives and will not change the physical and chemical composition of your samples. Selecting equipment based on cost and time savings alone can be far more expensive in the long run if the equipment yields false positive or false negative analytical results; malfunctions often; is difficult to use and service; provides data that does not meet regulatory and data quality objectives; or provides data that does not stand up to legal scrutiny.

Dedicated purging and sampling equipment - case studies

Meyer (1990) and Parker et al., (1992), have shown that using dedicated groundwater sampling equipment (devices "permanently" left in a well) may save time and money over using non-dedicated systems. In addition, dedicated equipment consistently collects high-quality samples. Both studies indicated that, although there was a high initial capital cost in purchasing the dedicated equipment, the systems paid for themselves in about three years.

Meyer (1990) conducted a three-year study comparing the technical and economic benefits of using dedicated and non-dedicated systems at the Weldon Spring Site – a 12-year, $400 million remedial action project in east central Missouri. Meyer's study used 33 dedicated bladder pumps in 33 of the 100 monitoring wells installed at the site. Sampling with the dedicated bladder pumps equated to a labor cost savings of $160 per well per year (based on $40/hr. labor) compared to the non-dedicated sampling systems. The dedicated bladder pumps provided an additional cost savings because decontamination quality assurance samples (i.e., field blanks) were not required. This garnered a savings of approximately $60 per well per year. Additional "hidden" economic benefits included fewer days spent in the field, less money spent on per diem expenses and, because less time was spent in the field, more time was available to work on other projects.

Parker et al., (1992) conducted a study comparing the technical and economic benefits of using dedicated low-flow submersible pumps and disposable bailers at the Union Pacific

Railroad Yard superfund site in Sacramento, California. Parker's study evaluated the use of disposable bailers vs. dedicated Grundfos Redi-Flo2® submersible pumps installed in nine monitoring wells. Ninety samples were collected from the nine wells using the dedicated pumps and disposable bailers. Samples were collected quarterly from each well and analyzed for VOCs. Comparison of labor costs for sampling indicated an approximate cost savings of $100 per well per sampling event using the dedicated pumps vs. the disposable bailers. Annual labor cost savings were projected to be $12,000 if dedicated pumps are installed in all of the site's 42 monitoring wells. Costs of the dedicated pumps were projected to be recovered in approximately three years due to labor cost savings.

Cost savings for both studies were realized due to reduced time for equipment setup, sampling and removal; virtual elimination of decontamination procedures; and a reduction in the number of quality assurance samples required. Equipment replacement or repair costs due to continued insertion and removal and decontamination associated with non-dedicated equipment were eliminated. The quality of data collected with dedicated pumps was very high because the wells were purged at consistent depths and flow rates and the potential for cross-contamination between wells was greatly reduced. Quality assurance audits for Meyer's study went smoothly using dedicated equipment and its use helped eliminate numerous uncertainties regarding sample quality typical of non-dedicated equipment.

Materials

The materials that purging and sampling equipment are made of can adversely affect sample quality. The choice of equipment materials should be based on: 1) the chemistry of the groundwater in the well (e.g., low pH, high dissolved oxygen, hydrogen sulfide, dissolved solids, high carbon dioxide and high chloride); 2) the type, form (i.e., dissolved or free product) and concentration of contaminants in the well; 3) whether the equipment's materials may leach or sorb contaminants; and 4) whether the equipment's material may degrade or otherwise change the chemical composition of samples by physical, chemical and biological processes.

Parker (1992) provides an excellent discussion and literature review of several commonly available materials and their resistance to chemical attack, sorption of metals and organics and leaching of metals. Parker (1992) focuses on Teflon®, PVC and stainless steel used in samplers and well casing materials.

Common materials used in purging and sampling equipment include (from most inert to least): polytetrafluorethylene (PTFE), commonly available as Teflon®; rigid polyvinyl chloride (Type I PVC); flexible polyvinyl chloride (Type II PVC); stainless steel (#304 and #316); Viton®; polyethylene; polypropylene; acrylonitrile butadiene styrene (ABS); low-carbon steel; galvanized steel; carbon steel; and silicone rubbers. Teflon®, rigid PVC and stainless steel are the most commonly used and the most inert materials. Table 4A and 4B lists the relative inertness (i.e., ability to adsorb or leach contaminants and resistance to chemical reaction and degradation) of several rigid and flexible materials. Tables 4A and 4B are arranged so the most inert material is listed first and the least inert material is listed last.

Table 4A: Relative Inertness of Rigid Materials
        (After Nielsen & Yeates, 1985 and Parker, 1992)

        Teflon® (polytetrafluoroethylene, PTFE)
        Stainless steel 316
        Stainless steel 304
        Polyvinylchloride (PVC)
        Low-carbon steel
        Galvanized steel
        Carbon steel
        Brass

Table 4B: Relative Inertness of Flexible Materials
        (After Nielsen and Yeates, 1985)

        Teflon® (polytetrafluoroethylene, PTFE)
        Polypropylene
        Flexible PVC/Linear polyethylene
        Viton®
        Conventional polyethylene
        Tygon®
        Silicone/Neoprene

Sample tubing - case study

Barcelona et al., (1985), conducted laboratory sorption experiments for five flexible tubing materials (Teflon®, polyethylene, polypropylene, polyvinylchloride (PVC) and silicone rubber) to determine sorption bias of chloroform, trichloroethylene, trichloroethane and tetrachloroethylene. Results of the experiments showed that all five materials sorbed the test compounds under short exposure periods; however, Teflon® showed the least adsorption and leaching problems followed by polypropylene, polyethylene, PVC and silicone rubber, which exhibited the worst adsorption and leaching problems.

2.4.2 Grab Samplers

Grab samplers collect a sample at a discrete depth in a well without the sample being pumped or being lifted to the surface by a gas or by air. Typical grab samplers include bailers, syringe samplers and thief samplers. You lower these devices into a well by rope, cable or tubing to collect a sample at a discrete depth. You can use bailers for both purging and sampling a well. Most other grab samplers are designed for sampling only.

Bailers

Two common styles of bailers include the single check valve or "standard" bailer and the dual or double check valve bailer, also known as the point-source bailer. Point-source bailers may reduce mixing of the sample with the water column as the bailer is removed from the well.

Some researchers have shown bailers capable of collecting high quality samples (e.g., Baerg et al., 1992; Imbrigiotta et al., 1988); however, researchers have cautioned that the quality of samples collected with bailers (and disturbance of fines around the well during purging) *highly depend* on the skill, care and consistency of the operator using the bailers. Some researchers believe that bailers are inappropriate for collecting substances such as VOCs and redox-sensitive trace metals (Houghton and Berger 1984; Yeskis et al., 1988; Stolzenburg and Nichols 1985) because bailers can change sample chemistry, cause contaminant loss and increase sample turbidity. Imbigiotta et al. (1988), Muska, et al. (1986), Yeskis (1988) and other researchers have found that bailers tend to have the greatest variability in VOC results (low precision) compared to other common sampling devices (e.g., bladder pump, submersible pump, peristaltic pump, etc.,).

Bailers are effective for collecting stable substances not affected by sample aeration or changes in a sample's redox state (e.g., chloride).

WDNR conducted a study between 1994 and 1995 to evaluate differences in VOC analytical results attributable to samples collected with a Teflon® bailer equipped with a bottom-emptying device and samples collected with a portable (non-dedicated) Keck® helical-rotor pump operated at low-flow pumping rates (< 500 ml/min). Nine monitoring wells that had a history of VOC contamination were sampled at three landfills. Only small differences in VOC analytical results were found between samples collected with the bailer and samples collected with the low-flow pump. The small differences in VOC analytical results could not be attributed to the use of the equipment or the purging and sampling procedures. Great care was taken to slowly and gently lower and raise the bailer in and out of the water column. A pulley was used to lift the bailer straight up and out of the well and a bottom-emptying device was used to decant samples to their respective VOC vials.

The study recommended: 1) using a bailer equipped with a bottom-emptying device or a low-flow pump for collecting VOC samples from monitoring wells; 2) using a bailer at sites where wells are not easily accessed; 3) using a bailer for sampling on days below 20°F; and 4) using a dedicated system if a low-flow pump is used to collect samples. On average, it took four times longer to collect samples with the portable low-flow pump than with the portable bailer: The portable low-flow pump is heavier and bulkier; includes more equipment and accessories (e.g., power source, pump and sample tubing, flow-through cell, etc.), and takes longer to set up, decontaminate and dismantle.

Design and Materials

Figure 9 illustrates a variety of bailers and bottom-emptying devices. Bailers come in a wide variety of styles, lengths, diameters and materials. They are typically 3 to 7 feet (1 to 2 meters) but may be constructed to almost any length. Common materials used in constructing bailers include high grade stainless steel, rigid PVC and various fluorocarbon materials such as Teflon®. Bailers should be made of relatively inert materials that will not sorb contaminants onto the bailer or leach contaminants out. The same holds true for choosing bailer rope or cable. Polypropylene or nylon rope, stainless steel cable, or Teflon®-coated wire are good choices under most conditions. If you use cotton or other sorptive rope or cable, discard it after a single use or cut off and dispose of those portions that touched any contamination.
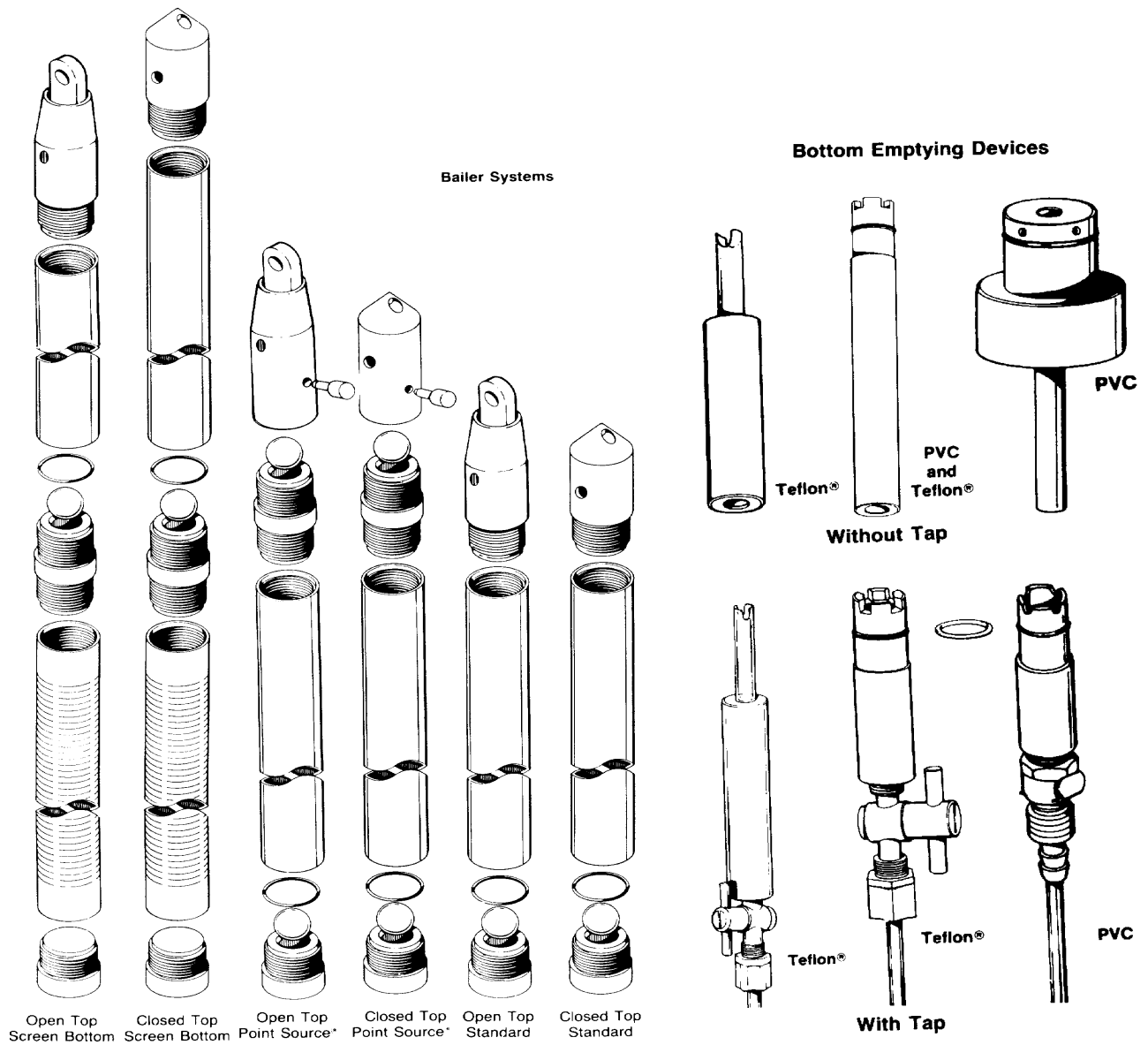
Figure 9: Bailer system and botem emptying devices. (Diagrams courtesy of TIMCO^{TM})

Operation

A bailer is essentially a hollow rigid tube that fills from the bottom up as you lower it into the water column. You attach a bailer to a line or cable and slowly lower it into the water column. Slowly lowering and raising the bailer is essential to minimize sample turbulence, agitation, degassing, aeration and turbidity. *NEVER* let a bailer free-fall into the water and *NEVER* rapidly raise the bailer out of the water column! These activities severely agitate the samples collected from the well. In addition, these activities may over-develop the well or damage the well's filter pack.

After slowly raising the bailer out of the water column, lift it straight up and avoid banging it against the casing wall. To accomplish this, you can place a tripod and pulley over the well or use vertical hand-over-hand lifting. The bailer lifting method known as "helicoptering," or grabbing the rope with alternating horizontal hands, causes the bailer to bounce from side to side within the well casing. This can cause sample agitation, the gain or loss of dissolved gasses in the sample, and loss of VOCs by volatilization.

To avoid sample aeration, use a bottom emptying device when decanting samples from a bailer. Pouring the sample from the top of a bailer is unacceptable under most circumstances due to excessive sample agitation and aeration.

Advantages of bailers

- Can be constructed of almost any material.
- Relatively inexpensive to purchase or construct.
- Simple to operate and durable with few parts to break.
- No depth or well diameter limitations.
- Light, portable and easy to disassemble and decontaminate in the field.
- Requires no power source or controller box.
- Ideal for collecting samples on days when the temperature is below freezing.

Limitations of bailers

- May lose VOCs or alter redox-sensitive samples.
- May artificially mobilize colloids and particulates near the well screen during its operation.
- Sample quality **highly** depends on the skill and care of the bailer's operator.
- Time consuming and labor intensive, especially for deep wells and wells requiring purging of many well volumes.
- Check valve ball may leak when collecting silt- or sand-laden samples.
- Direct, in-line filtration is possible but may be time consuming.
- Heavy use of a bailer may cause the bailer's surface materials to become rough and scratched, which makes it difficult to properly decontaminate the bailer.

Syringe Samplers

You can use these devices at any depth and thus sample at discrete depths. Syringe samplers cannot be used to purge a well. Samples collected with a syringe device do not contact atmospheric gases, are subject to very slight negative pressure and therefore, neither aeration nor degassing of samples should

occur (Herzog et al., 1991). However, Imbrigiotta et al., (1988) found that the syringe sampler had poor recovery of VOCs in comparison to six other sampling devices.

Design and Materials

A variety of designs for syringe samplers are available on the market. Most work with a moveable plunger, piston, or float mechanism operated mechanically, pneumatically or by hydrostatic pressure. Common materials used in the construction of syringe samplers include flexible tubing, stainless steel ballasts and tubes and PVC or polyethylene syringe chambers. As with any other sampling device, make sure that the design, operation and material of the device do not adversely affect the samples being collected.

Operation

Syringe samplers function much like a medical syringe. After you lower the device into a well's water column, a plunger or piston is pulled up either mechanically or pneumatically, thus allowing water to enter the lower sample chamber. After the piston rises to the top and the sample chamber is full of water, pull the device to the surface and decant it into sample containers.

Modifications to the syringe sampler allow it to become a simple syringe pump (**Figure 10**). It is, therefore, no longer a grab sampler. Alternating vacuum and pressure drive the piston or plunger up and down. The intake port may be faced upward to ensure that any gas in the sample chamber is released before sample collection. A pair of check valves, one below the sample intake and one on the sample line, allows the sample to be drawn in under vacuum and then flow to the surface through a separate line after pressure is applied to the piston. The main advantage of the syringe pump over the syringe sampler is that the pump allows you to collect unlimited sample volume without pulling the device from the well.

Advantages of syringe samplers

- Can be made of a wide variety of readily available materials.
- Relatively inexpensive to purchase or construct.
- Usually simple to operate and requires little operator training.
- Most have no depth limitations.
- Effective at collecting depth-discrete samples.
- Light and portable and usually easy to decontaminate in the field.
- Typically requires no power source (some syringe pumps may require an air compressor or electrical power source).

Limitations of syringe samplers

- Plungers may be prone to bind and leak, especially when collecting silt-laden samples.
- Operation may be difficult if the device is lowered into a deep well.

SAMPLE LINE TO SURFACE
SAMPLE INTAKE
CHECK VALVE

PRESSURE/VACUUM LINE

CLAMPS

PLUNGER

STOPPER

WEIGHTED COLLAR
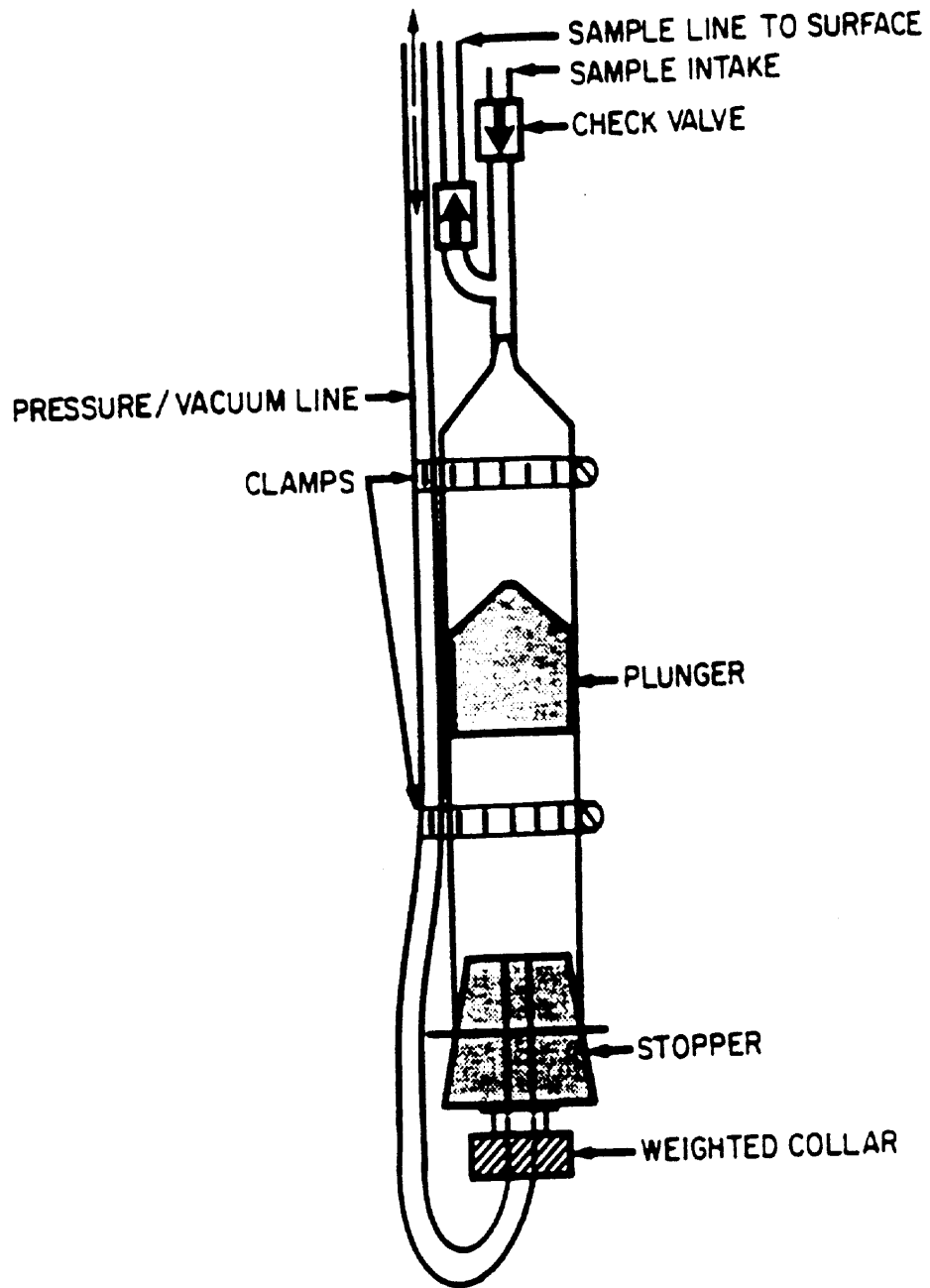
- Plungers are typically made of non-inert materials (rubber) unsuitable for VOCs and other sorptive contaminants.
- Sample transfer can be difficult.
- Degassing can occur while samples are being decanted.
- Syringe chambers usually have limited sample volume.
- Not widely available through commercial markets.

Other Grab Samplers

Other, less common grab samplers include the pressurized bailer, the Chismar® (surface bomb/pressurized bailer) samplers, the Westbay® sampler and the VOA trap sampler.

Thief samplers such as Kemmerer®, Van Dorn® and alpha bottle samplers are also grab samplers but are not commonly used or appropriate for groundwater sampling, although they are widely used for discrete-depth surface water sampling.

2.4.3 Suction-lift Pumps

Suction-lift pumps, especially surface centrifugal pumps, are considered unacceptable for collecting VOCs, dissolved metals, pH, Eh and other gas-sensitive or volatilizing substances or measurements. The vacuum applied on the sample during collection may cause degassing. Suction-lift pumps are considered acceptable for collecting major and minor ions that are not gas-sensitive (refer to Section 2.6.7). Peristaltic and surface centrifugal pumps are two common types of suction lift pumps. Of these two suction-lift pumps, the peristaltic pump is far less likely to adversely affect samples compared to surface centrifugal pumps.

As suction-lift implies, these pumps work by creating a vacuum or suction (in the sampling tube) that pulls groundwater to the surface. In theory, suction-lift pumps should be able to lift water up to 32 feet (9.7 meters); however, in practice, anywhere from 15 to 25 feet (4.6 to 7.6 meters) is the upper limit of their effectiveness. Pumping rates for suction-lift pumps typically range from 0.03 to 15 gallons per minute (gpm) or 0.1 to 57 liters per minute (L/min). Peristaltic pumps commonly have the lower pumping range (0 to 8 gpm or 0 to 30 L/min) while surface centrifugal pumps have pumping rates as high as 40 gpm (150 L/min).

Peristaltic Pumps

Barker and Dickhout (1988) conducted laboratory research to evaluate the loss of volatile organic analytes from groundwater charged with dissolved gasses such as methane and carbon dioxide. A positive displacement bladder pump (Well Wizard®, QED, Inc.), inertial-lift pump (WaTerra® pump) and peristaltic pump were employed in sampling methane-charged groundwater from a monitoring well for volatile aromatic hydrocarbons and CO_2-charged water reservoir (i.e., an artificial laboratory well) spiked with known concentrations of volatile chlorinated hydrocarbons. In both the field and laboratory cases, the peristaltic pump provided samples with a significant negative bias (9 to 33 percent lower) relative to the bladder pump and inertial-lift pump methods.

Baerg et al., (1992) conducted laboratory research to evaluate the loss of volatile organic compounds (VOCs) caused by the sampling method used. Several devices (peristaltic pump, stainless and

Teflon® bailers, VOA trap sampler, bladder pump, inertial-lift pump and double valve sampler) were used to collect samples for VOCs from a laboratory monitoring well. VOC analytical results for the peristaltic pump were 7 percent to 12 percent lower than the control VOC concentrations. The inertial-lift pump performed the worst with VOC results up to 34 percent less than the control.

Imbrigotta et al., (1988) conducted a field evaluation of seven sampling devices for purgeable organic compounds (POCs) in groundwater. One of the devices tested was a peristaltic pump outfitted with Teflon® tubing and a glass Erlenmeyer receiving flask for sample collection. It was pumped at 600 ml/min (0.6 L/min) or less. Of the seven devices tested, the peristaltic pump consistently recovered lower POC concentrations than the other devices and had the lowest precision of the four pumps tested (gear submersible, bladder, helical-rotor and peristaltic pumps); however, it had a greater precision than all three grab samplers tested (syringe, open bailer and point-source bailer).

Tai et al., (1988) found good recoveries of VOCs under lab conditions using a peristaltic pump outfitted with Teflon® tubing and used under low lift conditions – 5 feet in this case.

In general, the lower the lift, the lower the pumping rate, and using non-sorptive tubing such as Teflon® will minimize the effects a peristaltic pump may have on a sample.

Operation and Materials

Peristaltic pumps are very easy to use. The sample tubing is usually 1/4 inches in diameter and open at both ends. Some kinds of flexible tubing (e.g., silicone and Tygon®) can leach plasticizers and sorb organic compounds that may adversely affect sample quality.

Place the suction end of the tube into the well to the desired depth. Place the discharge end in the sample container. You can attach a transfer vessel, a filtering device chamber or an in-line filter directly to the pump's discharge tubing. This is the recommend filtering method. Rotating two or more rollers along the sample tubing causes a vacuum on the tubing, thus lifting the water out of the well. Decontamination usually consists of running a detergent or disinfectant through the sampling tube, followed by appropriate decontamination rinses.

Advantages of peristaltic pumps

- Allows for easy, direct in-line filtration of samples.
- Portable, easy to use and little operator training is required.
- Readily available and relatively inexpensive.
- Variable flow rates are possible.
- Sample does not contact pump parts.
- Durable and reliable.
- Can be used in wells of any diameter.

Limitations of peristaltic pumps

- Requires a power source.
- Vacuum may cause volatilization and degassing in gas-sensitive ᴅ volatile samples.

- Lift restriction of 25 feet (8 meters) or less.
- Flexible sample tubing (e.g., silicone and tygon) may leach placticizers and adsorb or desorb organic compounds.
- Field repair may be difficult.

Surface Centrifugal Pumps

Surface centrifugal pumps are commonly used for well development. High pumping rates, sample alteration and sample contact with pump parts makes these devices unacceptable for most well monitoring and sampling applications. Do not use these pumps for collecting groundwater samples from monitoring wells.

Advantages of surface centrifugal pumps

- Can purge large volumes of water quickly.
- Easy to use and operate.
- Readily available.

Limitations of surface centrifugal pumps

- Difficult to adequately decontaminate.
- Generally unacceptable for collecting groundwater samples.
- Pump parts come into contact with sample.
- Lift restrictions limit effective purging and sampling depth to 20 feet (6 meters).
- Require a power source, usually an electric outlet or portable generator.
- High pumping rates may over-develop a well.
- May require priming before pumping.

Other Suction-lift Pumps

Other common suction-lift pumps include manual diaphragm-type pumps, pitcher pumps and eductor or jet pumps. These pumps are not typically used and are inappropriate for sampling monitoring wells. **Figure 11** illustrates these three pump types.

Manual Diaphragm and Pitcher Pumps

The manual diaphragm ("guzzler") pump consists of a lever-powered flexible diaphragm between 2 check valves. They are commonly self-priming to 20 feet (6 meters) and capable of moving considerable volumes of water. However, they are not acceptable for either purging or sampling monitoring wells. These pumps are difficult to decontaminate properly.

The pitcher pump is used for shallow water supply wells. Pitcher pumps apply a suction to a well's casing by a lever-operated piston and barrel mechanism. Pitcher pumps should not be used to collect groundwater samples; however, if you are interested in what contaminants a consumer of pitcher pump water may be exposed to, then you may collect groundwater samples from this type of pump. The pump's flow rate should be kept as low as possible during sampling.
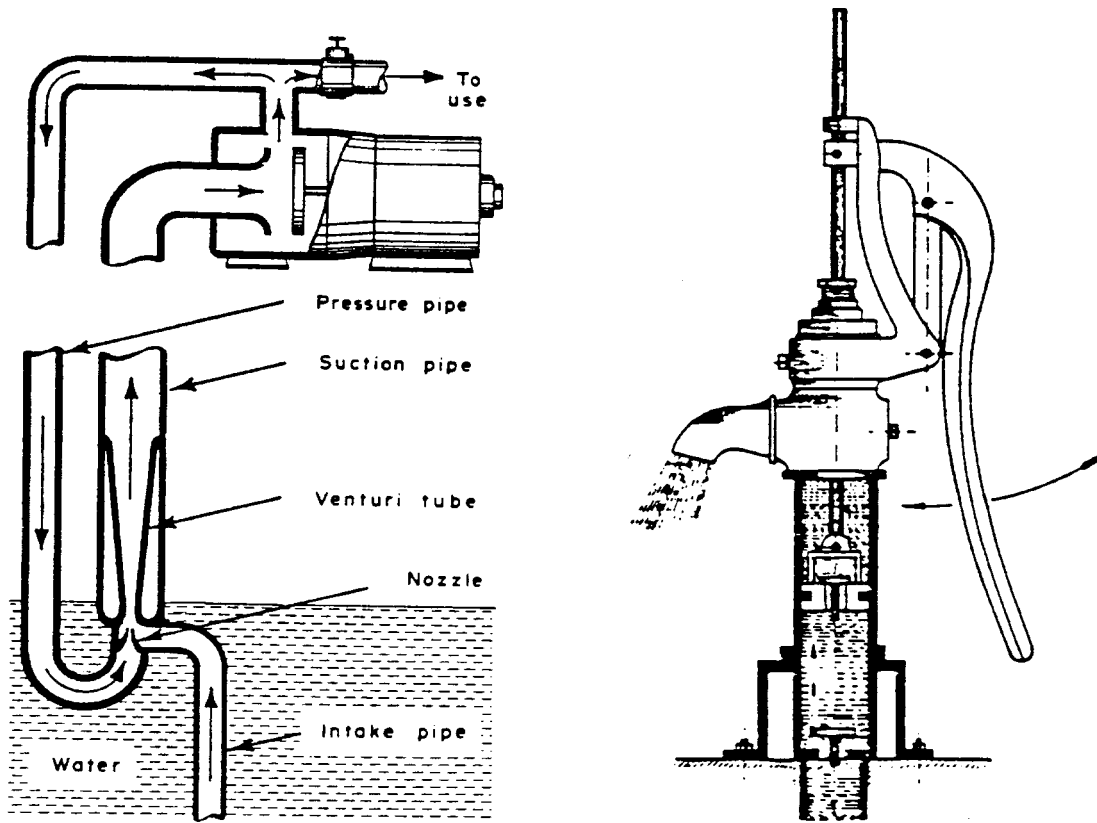
Figure 11: Suction-lift punps: a) jet pump, upper left; b) pitcher pump, upper right; and c) manual diaphragm pump, bottom.
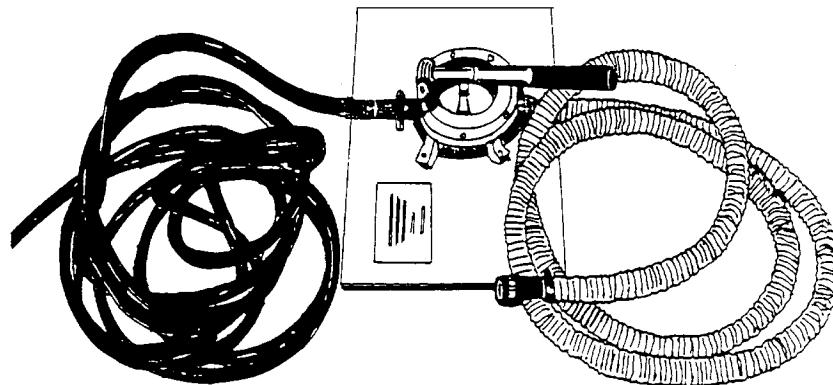
Jet or Eductor Pumps

A jet or eductor (venturi) pump is commonly used for water supply wells; however, this pump is only suitable for developing and purging monitoring wells. The operation of a jet or eductor pump causes a large pressure drop in the water passing through these pumps. Therefore, they should not be used for collecting gas-sensitive or VOC samples. These pumps are usually very bulky and require priming before they will operate.

2.4.4 Centrifugal Submersible Pumps

In the past, centrifugal submersible pumps, or impeller-driven pumps, were primarily designed for use in water supply wells. Recently, manufacturers have offered several models that work well for both the purging and sampling of 2-inch diameter monitoring wells. Centrifugal submersible pumps are categorized as a positive displacement device.

Design and Materials

A centrifugal submersible pump consists of impellers or vanes that are spun or rotated by a sealed electric motor. Pumps designed for 2-inch monitoring wells are usually cooled and lubricated with water rather than with hydrocarbon-based coolants and lubricants that could contaminate groundwater samples.

These pumps can be fabricated of stainless steel, PTFE (Teflon®), Viton® and other non-sorptive materials appropriate for collecting VOCs and other sensitive parameters. Pumps are now available that can achieve variable flow rates and flow rates as low as 100 ml/minute (0.1 L/min or 0.03 gpm). Several commercially available pumps capable of achieving low-flow rates are available for 2-inch monitoring wells.

Operation

Centrifugal submersible pumps operate by spinning or rotating an impeller or series of impellers that cause water to be accelerated outward and then upward into the pump's discharge line. **Figure 12** illustrates the movement of the impellers and water in this type of pump. The higher the pumping rate, the greater the potential for sample alteration by sample agitation, increased turbulence and pressure changes in the sample. Consider using a variable-speed pump when purging and sampling monitoring wells.

A centrifugal submersible pump is usually suspended in a monitoring well by its water discharge line, a support cable, or both. These pumps can be dedicated to above ground or flush mount wells (see Figure 12), thus eliminating the need to transport, set-up and decontaminate the pump. Dedicated pump systems also eliminate the need to collect quality assurance field blank samples.

Low-flow centrifugal submersible pumps appear to perform similarly to low-flow bladder pumps in preserving sample integrity during the well purging and sampling process.
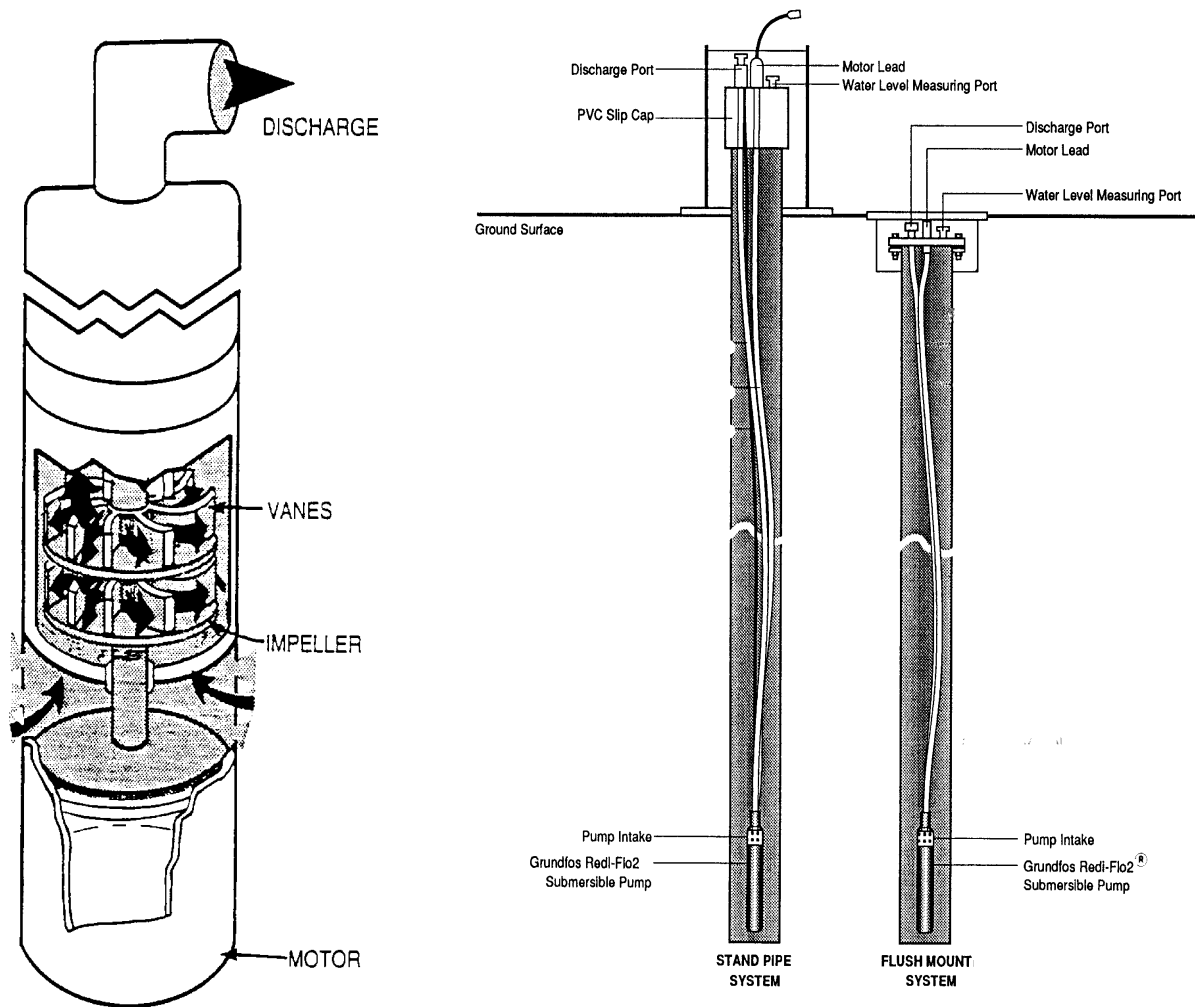
Figure 12: Centrifugal submersible pump: a) functional diagram, left (Courtesy of Grundfos Pumps Corp.); b) stand pipe and flush mount systems, right (Parker et al, 1992).

Advantages of centrifugal submersible pumps

■   When low-flow pumping rates are used, these pumps consistently collect high quality samples.
■   Motor is sealed from impellers thus protecting against contaminating the samples.
■   Capable of variable flow rate (typ. 0.1 - 30 L/min or 0.03 - 8 gpm).
■   May collect low turbidity samples (< 5 NTUs) when low pumping rates used.
■   Moderate to high lift capability, approximately 300 feet (90 meters).
■   Initial high capital cost may be recovered if dedicated pumps are used.
■   Priming is not necessary.
■   Models are available that are constructed of relatively inert materials.
■   Allows for easy, direct in-line filtration of samples.

Limitations of centrifugal submersible pumps

■   Models not capable of low-flow rates are not suited for collecting gas-sensitive and VOC samples.
■   Requires external power source - portable systems usually require a heavy generator typically powered by gasoline (potential extraneous contaminant source).
■   Some variable speed models must be started at high flow rates initially.
■   Purging and sampling from deep wells may be slow.
■   Relatively time consuming to disassemble and decontaminate.
■   Portable but may be bulky, heavy and difficult to transport over long distances and over rugged terrain.
■   Portable systems may freeze up in winterduring sampling and decontamination.
■   Transport, setup and decontamination time is high compared to bailers if the pump is not dedicated to the well.
■   Motor may slightly heat the samples.

2.4.5 Progressive Cavity (helical-rotor) Pumps

Progressive cavity pumps are categorized as a positive displacement device. They are commonly used for both purging and sampling monitoring wells. These pumps are appropriate for collecting sensitive samples if low-flow pumping rates are used.

Recent studies conducted by Gibs et al., (1994), Imbrigiotta et al., (1988) and Tai et al., (1991) found good precision and recovery of VOCs collected with a helical-rotor pump.

Operation and Materials

Figure 13 illustrates the design and operation of a common progressive cavity pump. An electric pump motor at the base of the pump turns a corkscrew-like helical rotor near the top. The helical rotor causes an upward movement of water trapped in the cavities of the rotor and the water moves up the discharge line. A check valve at the top of the pump ensures that the water in the discharge line (i.e., sample tubing) does not re-enter the pump. A controller box operated at the surface allows for variable pumping rates.

Models are available for use in 2-inch diameter monitoring wells and are made of materials

suitable for collecting sensitive samples, such as Teflon[®] and stainless steel. The

Pump Discharge Line → ←**Power Cord**

Electrically Operated
Power Source-12 volts D.C. at 5 Amps
Pumping Rate-0.36 PM at 125 ft.
               1.26 PM at 10 ft.
Pump Length-19.5"
Pump Diameter-1.75"
Weight-7 lbs.
Materials-Stainless Steel (304)
              Teflon
              EDPM

Rotor
Stator

Pump Intake

Pump Motor
(12V. D.C.)
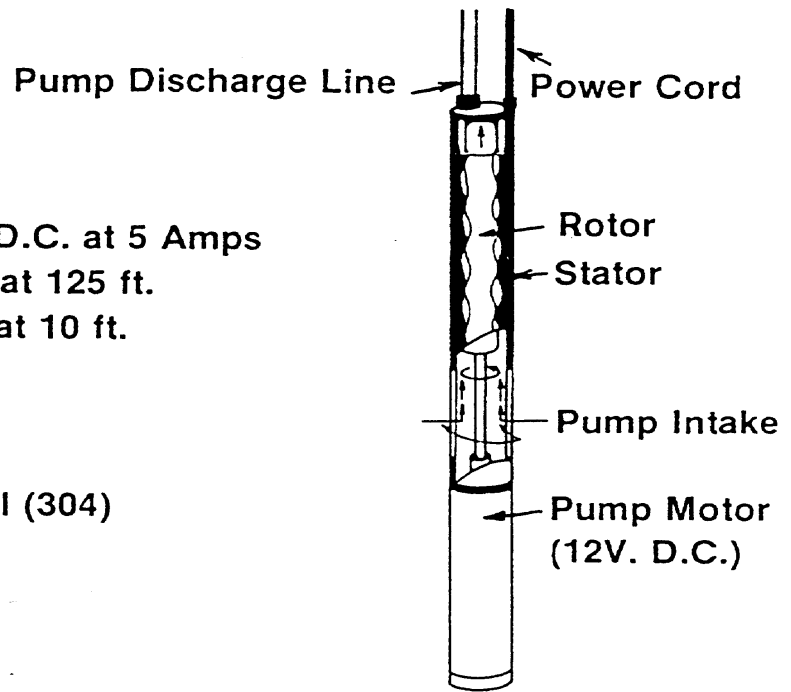
Keck® pump is one commercially-available helical-rotor pump capable of achieving low-flow rates and is available for 2-inch monitoring wells.

Advantages of progressive cavity pumps

- When low-flow pumping rates are used, these pumps consistently collect high quality samples.
- Models are available with variable flow rates and low-flow pumping rates.
- Initial high capital cost may be recovered if dedicated pumps are used.
- Models are available that are constructed of relatively inert materials.
- Lift capability is approximately 160 feet (50 meters).
- Allows for easy, direct in-line filtration of samples.

Limitations of progressive cavity pumps

- Pumps not capable of low-flow rates are not suited for collecting gas-sensitive or VOC samples.
- Portable but may be bulky, heavy and difficult to transport over long distances or over rugged terrain.
- Some variable speed models must initially be started at high flow rates.
- Pump may shut-off periodically at low-flow rates (< 200 ml/min).
- Requires external power source, usually a car battery or generator.
- Relatively difficult to disassemble and repair in the field.
- Transport, set-up and decontamination time is high compared to bailers if the pump is not dedicated to the well.
- Limited number of pumps available for 2-inch wells.
- Purging and sampling from deep wells may be slow.
- Rotor and stator may be damaged by turbid or silt-laden water.
- Portable system may freeze up in winter during sampling and decontamination.

2.4.6 Bladder Pumps (gas-operated squeeze or diaphragm pumps)

Bladder pumps are categorized as a positive displacement device. Bladder pumps are commonly used for purging and sampling monitoring wells for a wide variety of parameters, including VOCs and trace metals. They are typically considered among the best devices for collecting samples of VOCs, trace metals and other substances and parameters (Tai et al., 1991; Barcelona et al., 1984; Unwin and Maltby, 1988, Imbriogiotta et al., 1988; and Houghton and Berger, 1984). However, Yeskis et al., (1988) found that the bladder pump was one of the most difficult devices to decontaminate in the field.

Design and Materials

A bladder pump consists of a flexible, squeezable bladder encased in a rigid outer casing. Bladder pumps are designed so that the gas that squeezes the outside of the bladder does not come into contact with the samples. **Figure 14** shows the design of a common bladder pump.
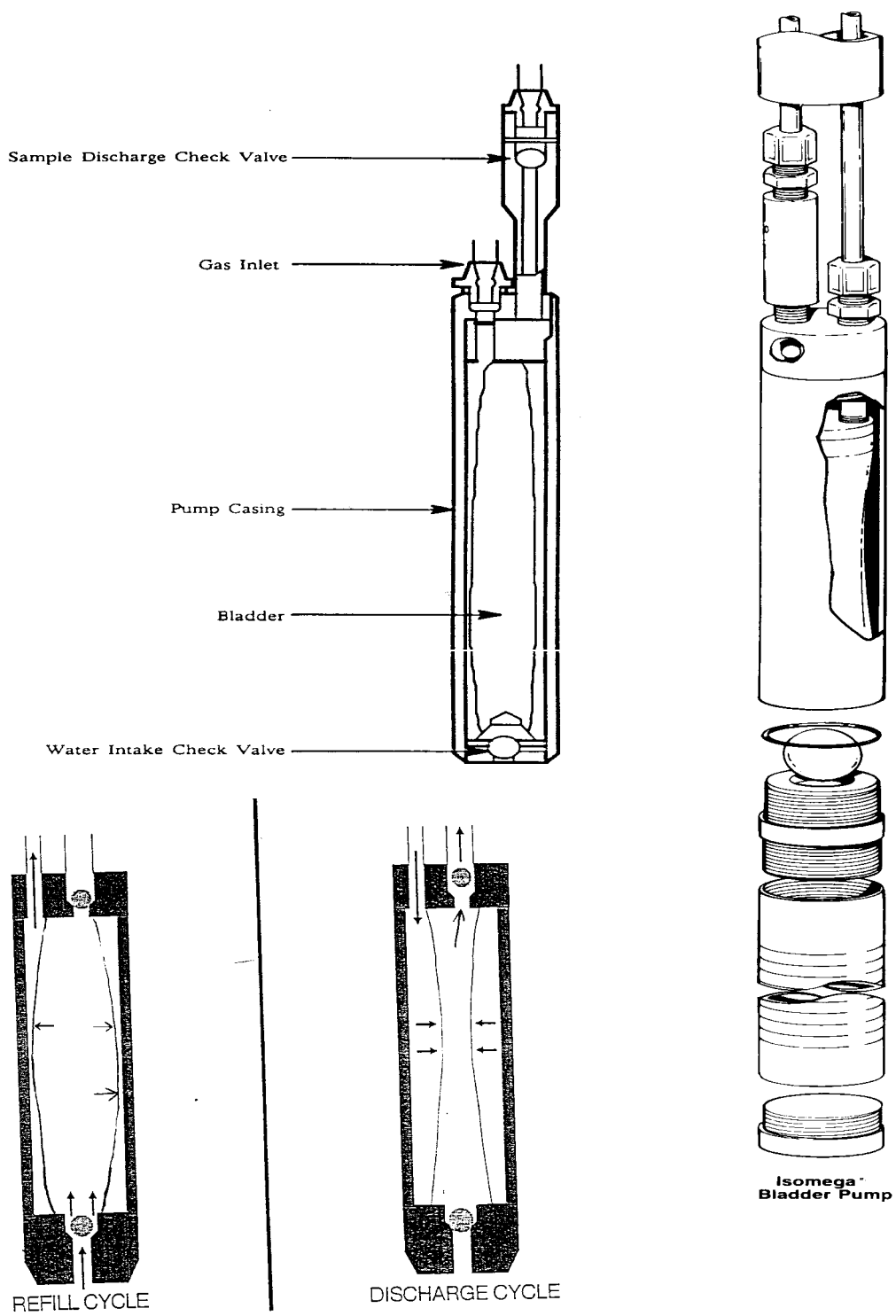
Figure 14: Bladder pump: a) cut-away diagram, upper left (Pohlmann et al., 1990); b) Isomega bladder pump, right (Courtesy of TIMCO^{TM}); and c) functional diagram, bottom.

Bladder pumps are commonly constructed of a stainless steel body and a flexible bladder. Bladder pumps are available for 2-inch diameter monitoring wells. As with centrifugal submersible pumps, bladder pumps can be dedicated to above ground wells or flush mount wells (see Figure 12), thus eliminating the need to transport, set-up and decontaminate the pump and collect quality assurance field blank samples.

Operation

A bladder pump operates much like a plastic squeeze bottle that has a liquid in it. Figure 14 illustrates the fill and discharge cycles of a common bladder pump. After you lower the device into the well's water column, water enters the bottom of the bladder under hydrostatic pressure through a check valve at the bottom of the pump. When the bladder is full, a check valve seals its bottom. A controller box at the well surface injects gas into the space between the pump casing and the outside bladder wall, thus squeezing the bladder. This squeezing causes the water to rise out of the bladder and up the sample tubing. When the bladder is nearly empty, the controller box releases the gas pressure and the bladder fills up again with water. A check valve at the top of the pump ensures that the water in the sample tubing does not re-enter the bladder. In some models, the water and air chambers are reversed.

A pneumatic controller box at the surface controls the gas injection and pressure release cycles that drive the pump. The controller box adjusts the purging and sampling flow rates by adjusting the injection and exhaustion cycles of gas in and out of the space between the outer casing and the bladder. The pump's lift capabilities are directly related to the pressure rating of the bladder and tubing and the ability of the pressure source (e.g., air compressor or compressed gas) and controller box to apply a sufficient force of gas at depth.

Advantages of bladder pumps

■ When low-flow pumping rates are used, these pumps consistently collect high quality samples.
■ Sample does not contact compression gas or mechanical parts of pump.
■ Flexible bladder may be constructed of relatively inert materials.
■ Capable of variable flow rate and low flow rates.
■ Capable of collecting very low turbidity samples (< 5 NTUs).
■ Allows for easy, direct in-line filtration of samples.
■ Very high lift capacity (1000 feet or 305 meters for some models).
■ Initial high capital cost may be recovered if dedicated pumps are used.
■ Pump is not damaged if run dry.
■ Easily repaired in the field and very reliable.
■ Lends itself to permanent dedication to a well.

Limitations of bladder pumps

■ Portable but may be bulky, heavy and difficult to transport long distances or over rugged terrain.
■ Requires compressed gas and controller box.
■ Purging and sampling from deep wells may be slow.
■ Depending on design, may be time consuming to disassemble and decontaminate.

- May cause changes in the CO_2 and pH of samples.
- Bladder may rupture when used in deep wells.
- Portable systems may freeze up in winter during sampling and decontamination.
- Transport, set-up and tear-down time is high compared to bailers if the pump is not dedicated to the well.

2.4.7 Gas-displacement or Air-displacement Pumps (also gas-drive pumps)

Gas-displacement or air-displacement pumps are categorized as a positive displacement device. Gas-displacement pumps (also called air-drive pumps) use a gas other than air (e.g., nitrogen gas) to drive the pump. Air-displacement pumps (or air-drive pumps) use air, typically supplied by an air compressor, to drive the pump. Gas-displacement or air-displacement pumps are more commonly used for purging than sampling monitoring wells. Do not use these pumps for collecting gas-sensitive, redox-sensitive or volatile samples. Do not confuse these devices with gas-lift or air-lift pumps. (Refer to Section 2.4.11.)

Operation and Materials

Figure 15 illustrates the design and operation of gas- or air-displacement pumps. As you lower a gas- or air-displacement pump into the water column, hydrostatic pressure opens an inlet check valve at the bottom and water fills the pump chamber. When the pump chamber is full, the inlet check valve seals itself. Gas or air pressure is applied at the top of the pump chamber and the gas or air pressure displaces the water in the chamber and forces the water up the sample tubing. After the chamber is empty, the gas or air pressure is released and the hydrostatic pressure of the water begins to refill the pump chamber again. A check valve at the top of the pump prevents water from re-entering the pump chamber. Adjusting the pressuring and venting cycles for these devices can be tedious and time consuming and must be redone whenever the depth of the pump is changed.

These pumps can be made of inert material to avoid sorption and leaching. These pumps can alter gas-sensitive, redox-sensitive and VOC samples. They may also change the pH of a sample because of increasing or decreasing CO_2 concentrations as gas or air pressure is applied to the water in the pump's chamber. Using an inert gas such as nitrogen (N_2) may minimize sample oxidation and volatilization.

Advantages of gas-displacement or air-displacement pumps

- Very portable and inexpensive.
- Available for wells as small as 1.25 inches in diameter.
- Acceptable for collecting non-sensitive parameters.

Limitations of gas-displacement or air-displacement pumps

- Air-displacement pumps may cause oxidation and volatilization of samples.
- Not very efficient for purging 2-inch diameter or larger wells.
- Require gas or air compressor, or compressed gas or air.
- Can be difficult to disassemble, repair and decontaminate in the field.
- Don't work well in deep wells.
- Pressuring and venting cycles must be adjusted every time pump's depth is changed.
- May cause changes in the CO_2 and pH of samples.

GAS- OR AIR-DISPLACEMENT PUMP

REFILL CYCLE

DISCHARGE CYCLE

Stainless Steel
or Teflon

Weighted
Bottom Section

PVC
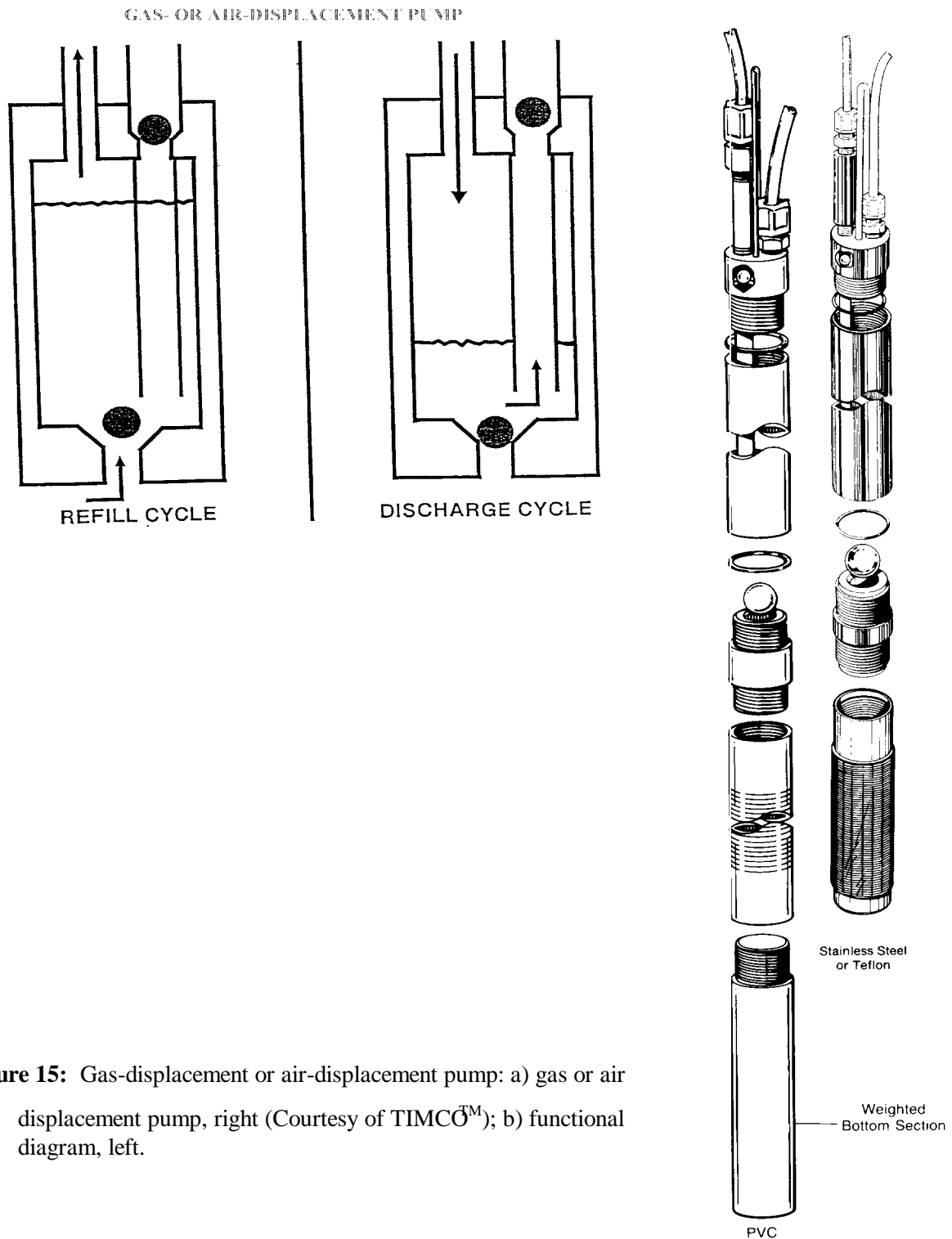
Figure 15: Gas-displacement or air-displacement pump: a) gas or air displacement pump, right (Courtesy of TIMCO^{TM}); b) functional diagram, left.

2.4.8 Piston Pumps (manual and gas-drive piston pumps)

Piston pumps are categorized as positive displacement devices. You may use a piston pump to purge and sample monitoring wells depending on their design, materials and mode of operation. Knobel and Mann (1993) and Yeskis et al., (1988) found that the air-operated reciprocating piston pump recovered VOC concentrations comparable to those found using a submersible centrifugal pump and bladder pump. However, a previous study conducted by Nielsen and Yeates (1985) found that the intricate valving mechanism of these pumps, which can cause a series of pressure drops, can lead to pH changes and degassing in the sample.

Operation and Materials

Piston pumps may be mechanical or pneumatic and may have one or more pistons (plungers). The design of most piston pumps consists of a single-direction or dual-direction piston. With the single-direction piston design, as the piston travels up and down the pump chamber, it draws water into the chamber under suction on the up stroke and then forces the water out of the chamber and up the sample tube on the down stroke. With the dual-direction piston design, water is simultaneously sucked in and forced out as the piston(s) is moved in both the up and down direction. **Figure 16** illustrates the design and operation of a dual-direction piston pump.

Piston pumps can provide representative samples for non-gas and non-pressure sensitive samples. The action of the piston may create pressure changes on the sample that may cause degassing and changes in sample chemistry; however, if the pump cycling rate is decreased, these affects can be minimized. The piston (plunger) and O-ring seals equipped on most piston pumps may sorb various VOCs that make decontamination of these pumps difficult.

Advantages of piston pumps

- High lift capabilities - 500 feet (150 meters) for mechanical designs and 1000 feet (305 meters) for pneumatic designs.
- Allows for easy, direct in-line filtration of samples.
- Can be constructed of relatively inert materials.
- Models with variable flow rate capabilities are available.
- Moderately easy to operate.
- Models available for 2-inch diameter and smaller wells.

Limitations of piston pumps

- Susceptible to damage, binding or failure in silt-laden and turbid water.
- May be damaged if pump is run dry.
- Requires external power source or pressurized-gas source.
- Difficult to disassemble, repair and decontaminate in the field.
- Equipment is moderately bulky, heavy and not very portable.
- Contact with the pump's mechanisms can cause contamination.
- Moderately expensive to purchase and operate.

AIR EXHAUST TUBE — releases exhaust air at surface.

AIR SUPPLY TUBE

WATER DISCHARGE TUBE

WATER LEVEL INDICATOR — contact probe.

VALVE BODY

MOTOR PISTON

PISTON ROD — stainless steel — connects motor piston to pump piston.

ROD SEALS — prevent air in motor from entering fluid pump.

FLUID INLET VALVE

FLUID DISCHARGE VALVE

DOUBLE ACTING PUMP PISTON
fluid discharge on up
and down stroke

PUMP PISTON

FLUID DISCHARGE VALVE

FLUID INLET VALVE
ACETYL PLASTIC

INLET SCREEN
stainless steel - 100 mesh

ARROWS SHOW FLUID
FLOW THROUGH PUMP

HAND BRAKE

TUBE BUNDLE

AIR SUPPLY LINE
& FILTER

REEL LOCK

WATER LEVEL
INDICATOR

LOW FLOW
SAMPLE TUBE

REEL
DRIVE

WATER
DISCHARGE TUBE

ROTARY SWIVEL
(inside console)

ROLLER
HEAD

FLOW METER

AIR PRESSURE
REGULATOR

TUBE BUNDLE MEASURING SYSTEM

BENNETT SAMPLE PUMP

Figure 16: Piston pump: a) automatic reciprocating piston pump, upper left; and b) portable piston pump system, lower right. (Both diagrams courtesy of Bennet Sample Pumps, Inc.)

2.4.9 Gear-drive Pumps

The gear-drive pump is categorized as a positive displacement device. Historically, gear-drive electrical submersible pumps have not been used for groundwater sampling; however, they do show promise for this purpose because they are very portable and serviceable under field conditions. In theory, these pumps, if operated at low-flow rates, should consistently collect high quality, representative samples; however, research and literature is limited on their abilities and limitations. Imbrigiotta et al. (1988) conducted a field evaluation of seven sampling devices for POCs in groundwater and found that the gear submersible pump had the highest precision and recovery of POC concentrations in comparison to the three other pumps and three grab samplers.

Operation and Materials

Figure 17 illustrates the design and operation of a gear-drive pump. This type of pump operates using a small high-efficiency electric motor that rotates a pair of meshing gears. The meshing gears have teeth that trap and move the water in either a clockwise or counter clockwise direction. Water enters through the bottom of the pump and exits through the top and into the sample tubing.

Flow rates cannot be controlled with conventional gear-drive pumps; however, there are now gear-drive pumps that allow variable flow rates. These pumps are available with either a self-contained power source (typically six hours of operation before recharging is required) or require an external electric power source. The body of gear-drive pumps is commonly constructed of stainless steel and the gears are commonly constructed of PTFE (Teflon®).

Gear-drive pumps may not be appropriate for purging large volumes of water. If a gear-drive pump is not capable of low-flow rates, it may not be appropriate for collecting sensitive samples.

Advantages of Gear-drive Pumps

- Can be constructed of relatively inert materials.
- Very portable and totally self-contained.
- Easy to operate, disassemble, repair and decontaminate in the field.
- Inexpensive to purchase andoperate.
- Allows for easy, direct in-line filtration of samples.

Limitations of Gear-drive Pumps

- Ability to control flow rate may not be available for some models.
- Silt-laden or turbid water quickly wears down gears.
- Requires a power source.
- Potential for pressure changes in samples due to cavitation from pump gears.
- Some models are not available for 2-inch diameter wells.
- Lift capability of 200 feet (60 meters) or less.

Quick-connect Fitting

Power Cord

Pump Discharge

Screen

Pump Intake

Gear Drive

Electrically Operated
Power Source-24 volts D.C. at 5 Amps
Pumping Rate-0.5 GPM at 100 ft.
        1.0 GPM at 50 ft.

Pump Motor
(24 V. D.C.)

Motor Housing

MESHING TEETH FORM
A SEAL THAT FORCES
WATER INTO DISCHARGE LINE

WATER CARRIED
AROUND BOTH
SIDES OF PUMP

WATER CARRIED
AROUND BOTH
SIDES OF PUMP

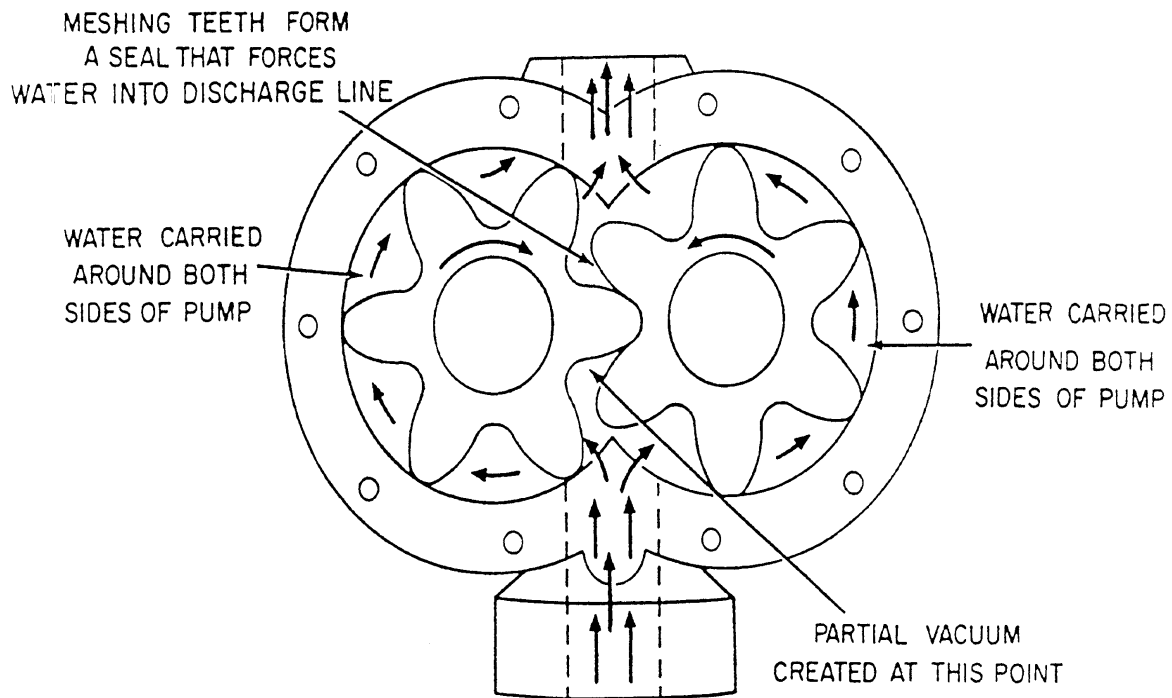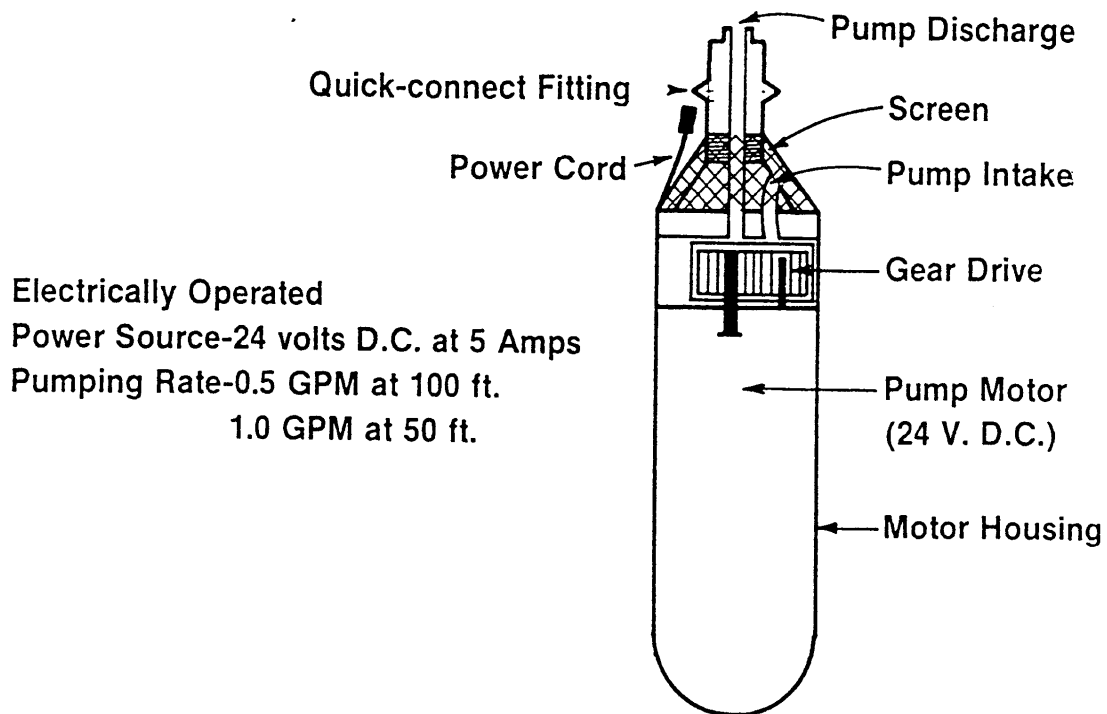PARTIAL VACUUM
CREATED AT THIS POINT

Figure 17: Gear-drive pump: a) cut-away diagram, top; and b) functional diagram, bottom.

2.4.10 Inertial Lift Pumps

Inertial lift pumps function adequately for both purging and sampling of monitoring wells; however, using these devices causes a surging action, which may cause increased turbidity, loss of volatiles, aeration, and degassing of samples. You may use these pumps to collect representative non-sensitive samples; however, do not use them to collect VOCs or gas-sensitive samples.

Operation and Materials

The inertial lift pump operates by either moving sample tubing up and down in a well or by moving a rigid inner pump casing up and down (e.g., TIMCO® or Water Hand Pump, Brainard•Kilman® Hand Pump). Both the sample tubing design and the rigid inner pump casing design are equipped with a check valve at the bottom.**Figure 18** illustrates both the sample tubing inertial lift pump design and the inner/outer inertial lift pump casing design. An electric or gasoline-powered motor can provide a continuous up and down motion for either design. Manually operating inertial lift pumps can be quite difficult.

A rapid up and down motion moves water up these pumps by lift and inertia. A rapid upstroke lifts the water in the tubing or casing. At the end of the upstroke, the water in the tubing or casing continues to move slightly upward by inertia. On the downstroke, the check valve at the bottom of the tubing or casing opens, which allows additional water to enter the device. This cycle continues on each up and down movement until water moves up and out of the device.

Because operating these pumps requires that the sample tubing or casing be rapidly raised and lowered, samples are often artificially high in turbidity. The rapid movement may also cause some sample alteration through loss of volatiles and degassing; however, these devices should be able to collect non-sensitive samples without significant sample alteration.

Materials used in the construction of inertial lift pumps rigid or flexible PVC, polyethylene, or PTFE materials.

Advantages of Inertial Lift Devices

- Simple design and easy to operate.
- Fairly portable if used in shallow wells (e.g., < 20 feet to water).
- Relatively inexpensive.
- Models are available for small diameter wells.
- Capable of controlled flow rate.
- Can be constructed of relatively inert materials.
- Satisfactory for non-sensitive sample parameters.
- Direct, in-line filtration of samples is possible but may be difficult.
- Manual pumps are effective up to 100 feet (30 meters) and motor-driven pumps up to 200 feet (60 meters).
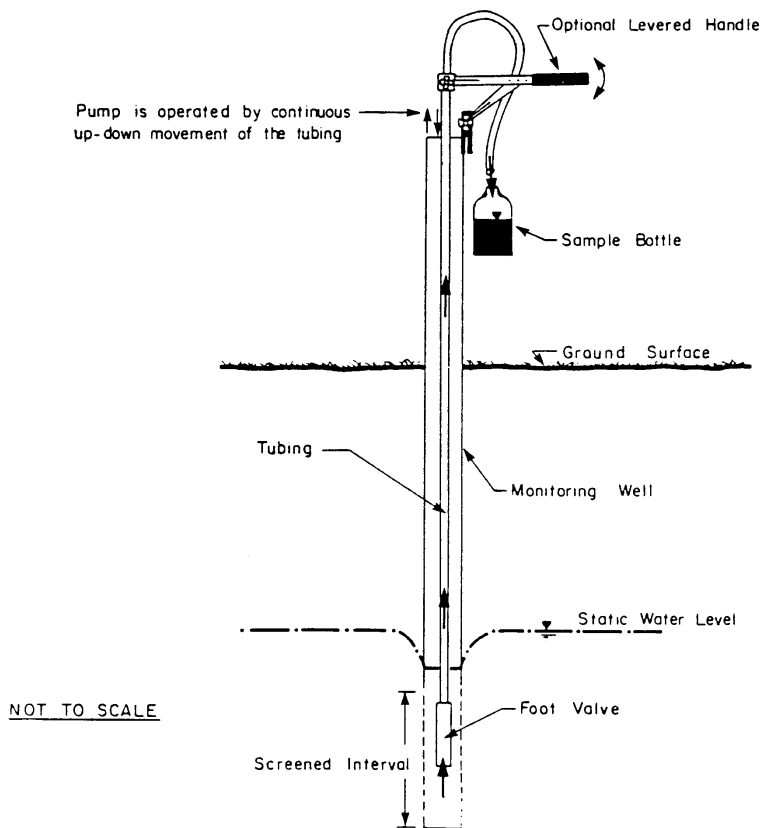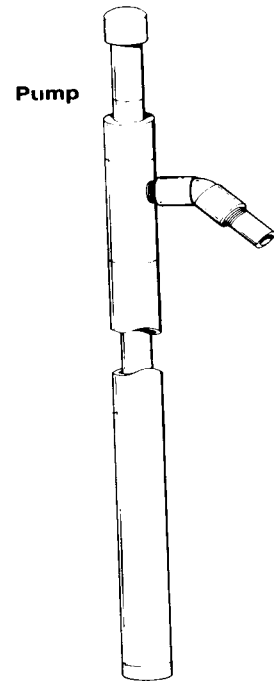
Pump

Figure 18: Inertial lift pumps: a) p in operation, upper left (Courtesy of Brainard Kilman^{TM});

b) functional diagram, upper right; c) single-tube hand pump, bottom.

61

Limitations of Inertial Lift Devices

- Field decontamination may be difficult and time consuming.
- Manual designs are labor intensive.
- Silt and sand may cause leakage around the check valve.
- Their use may artificially increase sample turbidity.
- Check valve wears with heavy use.
- External motor and power source are not very portable.
- Ineffective in purging large volumes of water.
- Limited lift capabilities make these devices ineffective for deep wells.
- Not very portable if used in deep wells (e.g., > 20 feet to water).

2.4.11 Gas-lift or Air-lift Pumps

These pumps operate by bubbling air or gas (e.g., nitrogen) through the water inside them. The rising of the air or gas lifts the water to the surface. While these pumps are not recommended for collecting groundwater samples – especially gas-sensitive and volatile samples – you can use them for purging. **Figure 19** illustrates some common gas-lift and air-lift pump designs.

2.5 PURGING AND SAMPLING PROCEDURES

Groundwater professionals, when initiating a groundwater monitoring program, set out to obtain measurements and samples representative of unaltered groundwater conditions. Several factors, especially purging and sampling procedures and equipment, can degrade the physical and chemical characteristics of the measurements and samples. Always try to collect the best measurements and groundwater samples possible.

The laboratory analytical method and limit of detection established for a contaminant should indicate the level of care needed in sampling. For example, if contaminants are present near the analytical detection limit or the regulatory limit, pay particular attention to adopt sampling procedures that avoid contaminating the sample or losing the contaminant.

> **Important note:** Collect groundwater data from all project wells using the same sampling and purging procedures and equipment throughout the project's life. This should generate groundwater data that is complete, with few, if any, "outliers;" is representative, reflecting conditions in the groundwater; and is comparable to other data sets. Comparability of data collected from a project's wells is important when performing trend analysis. Dedicated (left in the well) low-flow sampling systems typically produce groundwater data that are complete, representative, comparable and of high quality. Summers et al., (1987) provides a good discussion on the accuracy, bias, precision, representativeness, completeness and comparability of groundwater data collected from monitoring wells.
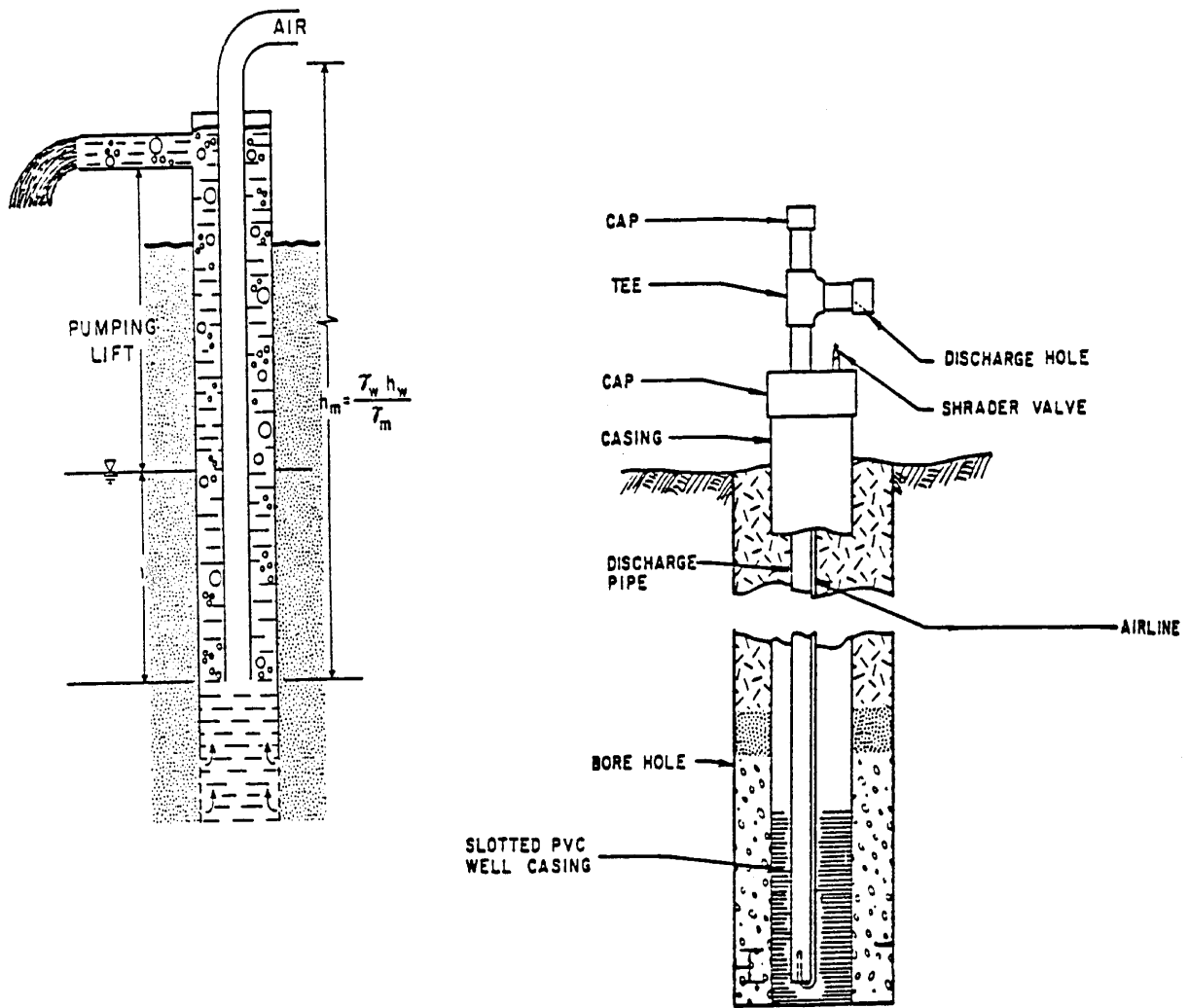
Figure 19: Gas-lift or air-lift pumps: a) annulus type, left (Gillham et al., 1983); and b) riser type, right (Gillham et al., 1983).

If the method or equipment used to purge and sample a well changes during a project's life, consider this change in protocol when comparing the well's laboratory analytical data and evaluating data trends.

2.5.1 Objectives and Considerations

Proper Well Construction, Development and Maintenance

Wells must be designed, constructed and developed according to procedures established in ch. NR 141 Wis. Adm. Code. These three factors can greatly influence the quality and representativeness of groundwater samples. Pay special attention to s. NR 141.15, which discusses drilling methods and drilling fluids that may be used in well construction. In addition, Driscoll (1986) provides a comprehensive discussion of well hydraulics, drilling methods, drilling fluids, well screens and sizing, and well development. Excessive disturbance of the formation during well construction can create artificial low-flow zones surrounding a well and may make proper development of a well very difficult, if not impossible.

Proper well development is important to ensure that a good hydraulic connection exists between the well and the surrounding groundwater system. Proper well development is also essential to avoid or minimize turbidity in groundwater samples and is essential for collecting representative, high quality samples. Proper well development removes artifacts created during the drilling process such as disturbed fines near the borehole and silts and clays that have been "smeared" along the walls of the borehole. Unless these disturbed and smeared fines are removed by proper well development, the hydraulic connection between the well and the surrounding groundwater system will likely be poor.

Materials used to construct a well, including the filter pack seal, well screen and well casing, should be made of clean, non-reactive materials. Improperly constructed wells may cause a biofilm (excessive growth of microorganisms) to develop around a well. A biofilm can clog the surrounding area, thus creating "dead zones" around the well. Biofilms can degrade sample quality. If a well's casing joints leak or if its annular space seal allows leakage around the casing, the well may act as a conduit for contamination or groundwater movement between naturally-separated aquifers.

> Special Note for Newly Constructed and Developed Wells
>
> Before purging and sampling a newly constructed and developed well, wait at least one week to allow the well to equilibrate with groundwater chemistry. Wells constructed in low-permeability silt and clay formations may require a month or more for proper equilibration. Palmer (1987), provides insight on allowing a well's filter pack to come into equilibrium with groundwater chemistry.

Inspect and maintain wells routinely as part of a site's sampling plan. Structural damage, siltation and biofouling (iron bacteria clogging a well) can significantly interfere in collecting representative groundwater samples. Total well depth, casing straightness and relative water recovery rates are good indicators of well condition and should be logged in field notes. If total well depth decreases with time, silt or sand may be settling out in the bottom. Reducing well recovery rates over time may

indicate biofouling of a well's filter pack. Well repair, redevelopment, or rehabilitation will typically rectify these problems; however, well replacement may be necessary if routine maintenance has not been done.

Reasons for Purging a Well

The primary objective of purging a well is to remove any stagnant water residing in the well screen and casing before collecting any samples. Always purge a well before sampling because standing water likely does not represent true groundwater chemistry. Appendix A includes a detailed literature review and evaluation of the three most common well purging techniques: 1) purging a specified number of well volumes; 2) low-flow pumping and monitoring indicator parameters for stability; and 3) well purging volume based on well hydraulics and aquifer transmissivity. Appendix A also includes a list of articles and publications and a brief description of the well purging and sampling equipment and procedures discussed in the article or publication.

Water in the well may have interacted with the air column in the well. This interaction can change the dissolved gas content (e.g., DO and CO_2) of well water. Air interacting with the water can cause oxidation (e.g., precipitation of iron and manganese and co-precipitation of arsenic with iron hydroxide) of some metals (Summers and Gherini, 1987). The stagnant water in the unscreened portion of a well (i.e., well casing) will not reflect the changes in the type and concentrations of contaminants that have flowed through the aquifer and well screen.

Potential interactions of the stagnant water with the well casing include: sorption of trace contaminants onto the casing; leaching of chemicals out of the well casing; and corrosion and degradation of the casing. The degree to which these reactions may occur will depend on the chemical environment in the well casing and the casing materials used. Foreign material may have entered the well and reacted with the stagnant water. Purging the well will either remove the foreign material that fell into the well or remove the stagnant water that has reacted with the foreign material in the well.

Collecting Representative Samples and Maintaining Sample Integrity

The primary objective of sampling is to collect an unaltered groundwater sample that represents the physical and chemical composition of the groundwater. Because groundwater is almost always under different temperature, pressure, dissolved gas content and oxidation-reduction (redox) state than conditions above ground, precautions must be taken to ensure that samples undergo minimal alteration during the sample withdrawal and collection process.

Some contaminants and parameters that may be altered or lost during the sampling or measurement process include the following: pH, Eh, dissolved oxygen, inorganic carbon, alkalinity, total organic carbon (TOC), VOCs, ammonium, nitrate/nitrite, sulfide, cyanide, molybdenum, mercury, selenium, dissolved iron, manganese, zinc, cadmium, lead, vanadium, arsenic and phosphate (Stolzenburg and Nichols, 1985).

Volatilization of contaminants is a primary concern during VOC sampling. Oxidation and precipitation/coprecipitation reactions are of primary concern when collecting dissolved metal samples.

Sampling equipment must not react with any contaminants you are collecting. Operate your equipment to cause the least disturbance to the samples. Equipment must deliver samples to the surface with

minimal agitation and aeration. Refer also to Sections 2.4, 2.5.2 and 2.5.3.

Once you collect your samples, it is imperative to maintain their physical and chemical composition and quality until they can be measured or analyzed. Refer also to Sections 2.6, 2.7, 2.8, 2.9 and 2.10.

2.5.2 Wells that do NOT Purge Dry

This section applies to wells that take less than ~ 1 hour for the water level in the well to recover (or nearly so) after they have been purged.

The following recommended procedures can assist you when you are considering which purging and sampling techniques are best suited for a project. While flexibility and site-specific modifications to the suggested purging techniques are allowed, make any modifications based on contaminants encountered, hydrogeology, regulatory objectives and the level of data quality required.

The following purging and sampling procedures are recommended for wells that do not purge dry. The first procedure listed consistently yields the *highest level of data quality.* The last procedure listed may yield a *lower level of data quality*:

1) **Low-flow purging < 1 L/min (0.26 gpm), low-flow sampling < 300 ml/min (0.3 L/min or 0.1 gpm) and the monitoring of indicator parameters for stability in a closed flow-through cell.** To obtain the highest-quality, most representative, and consistent groundwater quality measurements and analytical data, purge the well at an average rate of 1 liter/minute (L/min) or less, sample at an average rate of 300 ml/min (0.3 L/min) or less and monitor indicator parameters in a closed flow-through cell until their stability is reached. This procedure can usually be enhanced by using a dedicated pumping system (left in the well "permanently").

   Purging and sampling rates should be at or less than the natural flow conditions existing in the aquifer influenced by the well. Drawdown during purging should be minimal and the water level in the well should stabilize before the flow rate is decreased to 300 ml/min or less to commence sampling. While maintaining a sampling flow rate of 300 ml/min or less, the water level should be stable or preferably recovering as samples are collected (this ensures that any remaining stagnant water above the pump is not incorporated into the water collected for samples). Information collected on the well hydraulics, aquifer transmissivity and observed drawdown and recovery rates for the well can assist in determining appropriate purging and sampling flow rates.

   Do <u>not</u> reduce a pump's flow rate by using valves. The resulting pressure drop across the valve (also known as an "orifice effect") can alter sensitive samples, usually by degassing.

Purge the well until at least three consecutive readings, spaced ~ 2 minutes or ~ 0.5 well volumes or more apart, are within the following indicator parameter ranges:

Dissolved Oxygen	± 0.2 mg/L
Specific Conductance	± 5.0 µmhos/cm for values < 1000 µmhos/cm
	± 10.0 µmhos/cm for values > 1000 µmhos/cm
pH	± 0.1 pH units
Temperature	± 0.1 ^{o}C
Turbidity	< 5 NTUs (**Required** if metals samples will not be filtered. **Recommended** if sorptive compounds or elements are collected. **Optional**, but recommended if other compounds or elements are collected)
Eh **(optional)**	± 30 mv

Stable dissolved oxygen, specific conductance and turbidity readings are considered the most reliable parameters for indicating that stagnant water has been replaced by formation water. You may adjust the ± ranges and indicator parameters used to indicate replacement to reflect site-specific data, geochemistry, and hydrogeologic conditions.

Turbidity stabilization and NTU readings below 5 are required if metals samples will not be filtered. Low turbidity readings (i.e., < 5 NTUs), when measured using low-flowing pumping techniques, should represent colloids and particulates naturally mobile in groundwater under natural flow conditions. Turbidity stabilization should also be monitored when collecting sorptive, hydrophobic, or high octanol-water partition coefficient (Kow) compounds or elements.

Or: Purge the well until the readings for each indicator parameter listed above vary within ± 10 percent, over three or more consecutive readings spaced ~2 minutes or ~ 0.5 well volumes or more apart.

Collect samples from the pump's discharge line before the water enters the flow-through cell. Air pockets in the flow-through cell and probes inserted into the flow-through cell can degrade sample water quality. Either disconnect the sample tubing from the flow-through cell before collecting samples or connect a "tee" junction with an on/off sampling valve between the well and the flow-through cell to collect samples. **Figure 20** illustrates a "tee" valve outfitted with a direct, in-line disposable filter.

Low-flow purging/sampling may not be necessary or may be impractical under the following circumstances:

- Well purges dry before indicator parameters stabilize.
- Parameters are not affected by aeration, agitation, or the gain or loss of dissolved gasses (and subsequent change in sample pH, etc.,).
- Data quality objectives for a project do not require th level or rigor and stringency inherent in low-flow purging/sampling.
- An alternative purging and sampling technique has been proven to meet the data quality objectives for the project.
- Procedures are extremely burdensome and time consuming.
- Equipment is too cumbersome to be transported to distant wells.
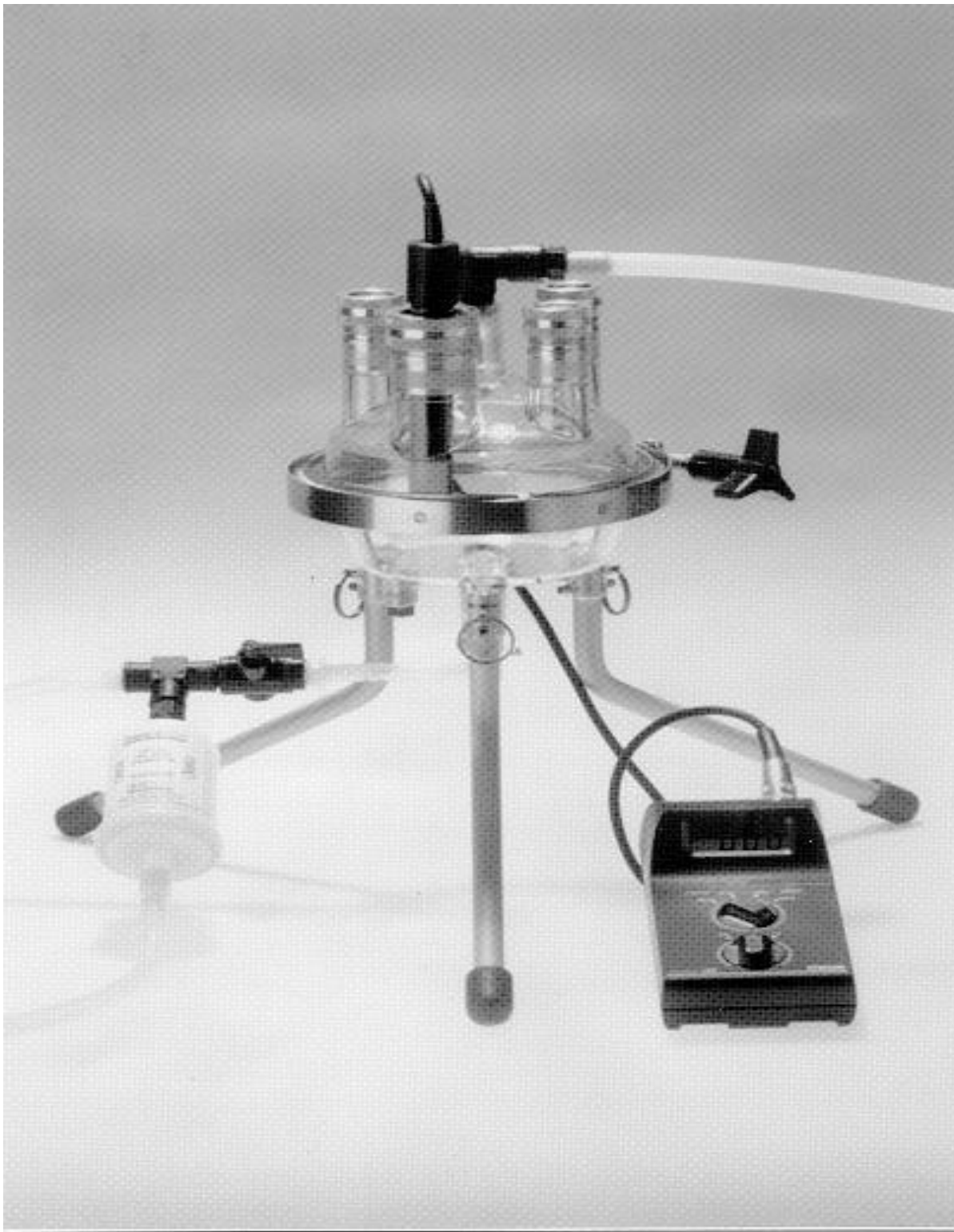
Figure 20: Closed flow-through cell outfitted with a direct, in-line filter.

- Weather conditions cause portable equipment to freeze up.
- The required equipment is excessively expensive.
- A bailer is the only device available to purge and sample a well.

2) **Purging FOUR well volumes and then sampling with a standard pump** You may use this method with a purging and sampling pump not capable of achieving low-flow rates, when equipment is not available to monitor indicator parameters for stability, or when you are sampling non-sensitive parameters. As with the low-flow purging and sampling technique, the purging and sampling rate should still be kept low and should not exceed the natural flow conditions of the aquifer, if possible. The sampling flow rate should be less than the purging flow rate.

3) **Purging FOUR well volumes with a standard pump and sampling with a bailer or similar grab sampler**. Conduct purging and sampling with the same equipment when possible; however, in cases where large volumes of water must be purged from a well or the depth to water is deep, a pump may be appropriate. This method may be appropriate when low-flow pumping equipment is not available but sensitive samples will be collected.
Under this scenario, you purge four well volumes and then collect samples with a bailer or similar grab sampler. As you are purging the well, *slowly lower the pump* so that, after four well volumes are purged, the pump's inlet is near the bottom of the well (within ~ 1 foot). When using this method, it is essential to lower the pump while purging, thus removing stagnant water before collecting samples with the grab sampler. If you are collecting sensitive samples (e.g., VOCs or trace metals), keep the purging rate as low as possible. In addition, lower and raise the bailer or similar device out of the water column slowly and carefully; and use a bottom-emptying device to dispense samples.

4) **Purging FOUR well volumes with a bailer and sampling with a bailer or other grab sampler.** The quality of samples collected with a bailer highly depends on the skill and care of the operator using it. Take great care when lowering a bailer in and out of the water column. Carefully lift the bailer up and out of the well without allowing it to bang against the casing and use a bottom emptying device to dispense samples.

2.5.3 Wells that Purge Dry

This section applies to wells that take ~ 1 or more hours to recover (or nearly so) after they have been purged dry (or nearly so).

Ideally, sample and purge wells at flow rates at or less than the natural flow conditions in the aquifer influenced by the well. Drawdown and turbidity during purging and sampling should be minimal; however, for wells that recover slowly, attaining little drawdown and low turbidity may be nearly impossible. Slowly-recovering wells should still be purged and sampled with minimal disturbance to the water and fines in and around the well and to obtain samples with the lowest turbidity and oxygenation possible.

For slowly-recovering wells that purge dry, bail or pump the well dry, or nearly so, and allow it to recover at least once before collecting samples. If time permits, purge the well a second time. If recovery permits, collect samples from the well within 24 hours of the final purging.

If you are collecting sensitive samples such as VOCs and trace metals, the following procedure should yield samples with the highest data quality. Purge the well dry, or nearly so, using a very low purging rate (< 300 ml/min or 0.1 gpm). Allow the well to recover, or nearly so, at least once before collecting samples. If time permits, purge the well a second time and collect samples within 24 hours. Low-flow pumping should minimize the disturbance of fines in and around the well during purging and sampling and should therefore minimize sample turbidity. If you use a bailer to purge and sample, take extra care to purge and sample very slowly and gently.

> Case study
>
> Hergoz et al., (1988) conducted a study to determine the best time to sample a well for VOCs after it has been purged dry. There were two main conclusions: 1) VOC concentrations were significantly lower before purging than after, and 2) VOC concentrations were **not** significantly different when collected two, four, six and 24 hours after purging; however, the highest VOC concentrations were collected at four and six hours after purging.

2.6 SAMPLE COLLECTION

2.6.1 Objectives and Considerations

During sampling, primary objectives and considerations include minimizing sample disturbance, avoiding sample exposure to air and extraneous contamination, and preserving sample integrity throughout collection.

2.6.2 Filling Sample Containers

Although the procedures used to fill sample containers may seem a minor consideration, filling them improperly can jeopardize all the careful work that went into collecting minimally-disturbed, representative samples. Filling sample containers exposes the samples to air, agitates the samples, may change their composition, may cause the loss of contaminants by volatilization or degassing, and may expose the samples to extraneous contamination.

Order of Filling Sample Containers

Collect sample parameters in the following order:

1. Unfiltered samples for in-field water quality measurements (not necessary if down well or flow-through cell measurements are taken).
2. Volatile organic compounds (VOCs).
3. Non-filtered, non-preserved (e.g., sulfate, chromium VI, mercury, semi- and non-volatiles,

pesticides, PCBs).
4. Non-filtered, preserved (e.g., nitrogen series [ammonia, nitrates, nitrites, etc.], phenolics, total phosphorous, total metals, cyanide, total organic carbon).
5. Filtered, non-preserved (e.g., dissolved chromium VI).
6. Filtered, preserved immediately (e.g., dissolved metals).
7. Miscellaneous parameters.

Collect sulfate samples before sulfuric acid preserved samples (e.g., nitrogen series). Collect nitrogen series samples before nitric acid preserved samples (e.g., boron, dissolved metals). This will prevent accidental contamination of a sample with a preservative intended for another sample (e.g., sulfuric acid preservation contaminating an unpreserved sulfate sample).

Procedures for Filling Sample Containers

There are correct and incorrect ways to fill sample containers. The more sensitive the parameter being collected (e.g., VOCs and redox-sensitive metals), the more cautious and rigorous the filling procedures should be.

Before opening and filling sample containers, check the sampling area for potential sources of extraneous contamination. Make sure the area around the well is clean and that contaminated equipment is kept away from the well. Protect the samples from airborne contaminants such as engine exhaust, blowing dust and organic fumes (e.g., gas cans); sample upwind of these contaminants or remove them before sampling. Choose gloves appropriate for the contaminants you encounter. Change into new, clean gloves every time you sample a new well or suspect your gloves have become contaminated. Do not attempt to decontaminate or reuse gloves; use disposables.

Do not open sample containers until it is time to fill them. Immediately after filling a sample container, if you haven't already done so, add any required preservative – filter first, if required – replace the cap, label the container and place the sample on ice in a cooler. Following these procedures will help minimize sample turbulence, agitation, volatilization, degassing, atmospheric exposure, biodegradation, exposure to extraneous contamination and heating of samples.

2.6.3 Volatile Organic Compounds (VOCs)

As their name implies, volatile organic compounds (VOCs) may volatilize from a sample under normal surface pressure and temperature conditions. Take care to ensure these compounds do not volatilize during sampling. Appendix B includes a table of Henry's Law Constants for most compounds listed in ch. NR 140, Wis. Adm. Code. Henry's Law Constants describe the likelihood that a dissolved organic compound will volatilize from a water sample and is equal to the vapor pressure of the compound divided by the compound's solubility in water. Just because a compound is very volatile in its pure form does not mean it will readily volatilize after it is dissolved in water. For example, acetone (2-propanone) has a high vapor pressure (270 mm Hg) and therefore, readily volatilizes to the air in its pure form. However, acetone's water solubility is infinite so acetone favors the aqueous phase over the vapor phase. Therefore, its Henry's Law Constant is relatively low (3.9 x

10^{-5} atm-m^3/mole) and acetone dissolved in water will not readily volatilize out of the water and into the air.

Many VOCs listed in ch. NR 140 have very low groundwater standards. For example, vinyl chloride and benzene have enforcement standards of 0.2 and 5 µg/L, respectively. Many VOCs are known or suspected carcinogens. Because their consumption is a public health concern, take extra care to ensure that VOCs are not lost by volatilization when you fill VOC containers, and that extraneous VOCs are not accidentally added to a sample.

Because VOC samples are very susceptible to extraneous VOC contamination, before opening and filling VOC containers, make sure there are no nearby extraneous airborne sources of VOCs such as gas cans, exhaust fumes, solvents, cleaners, or degreasers upwind of the well. Try to sample upwind of these extraneous sources, remove them, or ventilate the area around the well. Document suspected but unavoidable extraneous VOC sources when collecting VOC samples. These sources could include perfumes and cosmetics, skin pharmaceuticals, suntan lotions, marking pens (e.g., Sharpie®), insect repellents, tobacco smoke and automotive products.

Filling VOC Containers

When practical, store empty VOC containers on ice until you use them. This will minimize the loss of VOCs when you fill the sample containers. Open only one VOC container or one set of containers at a time. This will minimize exposure of the VOC sample to extraneous VOC contamination. After you open an empty container, add preservative. Acid preservative inhibits biodegradation of VOCs in a sample.

When filling a VOC container, tip it at a slight angle and allow a slow steady stream of water to run down its inner wall. This will minimize agitation, aeration and volatilization of the VOCs. Fill the container until a positive meniscus forms at the top (see **Figure 21**). No air space (i.e., head space) should remain in the container. If any airspace remains, VOCs in the sample can volatilize to this space and may be lost before analysis.

After filling a VOC container and replacing the cap, invert the sample and tap it lightly to check for bubbles. If bubbles are present, discard this sample and fill additional VOC containers. If bubbles are unavoidable, collect numerous samples and save the ones with the fewest bubbles. Do not try to reopen and add more water to samples that have bubbles.

Remember, one trip blank is required per sample batch (i.e., per cooler) when sampling for VOCs.

2.6.4 Semi-volatiles and Pesticides

These organics are typically not very volatile; however, as with VOCs, they are often analyzed at very low detection levels (e.g., µg/L or ppb) and are a threat to public health if consumed. Some substances that fall under this category include base-neutral extractables (e.g., polynuclear aromatic hydrocarbons [PAHs]), acid-neutral extractables (e.g., cresols, phenols), phthalate esters, PCBs, pesticides and herbicides.
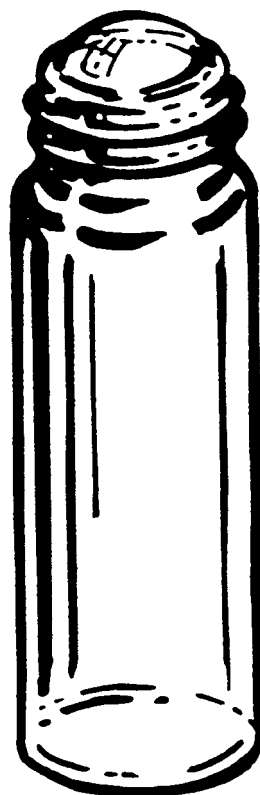
Figure 21: Positive meniscus formed on a VOC sample vial.

As with VOCs and dissolved metals, semi- and non-volatile organics are susceptible to extraneous background contamination and cross-contamination. These compounds are also susceptible to sorption and desorption reactions with the purging and sampling equipment. Equipment should be made of relatively inert material. Good decontamination procedures are necessary to avoid any cross-contamination between wells. These samples are not usually preserved or filtered; however, you should cool them to $4^{o}C$ immediately after collection.

2.6.5 Inorganics

Inorganic samples (e.g., dissolved metals) are typically quite susceptible to aeration, oxidation, precipitation, coprecipitation, extraneous contamination and cross-contamination during sampling, filtering and handling. Aeration of a sample, usually caused by excessive turbulence, can alter a sample's water quality by saturating it with oxygen. If proper care is not taken, the equilibrium of dissolved metals, which are usually in a reduced state in groundwater, can be shifted to a more oxidized state. Precipitation of metal oxides can lead to the adsorption, co-precipitation, or both, of other dissolved cations and anions, thereby causing a decrease in the concentrations of dissolved metals in a sample.

Unless WDNR requires or approves otherwise, inorganic samples must be filtered and preserved immediately after collection. WDNR's Wastewater permitting program requires total recoverable metals results, which are not filtered, when evaluating potential impacts of a groundwater remediation system discharging its effluent to a surface water. If sample filtering is required, refer to Section 2.8.

2.6.6 Major and Minor Ions

WDNR typically requires monitoring of major and minor ions as indicators of groundwater quality at a site or facility (e.g., solid waste landfill). Section NR 140.20, Table 3 lists indicator parameters that WDNR may require a site or facility to monitor. Some parameters that represent overall groundwater solution composition include total dissolved solids (e.g., chloride, sulfate, sodium and bicarbonate), conductivity, pH, alkalinity, major cations (calcium [Ca^{2+}], magnesium [Mg^{2+}], potassium [K^+] and sodium [Na^+]),and major anions (chloride [Cl], nitrate [NO_3] and sulfate [SO_4^{2-}]).

Ions such as Na^+, Mg^{2+}, K^+ and Cl, are usually analyzed at high limits of detection, are relatively stable and are not subject to the same degree of alteration during collection and handling as VOC and dissolved metal samples. These ions are usually analyzed and regulated at milligrams per liter (mg/l) or parts per million (ppm). Collection, handling and decontamination procedures for these ions can be less stringent than that which is required for VOCs and dissolved metals.

Other ions such as manganese (Mn^+), ferrous iron (Fe^{2+}), carbonate (CO_3^{2-}) and bicarbonate (HCO_3^-), although typically analyzed at the mg/l or ppm level, are unstable and subject to alteration, usually from aeration and therefore require rigorous collection and handling procedures similar to those required for VOCs. However, equipment decontamination procedures do not need to be as stringent as is required when collecting VOC samples.

When a groundwater sample is brought to the surface, dissolved Fe^{2+} and dissolved Mn^{+} in the sample may react with oxygen and precipitate out of solution. In addition, CO_3^{-} and HCO_3^{-} ratios may change quickly after a sample is brought to the surface. This reaction may cause calcium carbonate to precipitate out of solution, carbon dioxide to degas from solution and may cause a subsequent rise in sample pH.

2.6.7 Other Sample Parameters

Other parameters that may be altered due to aeration and degassing during sampling and handling include pH, Eh, dissolved oxygen, inorganic carbon, alkalinity, TOC, VOCs, ammonium, nitrate/nitrite, sulfide, cyanide, molybdenum, mercury, selenium and dissolved iron, manganese, zinc, cadmium, lead, vanadium, arsenic and phosphate (Stolzenburg and Nichols, 1986). Chromium and sulfide are also subject to alteration during sampling and handling.

For those who wish to monitor indicators of potential biodegradation that may be occurring in groundwater at a site, vendors offer various colorimetric field kits for quantifying nitrate, sulfate, ferrous iron, manganese and alkalinity. Follow the field test kit's manufacturer's instructions regarding the proper procedures for taking such measurements.

For the collection, preservation and handling of parameters not discussed in this document, refer to other published groundwater sampling procedures documents or articles. Gerba (1988) provides guidance for collecting virus samples from groundwater.

2.7 FIELD WATER QUALITY MEASUREMENTS

2.7.1 Technical Considerations

Several water quality parameters are subject to rapid alteration (caused by aeration, oxidation and the loss or gain of dissolved gasses) when groundwater is removed from a well and exposed to oxygen and atmospheric pressure. Water quality measurements that may be subject to rapid change include, but are not limited to, specific conductance, pH, dissolved oxygen, Eh and alkalinity.

Take water quality measurements while purging, using a closed flow-through cell and parameter-specific monitoring probes (Figure 20). Using a down-well measuring probe is also recommended; however, well water must be flowing past the probe during measuring (i.e., the probe is near pump inlet during purging or you lower and raise it in the water column as you measure). These two methods minimize any contact between groundwater and atmospheric conditions (air and pressure), thus limiting any alteration while you are measuring. If you cannot use either of these methods, take water quality measurements *immediately* after collecting a sample. Otherwise, clearly document that you did not take measurements immediately.

Specific procedures you may use to collect and measure the following water quality parameters are included in the *Groundwater Sampling Field Manual, PUBL-DG-038 96*, the most recent version of *Standard Methods for the Examination of Water and Wastewater*, and the manufacturer's instructions for the equipment.

2.7.2 Temperature

Temperature is an important measurement because it affects the rate of many biological and chemical reaction rates. The temperature of groundwater in Wisconsin commonly remains fairly stable throughout the year at approximately 13°C (55°F). However, shallow groundwater temperatures may fluctuate with changes in seasonal temperatures and in response to precipitation. During spring, summer and fall, shallow groundwater temperatures may elevate in response to a recent rain or surface water (e.g., stream) flowing into the groundwater system in response to a flood crest. Deep groundwater temperatures usually do not fluctuate much and are less susceptible to seasonal temperature fluctuations and the effects of precipitation.

In-field Measurement of Temperature

Whenever possible, measure temperature during or immediately after purging a well. Temperature should be read to the nearest 0.5^{o}C (approx. 1°F); however, instruments having an accuracy of $\pm$ 0.1^{o}C (approx. $\pm$0.2^{o}F) are recommended for determining small differences in groundwater temperatures. Temperature is commonly measured in the field by using one of the following three methods:

1) **Lowering a temperature probe into the water column of a well.** This is an in-situ measurement. Take readings during or immediately purging. This method ensures that your temperature values most closely represent actual groundwater temperature. Submerse the probe in the water long enough for it to equilibrate with the groundwater temperature. A couple of minutes usually suffices.

   In many cases, other instruments' probes (e.g., conductivity, pH, dissolved oxygen) provide temperature readings along with the primary parameter being measured. Probes that measure temperature must have their accuracy periodically checked against a good mercury-filled thermometer or a precision thermometer certified by the National Institute of Standards and Technology.

2) **Inserting a temperature probe into a closed flow-through cell.** If you use low-flow purging while monitoring indicators parameters, you can measure temperature as part of this process.

   During low-flow purging on a very hot or cold day, the sample will artificially warm up or cool down as it travels through the sampling tube and flow-through cell. After you collect samples, increase the purging rate until the water temperature once again stabilizes. Record this new stabilized reading as the actual groundwater temperature. You can usually minimize or avoid this problem by using a short sample tube and shielding or insulating the flow-through cell from heat and cold.

3) **Inserting a good thermometer into a sample.** The thermometer should be marked for every $0.1^{\circ}C$ (approx. $\pm 0.2^{\circ}F$). Protect the thermometer from breakage during use and transport.

For this method to work effectively, measure the temperature from the sample soon after collecting it (e.g., within five minutes) or while purging. If measuring temperature while purging, allow the water to overflow from the sample container while measuring. Wait until you've collected at least three stable readings to record the final temperature. If the water you are sampling is hazardous, properly collect, contain and dispose of the overflow water.

2.7.3 Specific Conductance (Electric conductance and conductivity)

Conductivity measures an aqueous solution's ability to conduct or carry an electric current. This "ability" depends on the presence, total concentration, mobility and valence of charged ionic species (e.g., Ca^{2+}, Na^+, Mg^{2+}, HCO_3^-, Cl^-), and the solution's temperature. Most soluble inorganic compounds are good conductors. Specific conductance is measured between two chemically inert probes spaced a fixed distance apart.

Changes in a well's groundwater conductivity frequently indicate groundwater contamination (e.g., landfill monitoring). Conductivity measurements approximate total dissolved solids (TDS) in a sample. The TDS of a sample can be approximated by multiplying the sample's conductivity (in µmhos/cm) by an empirical factor ranging from 0.55 to 0.9. This factor depends upon the soluble substances in the sample and its temperature (Standard Methods, 19th Ed., 1995).

Conductivity measurements are usually recorded as micromhos per centimeter (µmhos/cm). For instruments providing readings in the International System of Units (SI):

1 mS/m (milisiemens/meter) = 10 µmhos/cm and, conversely,
1 µmhos/cm = 0.1 mS/m

In-field Conductivity Measurements

Before use, the conductivity instrument and probe must be calibrated against a standard potassium chloride (KCL) solution. This can be done in the laboratory or in the field. Use the calibration procedures described in the manufacturer's instructions for the instrument and refer to the most recent version of *Standard Methods for the Examination of Water and Wastewater.* Measure conductivity <u>before pH</u> because salts contained in the pH probe may artificially increase sample conductivity.

Because conductivity depends on temperature, be sure to convert all conductivity measurements to $25^{\circ}C$ if your instrument doesn't automatically do so. Measurements collected at various temperatures can thus be compared. The farther the sample temperature deviates from $25^{\circ}C$, the greater the possible error in converting the reading to $25^{\circ}C$. According to *Standard Methods*, 19th Ed., 1995, the conductivity of a sample measured at a temperature other than $25^{\circ}C$ can be converted to conductivity at $25^{\circ}C$ by:

Specific Conductance @ 25°C =   sample conductivity (µmhos/cm)
$$\text{1 + 0.0191 } x \text{ (sample temp. }^o\text{C - 25)}$$

Conductivity meters that do not automatically correct readings to 25°C usually include a conversion table or chart to allow for this correction. In addition to temperature, a sample's conductivity can change as the sample is exposed to the atmosphere. Therefore, make sure you measure conductivity in the field as soon as possible after purging. Some meters must have their "zero" and "red line" checked and adjusted before use. Check the manufacturer's instructions before using the meter.

Most problems related to collecting poor conductivity data include fouling of the electrode, improper or no instrument calibration, not allowing the probe to equalize with the sample temperature, and improperly or not converting readings to 25°C.

Some common and acceptable methods for measuring conductivity in the field include:

1) **Lowering a conductivity probe into the water column of the well.** This is an in-situ measurement. Take readings during or immediately after purging. This method ensures that your conductivity values most closely represent actual groundwater conductivity. Submerse the probe in the water long enough for it to equilibrate with the groundwater temperature. A couple of minutes usually suffices.

   If you use this method before disturbing the water column (e.g., pumping or bailing), you may be able to detect conductivity stratification, which may indicate the well is screened in multi-layered strata.

2) **Inserting a conductivity probe into a closed flow-through cell.** You can do this in conjunction with the low-flow purging method.

   During low-flow purging on a hot or cold day, the sample will artificially warm up or cool down as it travels through the sampling tube or flow-through cell. Use a short tubing and insulate or shield the flow-through cell to minimize these effects.

3) **Inserting a conductivity probe into a sample.** For this method to work effectively, measure the conductivity from the sample soon after collecting it (e.g., within five minutes) or while purging. If measuring conductivity while purging, allow the water to overflow from the sample container while measuring. Wait until you've collected at least three stable readings to record the final conductivity. If the water you are sampling is hazardous, properly collect, contain and dispose of the overflow water.

2.7.4 pH

pH measures a solution's hydrogen ion concentration and is also referred to as a solution's degree of acidity or alkalinity. A ph value of 7.0 is considered neutral, while pH values progressively lower than 7.0 are acidic (increased concentration of H^+) and pH values progressively higher than 7.0 are basic or alkaline (decreased concentration of H^+). pH plays a very important role in the chemical composition and valence state of groundwater constituents. A sample's pH will influence and affect

chemical composition, chemical reaction rates, and biological (e.g., biodegradation) processes. For example, pH measurements provide information on the solubility of metals and the valence state of many compounds. As a sample's pH changes, many precipitation, co-precipitation and sorption processes can occur that can alter the sample's chemical composition.

Because a sample's pH can change quickly after collection, it is important to take this measurement down the well, in a flow-through cell, or immediately after collecting a sample. Aeration, oxidation and the loss or gain of dissolved gasses can significantly alter pH. The partial pressure of dissolved carbon dioxide (CO_2) is usually quite different in groundwater than the partial pressure of CO_2 that exists in air at the land surface. The pH is sensitive to the amount of CO_2 dissolved in the sample. According to Shaver (1993), if dissolved CO_2 degasses from a sample, the pH increases (decrease in H^+) and bicarbonate (HCO_3^-) concentration decreases [$HCO_3^- + H^+ \Rightarrow CO_2$ (aq) + H_2O]. A change in sample temperature can also affect the pH by affecting the solubility of CO_2. Also, according to Shaver (1993), microbial respiration and associated CO_2 production in a groundwater sample can lower the pH and increase bicarbonate HCO_3^- [$CO_2 + H_2O \Rightarrow H^+ + HCO_3^-$]. Shaver (1993) provides a good discussion of the bias of pH and alkalinity measurements taken in the field versus later in a laboratory.

In-field pH Measurement

Before use, a pH instrument and probe must be properly calibrated with pH buffer solutions. Two fresh pH buffer solutions (7.00 and 4.00 or 7.00 and 10.00, based on the anticipated groundwater pH), with temperatures within $5^{\circ}C$ of the groundwater samples are required for instrument calibration. Properly fill the probe with salt solution, if required. Follow the manufacturer's instructions for proper calibration and the frequency of calibration for the meter you are using. Read and record pH measurements to the nearest ±0.1 pH units. Some common and acceptable methods for measuring pH in the field include:

1) **Lowering a pH probe into the water column of the well.** This is an in-situ measurement. Take readings during or immediately after purging. This method ensures that your pH values most closely represent actual groundwater pH. Submerse the probe in the water long enough for it to equilibrate with the groundwater temperature. A couple of minutes usually suffices.

    Lower into the well only those pH probes specifically designed to be completely submerged and that can withstand significant hydraulic heads.

2) **Inserting a pH probe into a closed flow-through cell.** You can do this in conjunction with the low-flow purging method.

    During low-flow purging on a hot or cold day, the sample will artificially warm up or cool down as it travels through the sampling tube or flow-through cell. Use a short tubing and insulate or shield the flow-through cell to minimize these effects.

3) **Inserting a pH probe into a sample.** For this method to work effectively, measure the pH from the sample soon after collecting it (e.g., within five minutes) or while purging. If measuring pH while purging, allow the water to overflow from the sample container while measuring. Wait until you've collected at least three stable readings to record the final pH.

If the water you are sampling is hazardous, properly collect, contain and dispose of the overflow water.

Checking and Adjusting the pH of a Preserved Sample

Two common and simple methods are available for checking and adjusting the ph of a sample. The easiest method is to insert a pH probe into a decanted portion of the preserved sample, and check and adjust pH if necessary. The second method involves using pH paper to check and adjust the pH of a decanted portion of the preserved sample if necessary. Section 2.8 of the *Groundwater Sampling Field Manual, PUBL-DG-038 96,* provides step-by-step procedures for checking and adjusting pH by these two methods.

Do **not** check the pH of VOC samples. Use sufficient preservative the first time to ensure the pH of a VOC sample is properly adjusted. Your laboratory should be able to instruct you on the amount of preservative that should sufficiently adjust the pH of VOC samples.

2.7.5 Turbidity

Turbidity measures the clarity, not color, of a water sample. Turbidity is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and microscopic organisms. Turbidity is determined by the ability of light to travel through a sample without being scattered or absorbed. The presence of light-absorbing materials such as activated carbon and the presence of dissolved, color-causing substances that absorb light may contribute to a sample's turbidity (Standard Methods, 19th Ed., 1995).

In-field Turbidity Measurements

Most commercially available turbidimeters and nephelometers give fairly accurate results for measuring a wide range of turbidity values. Most are not designed to be used in a flow-through cell. Report measurements taken with turbidimeters or nephelometers in nephelometric turbidity units (NTUs). According to Standard Methods, 19th Ed., 1995, turbidity should be measured on the day the sample is collected, but you can store the sample in the dark for up to 24 hours before measuring. Shake it vigorously to resuspend any particles before measuring. Use the turbidimeter or nephelometer according to the manufacturer's instructions. Read measurements to the nearest 0.1 NTUs, if possible.

When using a turbidimeter, make sure the glass sample vial is very clean, does not have condensation on it, and that there are few, if any, air bubbles present in the sample. These factors can all interfere with turbidity readings. In addition, if soluble compounds in the sample begin to precipitate out of solution (e.g., dissolved iron or manganese), then the turbidity measurements may be artificially high.

If you do not use a turbidimeter, you can measure turbidity qualitatively by indicating whether the sample has very little turbidity, moderate turbidity or is very turbid, or by a similar descriptive method. Keep in mind that this is a subjective and qualitative way to measure turbidity.

2.7.6 Dissolved Oxygen

Dissolved oxygen (DO) levels in water depend, in part, on the chemical, physical and biochemical activities occurring in the water. Oxygen has a limited solubility in water directly related to atmospheric pressure and inversely related to water temperature and salinity. Both the electrons and energy are transferred in biological and geochemical oxidation-reduction reactions (redox) reactions (Rose and Long, 1988). Low dissolved oxygen levels can limit the bacterial metabolism of certain organic compounds. Dissolved oxygen can significantly affect the valence state of trace metals.

Dissolved oxygen readings can be very useful when you are investigating groundwater contamination from biodegradable organic compounds. Careful DO readings will help delineate the 3-dimensional DO zonation that may be occurring in a contaminated aquifer.

In-field Dissolved Oxygen Measurements

Methods you may use to determine DO in the field include: the Winkler titration method, the electrometric (i.e., dissolved oxygen meter) method, and the colorimetric method. Under field conditions, both the precision and detection limit for DO are approximately 0.2 mg/L (Rose and Long, 1988). The DO meter is simple to use but may be subject to more measurement error than the Winkler method; however, the Winkler method is time-consuming and difficult to perform under some field conditions. Simple colorimetric methods (e.g., supplied by Hach® and CHEMetrics, Inc.), with sensitivity ranging from ±0.1 mg/L to ±1 mg/L, are also available. This method employs a substance (e.g., indigo camine) that reacts with DO in a water sample to form a color. The intensity of the color is directly proportional to the DO concentration in the sample.

If you use a DO meter, check the electrode membrane frequently and replace it at least once a month. Calibrate the DO meter and probe before use. To obtain high quality DO readings, use either the Winkler titration method or a DO meter. Periodically check the meter's performance against the Winkler titration method.

Because groundwater DO can change rapidly when exposed to air, lower a DO probe into a well and place it next to a pump's inlet while purging, or insert a DO probe into a closed flow-through cell (Garner, 1988 and others). Do **not** use suction-lift pumps and air-lift pumps to collect DO samples; loss or addition of dissolved oxygen in the sample is very likely.

Common and acceptable methods for measuring DO in the field include:

1) **Lowering a DO probe into the water column of the well.** This is an in-situ measurement. Take readings during or immediately after purging. To function properly, most DO probes require that water continually flow past the membrane while measurements are being collected. Therefore, if you take DO readings after purging, use either a DO probe equipped with a stirring rod or, less preferably, slowly raise and lower the probe in the water column while collecting readings.

> **Note:** If the drawdown in a water table well is excessive, be aware that cascading water through a well's filter pack and well screen can artificially increase the DO of the in-flowing groundwater.

2) **Inserting a DO probe into a closed flow-through cell.** You can do this in conjunction with the low-flow purging method.

    During low-flow purging on a hot or cold day, the sample will artificially warm up or cool down as it travels through the sampling tube or flow-through cell. Use a short tubing and insulate or shield the flow-through cell to minimize these effects.

3) **Inserting a DO probe into a sample.** For this method to work effectively, measure the DO from the sample soon after collecting it (e.g., within five minutes) or while purging. If measuring DO while purging, allow the water to overflow from the sample container while measuring. Wait until you've collected at least three stable readings to record the final DO. If the water you are sampling is hazardous, properly collect, contain and dispose of the overflow water.

2.7.7 Eh (Oxidation-reduction potential)

Oxidation-reduction (redox) reactions can affect chemical and biological reactions in water by the gain (reduction) or loss (oxidation) of electrons. A common redox reaction occurs when a reduced groundwater sample containing dissolved ferrous iron (Fe^{+2}) is subjected to an increase in the sample's dissolved oxygen content. The dissolved oxygen accepts an electron from Fe^{+2}, thus oxidizing the iron and changing it to ferric iron (Fe^{+3}). Ferric iron then precipitates out of solution as ferric oxide or oxyhydroxides; the dissolved ferrous iron concentration in solution is subsequently decreased.

Redox reactions can occur with elements or compounds existing in one or more valence states (i.e., substances capable of gaining or losing electrons). For a redox reaction to occur, one compound must be reduced while another is oxidized. Redox reactions influence the mobility of metal ions by changing the valence state of metals, which in turn changes the solubility of the metals, causing them to dissolve into or precipitate out of solution.

Microorganisms can act as catalysts to speed up otherwise very slow redox reactions. They use the redox reactions as a source of energy (Domenico and Schwartz, 1990). Under aerobic conditions, oxygen acts as the electron acceptor in biological redox reactions. Under anaerobic conditions, nitrate, sulfate, methane and carbon dioxide may act as the electron acceptor in biological redox reactions. Anaerobic redox reactions typically occur much more slowly than aerobic redox reactions. Many natural attenuation and biodegradation processes and rates depend on redox geochemistry. A thorough understanding of a site's geochemistry is essential to developing a remediation strategy for a site.

According to *Standard Methods*, 18th Ed., 1992 and 19th Ed., 1995, factors that may interfere with the collection and interpretation of Eh values include irreversible reactions, sorption and poisoning effects on the electrodes, sample handling and preservation, the presence of multiple redox couples, very small exchange currents, inert redox couples, and the lack of electrochemical equilibrium of natural groundwater systems. However, *Standard Methods*, 18th Ed., 1992, concludes that when Eh measurements are properly measured and interpreted, Eh values can provide useful information in developing a more complete understanding of water chemistry.

According to Walton-Day et al., (1990), field Eh values can facilitate a comprehensive analytical determination of groundwater redox conditions when used in conjunction with laboratory analyses of other compounds such as redox active metals and anions, total dissolved carbon, and chemical oxygen

demand (COD).

In-field Measurements of Eh

Field measurements of Eh (or redox potential) must be made in an air-tight flow-through cell or down the well. The water must not come in contact with the atmosphere while Eh is being measured. Read Eh meter measurements to $\pm$ 10 millivolts (mV). A positive Eh value indicates that the solution is oxidizing while a negative value indicates that the solution is chemically reducing. Set up and calibrate the Eh meter and electrodes according to the manufacturer's instructions and refer to the most recent version of *Standard Methods for the Examination of Water and Wastewater.* Recalibrate your instrument at least daily and more frequently for turbid, organic-rich, or high dissolved-solids samples (Standard Methods, 18th Ed., 1992). Make sure the reference electrode has sufficient solution for maintaining its salt bridge.

You can measure redox potentials in the field using an inert indicator electrode and a suitable reference electrode. Platinum electrodes are most commonly used. Alternative electrodes are made of materials such as gold and wax-impregnated graphite (WIG). Pretreat platinum and WIG electrodes carefully before field use. Store platinum electrodes in an oxygen-scavenging solution; the electrode may require frequent replacement when exposed to oxygenated groundwater (Walton-Day et al., 1990). The WIG electrodes show no sensitivity to oxygen; however, laboratory tests have indicated possible sensitivity to dissolved organic matter (Walton-Day et al., 1990).*Standard Methods*, 19th Ed., 1995, indicates that silver:silver-chloride or calomel electrodes are commonly used reference electrodes for groundwater samples. Refer to the most recent version of *Standard Methods for the Examination of Water and Wastewater* before attempting to collect and interpret Eh measurements.

Walton-Day et al., (1990) describes an inexpensive, portable, homemade, air-tight flow-through cell that you can use for rapid field determinations of redox potentials in addition to pH, conductivity, ferrous and total iron, nitrite, dissolved oxygen and temperature. Drawings and specifications for constructing the flow-through cell are provided. You can also purchase or rent commercially-available closed flow-through cells.

Relationship of Eh and pH

The relationship between Eh and pH is commonly expressed through Eh-pH diagrams. You can use an Eh-pH diagram to evaluate the stability for both solid and dissolved ionic species in a solution. If a solution has several ions present that can react or have different valence states, the valence state will depend on the Eh and pH of the solution (Fetter, 1993). Eh-pH diagrams show which ions, compounds, solid and dissolved phases, and redox conditions would be expected in an equilibrium solution at various Eh-pH values. Fetter (1993) and Domenico and Schwartz (1990) provide detailed discussions on Eh-pH relationships and diagrams.

2.7.8 Color

Color is measured qualitatively in the field. A change in water color may indicate changes in groundwater quality. "True color" is the color of water due to dissolved substances after colloids and particulates have been removed. Observe color against a white background after filtering a sample. Use common color descriptors (e.g., light gray, dark brown, etc.,) or standardized color descriptors (e.g., color comparison disk for water or *Standard Methods*) to describe sample color.

If you do not filter the sample, any color you observe will be "apparent color." Apparent color is the combination of the color of dissolved substances and the color of colloids and particulates. Even slight turbidity can make apparent color noticeably higher than true color (*Standard Methods*, 19th Ed., 1995).

2.7.9 Odor

Odor can serve as a general indicator of groundwater quality. However, WDNR does *not* require nor advocate smelling water samples. If you do not know the type and approximate concentration of substances in a sample, do not smell it. Some volatile organics, even at low concentrations, are considered hazardous if inhaled (e.g., vinyl chloride).

If you know that the type and concentration of substances are below safe values as established by the Occupational Safety and Health Association (OSHA) or the National Institute for Occupational Safety and Health (NIOSH) Pocket Guide to Chemical Hazards or other acceptable guide, then you may note sample odor. Carefully wave your hand over the sample opening and note any distinct odor. Describe the odor by commonly understood descriptors (e.g., light sweet odor, strong sewage odor, rubber odor, etc.,).

2.7.10 Other Measurements and Parameters

More accurate and detailed hydrogeochemical interpretations of groundwater may require that you determine additional measurements, parameters and constituents (e.g., alkalinity, hydrogen sulfide, carbon dioxide, etc.,) in the field. Include the need for such measurements and analyses in the project's sampling plan.

Alkalinity measures the acid neutralizing capacity of water and primarily includes carbonate (CO_3^{2-}), bicarbonate (HCO_3^-) and hydroxide (OH) ions.

2.8   SAMPLE FILTRATION

2.8.1 Objectives and Considerations

There is much debate among groundwater professionals, researchers and regulators regarding whether or not to filter inorganic groundwater samples. Organic samples are not filtered. The primary objective is to collect representative groundwater samples that include colloids,

particulates, turbidity, and adsorbed inorganic and organic constituents moving through the groundwater under natural flow conditions. A groundwater sample that contains artificially mobilized colloids and particulates may change the concentration of some of the dissolved constituents (e.g., dissolved metals), thus yielding a sample that does not represent true groundwater quality. If you add acid preservative to such a sample without filtering it first, the sample will likely be artificially high in dissolved inorganic constituents.

A great deal of research and discussion in recent years has centered on the causes, problems and solutions associated with artificially-mobilized colloids and particulates, and whether samples should or should not be filtered.

Causes, Problems and Solutions Associated with Artificially-Mobilized Colloids and Particulates

Unfortunately, the processes of drilling, constructing, developing, purging and sampling a well tend to mobilize colloids and particulates that are not moving through the groundwater under natural flow conditions. This artificially-mobilized material may have adsorbed contaminants on its surface and may be made up in whole or in part of naturally-occurring inorganics (e.g., iron, copper, zinc, arsenic, manganese, lead, etc.,).

One thing is clear, the amount of artificially-mobilized material can be reduced in many cases by properly drilling, constructing and developing the well and by using purging and sampling methods that minimally disturb the groundwater in and around the well.

Section 2.5 details the importance of proper well construction and development. It covers well purging and sampling procedures that provide samples with the least amount of artificially-mobilized colloids and particulates. Low-flow purging and sampling procedures consistently collect samples with the least amount of artificially-mobilized colloids and particulates.

To Filter or Not to Filter

Filtering inorganic samples should remove most of the artificially-mobilized colloids and particulates that may have been artificially incorporated into the groundwater samples collected from a well. Yet filtering may also remove colloids and particulates, and any contaminants sorbed to them, that are moving through the groundwater under natural flow conditions. If these naturally-mobile colloids and particulates are filtered out of a sample, the true types and concentrations of contaminants moving through the groundwater will not be known.

Depending on equipment and techniques used, the very process of filtering a sample may alter the chemistry and concentration of dissolved metals and other constituents in the sample. Filtering can change the partial pressure of dissolved gasses (e.g., oxygen and carbon dioxide), pH and redox-state. Filtering can add oxygen by agitation, remove dissolved gasses by negative pressure filtration, add dissolved gasses by positive pressure filtration, and subsequently alter the chemistry and concentration of a sample's dissolved constituents.

Unfortunately, literature available on filtering is inconclusive regarding when, where and under what specific circumstances filtering should or should not be required. The decisions appear to be very specific to each situation, depending primarily on: 1) the contaminants or constituents being collected

and their susceptability to alteration during filtration; 2) the hydrogeologic environment; 3) groundwater chemistry; and 4) the ultimate use and purpose of filtered versus unfiltered analytical results.

Reasons Why Samples Should be Filtered

1. Filtering removes much of the artificially-mobilized colloids and particulates that may be an artifact of the well construction and well purging/sampling process.

2. Wells that purge dry are often constructed in silt and clay formations. Regardless of the purging and sampling technique used, groundwater samples collected from these wells typically have artificially-mobilized colloids and particulates (i.e., high turbidity). Based on the reasons stated below, these samples should be filtered.

3. Some organic and inorganic substances adsorb onto materials (e.g., organic matter and charged materials) in the groundwater. If these adsorbed contaminants are artificially-mobilized but not filtered out before preserving the sample, then analytical results may be artificially high. Artificially high analytical results may cause expensive and unnecessary enforcement action against a site or facility.

4. If artificially-mobilized materials are made up, in whole or in part, of naturally-occurring inorganics (e.g., minerals or metals) and are not filtered out before preserving the sample, then analytical results for dissolved inorganics may be artificially high. Artificially high dissolved inorganic results may cause expensive and unnecessary enforcement action against a site or facility.

5. Artificially-mobilized materials, if not filtered out of a sample, may cause artificial fluctuations in analytical results and false trends in analytical data.

6. Unfiltered samples may clog and interfere with sensitive analytical equipment.

7. If filtering is done on a sample as it is being collected (e.g., direct, in-line filtration) or immediately after, any changes in the chemistry or concentration of constituents in a sample are usually minimal.

Reasons Why Samples Should Not be Filtered

1. Except in cases were a well produces artificially turbid samples regardless of the purging/sampling technique, if a well is constructed and developed properly and low-flow purging and sampling techniques are used, samples primarily consist of colloids and particulates moving through the groundwater under natural flow conditions.

2. Filtering of samples may cause significant alterations to the chemistry and concentration of constituents in a sample.

3. Filtering may remove colloids, particulates and sorbed-contaminants that are mobile under natural flow conditions. Therefore, filtering may cause an underestimation of the amount of contamination that is naturally mobile in the groundwater. Groundwater flowing through fractured bedrock and karst formations commonly has higher concentrations of

naturally mobile materials than does groundwater flowing through unconsolidated materials.

4.   Clogging of a filter membrane may decrease the nominal pore size of the filter, thus removing progressively smaller colloids and particulates. This reduces the consistency of the particle size that is being filtered out of a sample (e.g., 0.45 microns) and increases the chance that naturally mobile materials will be filtered out of a sample. Use of a pre-filter or a larger diameter filter will minimize this problem.

5.   Unless a sample is filtered immediately, the chemistry and concentration of contaminants in a sample will likely be altered.

2.8.2 Filtering Equipment

Many filtering devices on the market are appropriate for filtering groundwater samples. All filtering devices have one thing in common; samples are either pushed through a filter membrane by applying positive pressure, or samples are pulled through a filter membrane by applying negative pressure (vacuum). A filter membrane, also called "filter paper," must always be disposed of after one use. Disposable filtering devices are available, as are those that can be reused after being properly decontaminated.

Filter membranes come in a wide variety of shapes, diameters, surface areas and pore sizes. They are made from a variety of materials. For the filtering of dissolved inorganic samples (i.e., dissolved metals), WDNR requires that a 0.45 micron (µm) filter pore size be used. The filter membrane and pre-filter (e.g., glass microfiber filters) can be of any diameter, shape and surface area that suit the samples being filtered. Filter membranes are commonly made of cellulose acetate, cellulose nitrate, Teflon® or glass microfiber (pre-filters).
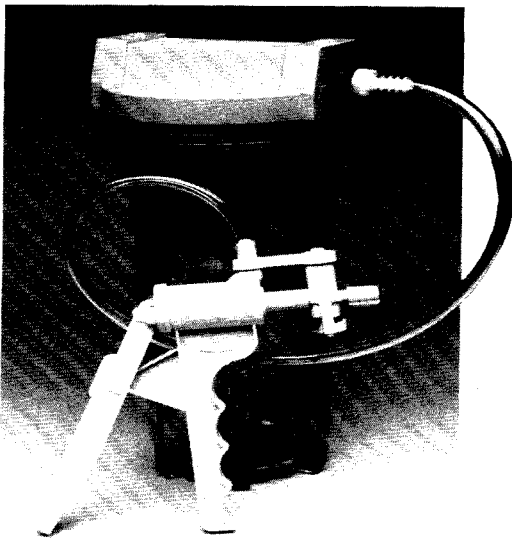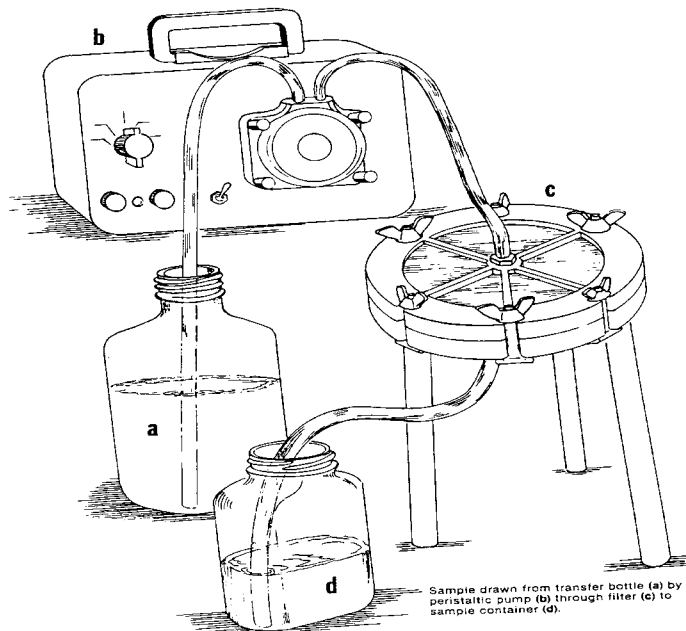
Figure 22 illustrates three positive pressure filtration systems.

2.8.3 Techniques and Procedures

IMPORTANT: Field filter all samples collected for dissolved metals analyses immediately after collecting the samples. There are three general exceptions:

1)   Total metals results are required. This requirement may be in a Wastewater permit, administrative rule, sampling contract or other requirement or agreement.

2)   WDNR grants a verbal or written approval to the responsible party, or its representative, which allows unfiltered metal sample results.

3)   Low-flow sampling procedures are used, three consecutive in-field turbidity readings (spaced ~2 minutes or ~ 0.5 well volumes or more apart) are all 5 NTUs or less **and** WDNR grants verbal or written approval to the responsible party, or their representative, which allows unfiltered metal sample results.

Sample drawn from transfer bottle (a) by peristaltic pump (b) through filter (c) to sample container (d).

Figure 22: Positive pressure filtration systems: a) reusable in-line filtration device outfitted with a sample transfer container, top; b) reusable transfer vessel and hand pump, lower left; and c) disposable, direct in-line filter attached to a pump's discharge line, lower right.

For filtering dissolved inorganic samples (i.e., dissolved metals), WDNR requires that a 0.45 micron filter pore size be used. Flush or rinse filter membranes and sample containers with a minimum of 500 milliliters (mls) of laboratory reagent grade water before use unless the manufacturer has already pre-washed and pre-rinsed filter membranes. In addition, discard the first 150 mls of sample that passes through the filter before filling sample containers. As a general rule of thumb, no more than 50 pounds per square inch (psi) should be applied to a sample to push or pull it through a filter membrane. Use positive pressure filtration rather than vacuum filtration, which causes excessive aeration and agitation of samples.

The filtering technique that consistently provides samples with the highest level of data quality is to use a direct, in-line filter attached directly to a pump's discharge line, pumping at a low-flow rate.

The following filtering procedures are recommended when filtering groundwater samples. The first procedure listed consistently yields the *highest level of data quality.* The last procedure typically yields a *lower level of data quality*.
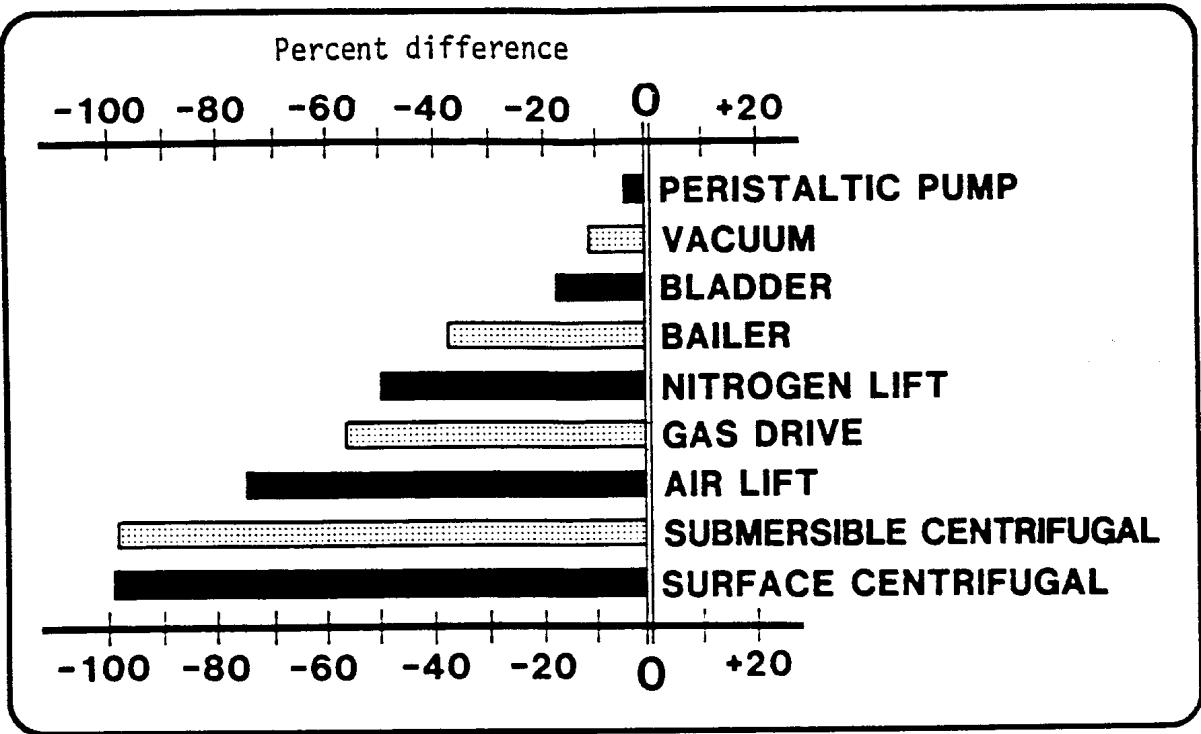
1) **Low-flow purging and sampling, no filtration and three consecutive turbidity readings of 5 NTUs or less.** This procedure involves purging a well at 1 L/min (0.26 gpm) or less and sampling the well at 300 ml/min (0.1 gpm) or less. The sample does not require filtering if its turbidity is 5 NTUs or less over three or more stable readings (spaced ~2 minutes or ~ 0.5 well volumes or more apart) *and* if WDNR staff has granted either verbal or written approval for no filtration.

    Under this scenario purging and sampling rates should be at or less than natural flow conditions existing in the aquifer. Low turbidity values (<5 NTUs) should reflect the naturally mobile colloids and particulates moving through the groundwater.
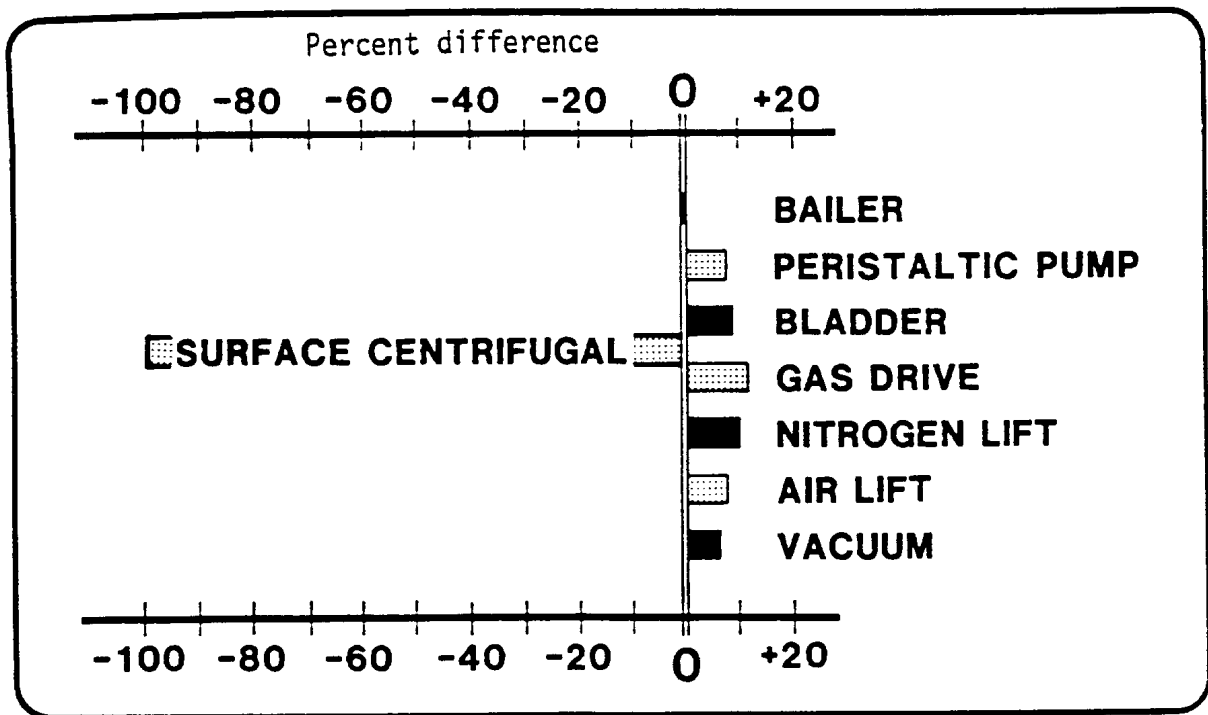
2) **Low-flow purging and sampling and in-line filtration device connected directly to the sample tubing.** This procedure involves purging a well at a flow rate of 1 L/min or less, sampling at a flow rate of 300 ml/min or less and connecting an in-line filter directly to the sample tubing.

    Under this scenario, purging and sampling rates should still be at or less than natural flow conditions existing in the aquifer; however, for certain wells constructed in tills, silts and clays, samples may be turbid even if low-flow techniques are used.

    Using a direct, in-line filter eliminates atmospheric contact with the sample and greatly reduces sample alteration during the filtering process. **Figure 23** illustrates the mean percent difference in filterable iron concentrations with in-line filtration and without in-line filtration; losses of filterable iron can approach 100 percent.

Percent difference

```
 -100  -80  -60  -40  -20    0   +20
```

	Method
▮	PERISTALTIC PUMP
▨	VACUUM
▮	BLADDER
▨	BAILER
▮	NITROGEN LIFT
▨	GAS DRIVE
▮	AIR LIFT
▨	SUBMERSIBLE CENTRIFUGAL
▮	SURFACE CENTRIFUGAL

```
 -100  -80  -60  -40  -20    0   +20
```

Without in-line filtration

Percent difference

```
 -100  -80  -60  -40  -20    0   +20
```

	Method
▮	BAILER
▨	PERISTALTIC PUMP
▮	BLADDER
▨SURFACE CENTRIFUGAL▨ ▨	GAS DRIVE
▮	NITROGEN LIFT
▨	AIR LIFT
▮	VACUUM

```
 -100  -80  -60  -40  -20    0   +20
```

3) **Purging and sampling with a bailer and in-line filtration device attached directly to the bailer.** If you use only a bailer for purging and sampling, you can equip the bailer with a gravity-fed or pressure-fed in-line filtration system (Figure 24). If the sample is excessively turbid or silt-laden, this process can be excessively slow and impractical.

4) **Sample is decanted to a container (e.g., transfer or holding vessel) or is poured into a filtering device and field-filtered immediately.** This procedure involves decanting the sample into a container or pouring the sample into the filtering device and then applying a positive pressure or vacuum (not recommended) to force the sample through a filter membrane. Filter **immediately** after collection to minimize sample alteration. Research has shown that iron precipitation can occur as fast as 30 seconds after sampling (Stolzenburg and Nichols, 1985). If possible, use nitrogen or another inert gas to push a sample through a filtering apparatus (note: don't use nitrogen gas if nitrogen compounds are being analyzed). Keep positive pressure as low as possible; less than 50 psi is recommended.

5) **Filtering not done immediately after collection.** Unless the constituents of concern are not subject to alteration by changes in partial gas pressures, pH, Eh and redox potentials, do not use this method. If the constituents being collected are subject to alteration while waiting to be filtered, the resultant analytical data will not represent the chemistry of the well's groundwater.

Geochemical Samples

Puls and Barcelona (1989) recommend that, for accurately estimating the ambient chemical constituents of an aquifer, you should perform filtration in the field with an in-line, non-metallic filter using a large (e.g., 142 mm) polycarbonate-type (thin with sharp pore-size cutoff) 0.1 µm filter. They emphasize minimizing air contact and acidifying samples to a pH of <2 immediately after filtration. Also use dedicated low-flow purging and sampling pumps and procedures when collecting and filtering these samples. Puls and Powell (1992) also recommended using in-line 0.1 µm filters with large surface areas and low-flow purging and sampling procedures for collecting constituents for geochemical modeling purposes.

2.8.4 Decontamination of Filtering Apparatus

If you are using an in-line disposable filtering device, decontamination is not necessary. Never reuse disposable filtering devices, even between "clean" wells.

Decontaminate non-disposable filtering apparatus between each sample you filter. As with any other piece of groundwater equipment, the rigor of decontamination will depend on the contaminants in the sample, regulatory requirements and the level of data quality required. Refer to Section 2.10.3 when decontaminating filtering equipment.
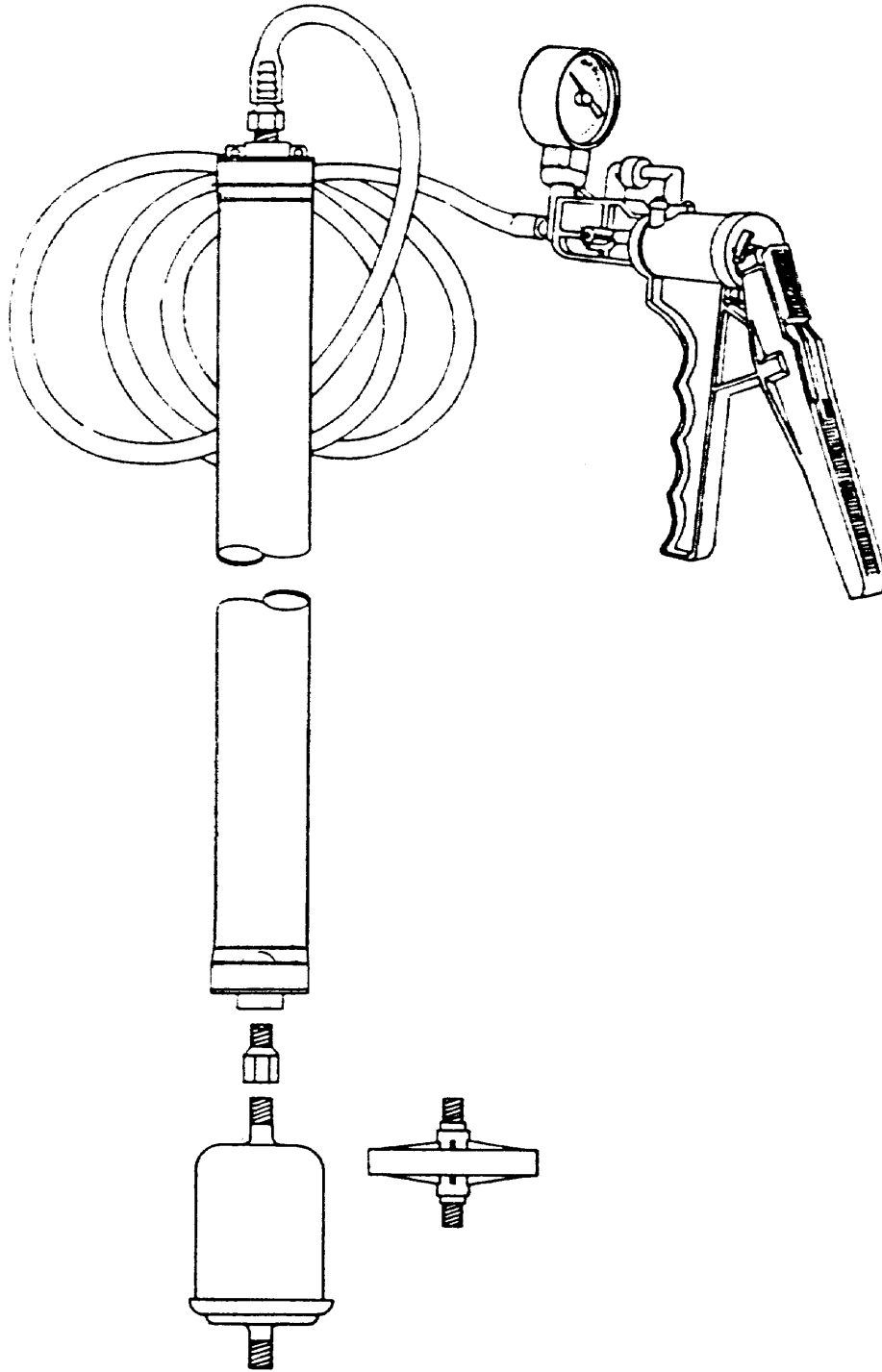
Figure 24:   Pressure-fed in-line filtration system for a bailer (Courtesy of Geotech™).

2.9   SAMPLE PRESERVATION AND HANDLING

2.9.1 Sample Containers and Preservation

Appendix C of the *Groundwater Sampling Field Manual, PUBL-DG-038 96,* lists common sample containers for a variety of compounds and parameters. In some cases, such as when collecting boron samples, using a boro-silicate based glass jar can actually contribute boron to the sample. Take care to ensure that sample containers do not adsorb contaminants onto the container, leach contaminants from the container into the sample, or otherwise change the chemical composition of the sample. Check with the laboratory that is analyzing your samples.

Sample containers may require special cleaning before use. For example, when collecting dissolved metal samples, thoroughly wash the sample containers with a non-phosphate detergent. Rinse with tap water, then nitric acid, again with tap water – then rinse with hydrochloric acid, tap water, and finally a reagent grade water. In most circumstances, the laboratory will do this or will purchase containers that have undergone this rigorous cleaning procedure. Either way, check with your laboratory to see if any special pre-cleaning procedures are necessary.

Appendix C of the *Groundwater Sampling Field Manual*, also lists sample preservatives suitable for a variety of contaminants and parameters. Preserving samples retards biodegradation reactions, hydrolysis reactions, precipitation and coprecipitation reactions and sorption reactions. Sample preservation usually involves reducing or increasing pH by adding an acid or base preservative. Samples are also preserved by cooling them to 4°C. Add preservatives to the container before or immediately after collecting the sample. If you add preservative before collection, take care to minimize sample overflow, which may dilute the preservative. If a sample requires filtration, add preservative <u>after filtration</u>, not before.

2.9.2 Sample Handling, Storage and Transport

After collecting, filtering (if required), preserving and labeling, place the sample immediately on ice in a cooler. Samples must remain at or below 4°C throughout handling, storage and shipping. Add sufficient ice or use another cooling method to keep the samples at or below 2°C. Avoid using frozen cold packs because they rarely keep samples sufficiently cool. If you must use frozen packs, precool the samples to 4°C and add a temperature blank before shipping. The laboratory will use the temperature blank to document the temperatures of the samples upon arrival.

Separate breakable sample containers (e.g., glass VOC vials) with bubble wrap, foam, ice, etc. At least a portion of each container must contact the ice, otherwise the protective layer (e.g., bubble wrap) may insulate the sample from the cooling effects of the ice. Placing samples in a plastic bag can help minimize the chance of cross-contamination among samples should a container break.

Be conscious of analytical holding times and minimize the time between sampling and delivery to the laboratory. Results for samples analyzed after holding times have expired are questionable at best. Laboratories are required to honor holding times. When samples arrive near the end of the holding time, the risk increases that holding times will not be met and you may incur additional costs

to expedite sample analyses. If the laboratory exceeds holding times, results should be flagged. If samples are submitted to the laboratory beyond the holding time, don't be surprised if you get a call suggesting resampling.

Reminder: Chain of Custody procedures are part of the handling procedures. See Section 2.10.5 for more details.

2.10 QUALITY ASSURANCE/QUALITY CONTROL

Following proper QA/QC procedures when collecting samples in the field will help minimize error, variability and bias in results attributable to sampling and handling. Both the equipment and procedures used in collecting and handling groundwater samples have limitations that introduce a certain level of error, variability and bias into the final analytical results.

Quality assurance (QA) procedures for collecting groundwater samples are the checks, such as documentation and quality assurance samples, that establish the type and quality of collected data. For example, a trip blank verifies whether samples were exposed to extraneous contamination during storage and transport, while a field blank verifies whether equipment decontamination procedures were adequate.

Quality control (QC) refers to the plans, equipment and procedures used to verify and maintain the quality of collected data. One important QC procedure – if dedicated or disposable equipment is not used – is to sample wells from least to most contaminated. Do this to avoid cross-contamination between wells and samples. Refer to Section 2.1 for further details.

2.10.1   Quality Assurance/Quality Control Plan

Incorporate QA/QC procedures into the entire sampling and monitoring process. Include the QA/QC procedures for a project in the site-specific sampling and analysis plan (SAP), or less preferably, create a QA/QC plan as a separate plan. The content and level of detail to include in a QA/QC plan will vary according to the project's data quality objectives. Important QA/QC procedures include:

1.   Following a site-specific sampling plan based on data quality objctives.
2.   Using appropriate purging and sampling equipment and procedures.
3.   Decontaminating and storing equipment properly.
4.   Collecting, handling and storing samples properly.
5.   Following sample chain of custody procedures.
6.   Documenting the entire sampling event.
7.   Following proper equipment calibration procedures and properly using and maintaining the equipment.

Other references for developing QA/QC procedures and plans include Van Ee and McMillion (1988) and Kent and Payne (1988). References for evaluating and documenting the quality of

groundwater data, field instruments and measurements include Campbell and Mabey (1985) and Mackiewicz (1990).

2.10.2   Quality Assurance Samples

Trip Blank

The purpose of the trip blank is to determine if any volatile samples have become contaminated with extraneous substances during storage and transport.

Trip blanks are only necessary when collecting VOC, gasoline range organics (GRO), and petroleum volatile organic compound (PVOC) samples. Trip blanks should be prepared and provided by the laboratory analyzing the VOC, GRO or PVOC samples. Trip blanks must be prepared with laboratory *reagent grade water* and analyzed by the same laboratory that is analyzing the volatile samples. *Do not* prepare trip blanks with water (even if distilled or deionized) purchased at a store; there is no guarantee that store-bought water is contamination-free. The trip blank should remain in the same cooler in which the groundwater samples are stored and shipped.

> **Note:** If trip blank holding times permit, trip blanks do not need to be analyzed if VOC, GRO and PVOC compounds are not detected in any of the groundwater samples. Trip blanks have the same holding time as samples.

Include one trip blank per sample batch, that is, at least one per sampling event and one per cooler. If you use more than one vehicle to transport the samples, or if samples are not shipped together, include one trip blank per vehicle or one trip blank per cooler. The easiest way to minimize the number of trip blanks necessary is to store, transport and ship all VOC, GRO and PVOC samples in one cooler.

Field Blank

Field blanks are also commonly called field rinsate blanks, decontamination blanks and equipment blanks. A field blank evaluates the effectiveness of decontamination procedures when equipment is not dedicated to a well or disposed of after one use. If decontamination procedures are effective, there should be no contamination in the field blanks. Field blanks are not required if dedicated sampling equipment or disposable sampling equipment is used.

A field blank consists of a sample of the reagent grade water supplied by the laboratory and used in the final rinse step of the equipment decontamination procedure. Process the field blank water through the equipment the same way you process any other final rinse water.

Collect one field blank for every 10 or fewer samples collected. Analyze the field blank for the same parameters as the samples. If possible, collect the field blank after sampling the most contaminated well.

Field Duplicate

A field duplicate sample is collected to determine the variability of analytical results caused by the sampling equipment and procedures used. Collect field duplicates for sensitive parameters such as VOCs, sorptive organics and trace metals. Try to choose wells in which the contaminant concentrations have been relatively stable over time and wells that are screened in relatively homogeneous material. This will minimize analytical variability caused by contaminant concentration gradients that may exist in the groundwater system.

Collect one field duplicate for every 10 or fewer samples collected. This frequency can be reduced if it is demonstrated to the satisfaction of WDNR that variability in duplicate samples has been consistently low (typical of low-flow dedicated pump samples). Collect and handle the original sample and field duplicate using the same procedures; however, label them differently so the laboratory cannot tell they are duplicates; thus minimizing any potential bias. If possible, collect the duplicate and original sample from the same grab sampler, from a water discharge splitter if pumping, or immediately after each other if you do not use a discharge splitter.

Field duplicates can provide valuable information for determining if a ch. NR 140 exceedance has occurred for substances that have PALs and ESs below the limit of quantitation (LOQ). If analytical variability of sample duplicates is low, then there is greater confidence that the analytical results represent true values; if not, re-sampling with better equipment or procedures may be appropriate.

> **Technical note:** WDNR reserves the term "replicate" to describe a practice required of laboratories. For the purposes of this document and the field manual, use the term "field duplicate."

Field Split Samples

Field split samples are analyzed at more than one laboratory. The samples should be analyzed by identical laboratory analytical methods to be comparable. Split samples determine the analytical variability between laboratories, not analytical variability caused by the sampling procedures. The technique for collecting split samples is critical and can contribute to variability in laboratory results. Therefore, make sure you collect, store and transport split samples in the same exact manner.

In most cases, samples are split between the site owner or facility and its laboratory, and the regulatory agency and its laboratory. The analytical results are then compared to evaluate variability caused by the two laboratories. Take care when comparing split sample results. Ideally, identical sample handling and analytical procedures are used at both laboratories. If not, consider these factors when comparing split sample results.

Split samples are only required if requested by a regulatory agency or required by state or federal rules or codes. However, you may wish to compare the analytical abilities of two or more different laboratories.

If you are not collecting volatile or oxygen-sensitive samples (e.g., dissolved metals in reduced groundwater), transfer a sample into one large container. Filter and preserve the sample if required

and then split it into two or more separate containers. The containers should be of the same material and volume. Add the same type and quantity of preservative to each container. To avoid using a transfer container, when pumping a sample, use a splitter that divides the water discharge. This will avoid the bias associated with using a transfer container. If you are splitting dissolved metal samples and filtering is required, use direct in-line filtration in combination with a discharge splitter. Do not transfer dissolved metal samples before splitting. Never filter or transfer organic samples, especially VOC samples.

Sequential Samples

Sequential samples are those taken from the same well at the same time but with different sampling equipment or procedures. Sequential samples evaluate analytical variability caused by different sampling equipment or procedures. For example, a facility may use its own bailer to purge and sample a well for VOCs and a regulatory agency may use a low-flow bladder pump immediately afterwards to purge and sample the same well. You can reverse the order that different equipment is used in a well and use field duplicates to further detect and evaluate analytical variability caused by different sampling equipment and procedures.

When collecting sequential samples, try to choose wells in which the contaminant concentrations have been relatively stable over time and wells screened in relatively homogeneous material. This will minimize analytical variability caused by contaminant concentration gradients that may exist in the groundwater system.

Handle, filter, preserve, store and transport a set of sequential samples in the same exact manner. Use only one laboratory and one analytical method to analyze the samples. This will reduce these factors as potential errors and biases.

2.10.3   Equipment Decontamination

Follow proper equipment decontamination procedures to minimize the potential for cross-contamination between wells and maintain data quality. According to Nielsen (1991), without effective decontamination procedures, any data generated by an investigation or remediation are subject to critical scrutiny.

The level of rigor and stringency required for equipment decontamination will depend on 1) the type, concentration, sorption and limits of detection of analytes being sampled; 2) the risk of equipment coming into contact with contamination during storage and transport; 3) regulatory objectives and requirements; and 4) the level of QA/QC procedures required.

Include equipment decontamination procedures in your site-specific sampling and analysis plan (SAP) or the QA/QC plan. Some simple sampling events may not need a QA/QC plan; however, decontamination procedures should still be documented.

All equipment contacting well water or any unclean surface should be properly decontaminated after contact. Examples of equipment that require decontamination include: water level instruments; well purging and sampling devices and accessories; filtration apparatus; and instruments used for field

water quality measurements (e.g., conductivity, pH, turbidity and dissolved oxygen probes and meters).

Address any health and safety issues related to decontamination chemicals, equipment and procedures in the site-specific health and safety plan (refer to Section 2.1.2).

Decontamination Procedures

The American Society for Testing and Materials (ASTM) Method D 5088-90 provides basic guidelines for the "Decontamination of Field Equipment Used at Nonradioactive Waste Sites." The ASTM Method D 5088-90 procedures recommend the following for decontaminating equipment that comes into contact with sample water:

<u>Minimum decontamination procedures</u>

1.   Wash sample contact equipment with a non-phosphate detergent solution (e.g., Alquinox®, Liquinox®).

2.   Thoroughly rinse the equipment with organic-free tap water.

<u>More rigorous decontamination procedures</u>

1.   Wash equipment with a non-phosphate detergent solution and scrub with an inert brush. For internal mechanisms and tubing, circulate the detergent solution through the equipment.

2.   Thoroughly rinse the equipment with organic-free tap water.

3.   For **organic** sampling, rinse equipment with an organic desorbing agent (e.g., pesticide grade isopropanol, acetone, methanol or hexane). For **inorganic** sampling, rinse with inorganic desorbing agent (e.g., dilute [0.1 Normal] reagent grade hydrochloric acid or nitric acid solution). For stainless and low-carbon steel, a more dilute hydrochloric acid solution (1 percent) is recommended.

>   **Note:** If organic or inorganic desorbing agents are to be used, check with your laboratory regarding potential analytical interferences or contamination potential and proper use of these desorbing agents.

4.   Rinse with organic-free tap water (only if inorganic desorbing agent used).

5.   Rinse with deionized (reagent grade organic free) water. Allow the equipment to air dry before next use.

6.   Place equipment in an inert container or wrap in clean plastic or aluminum foil for storage and transport.

In addition, disassemble the equipment as much as possible and wash/scrub it with a non-phosphate detergent during decontamination. Because disassembling equipment can take

time and be hard on the equipment, use your professional judgement to determine when this is necessary.

You may use the ASTM or similar decontamination procedures; however, some procedures may be substituted or modified to meet specific project requirements or more stringent regulatory requirements. Mickam et al., (1989) conducted an extensive survey of equipment decontamination procedures used or required by the U.S. Environmental Protection Agency (EPA) and state regulatory agencies. These procedures may prove to be a useful reference for a variety of decontamination needs.

Decontamination Documentation

At a minimum, decontamination*documentation* should include: 1) the location where decontamination occurred; 2) the individuals performing the decontamination; 3) the decontamination procedures, including the wash solution and rinse water used (e.g., tap water and reagent grade water); 4) equipment storage and transport procedures; and 5) the handling and disposal of decontamination wastewater. If you have already included this information in your site sampling plan, redocumentation is not necessary.

Disposal of Decontamination Wastewater

Depending upon the decontamination methods and solutions you use, your decontamination wastewater may be classified as a hazardous waste by virtue of the contaminants you encounter at the site and the solutions you use to decontaminate your equipment (e.g., hexane, acetone). This is usually not a significant problem if the decontamination wastewater can be treated on-site. If hazardous wastewater needs to be transported and treated/disposed of off-site, this will likely add additional cost to the project. Contact WDNR staff to determine if decontamination wastewater is considered a hazardous waste and the proper ways to manage it if generated.

If decontamination wastewater is classified as hazardous, the cost and time to properly treat and dispose of it can be substantial. A couple of methods for avoiding the generation of hazardous waste is to use dedicated equipment left in the well, thus minimizing or eliminating decontamination wastewater, or to use dedicated equipment not stored in the well but taken back to a laboratory after sampling to conduct proper decontamination procedures.

If the decontamination wastewater is not classified as hazardous waste, you may be able to dispose of it into a sanitary sewer,not a storm sewer. You must get approval from the receiving wastewater treatment plant (WWTP) beforehand. WWTP personnel will usually want to know the type and concentration of contaminants and the volume of wastewater in question. If approval is granted, make sure you don't pour silt-laden water into the sanitary sewer because silt may clog the sewer. Allow the silt to settle out and then decant the clear wastewater into the sanitary sewer. Non-hazardous wastewater may also be treated at an on-site groundwater treatment system, if appropriate.

2.10.4   Equipment Storage and Transport

Properly storing and transporting equipment protects it from a variety of extraneous solid, liquid and airborne contaminants including oils, greases, fuels, solvents, paints and other VOCs.

Examples of appropriate storage include wrapping the equipment in clean aluminum foil, placing it in plastic bags, or placing it in a PVC carrying tube outfitted with end caps. The storage/transport device should be made of relatively inert materials that will not contaminate the equipment. For example, if you use a PVC tube to transport bailers, do not fasten the end caps to the PVC tube with glues that contain VOCs.

You may designate one storage container for contaminated equipment and another for decontaminated equipment. Clearly label the containers as such.

2.10.5   Chain of Custody, Sample Tracking and Security

Following proper chain of custody, tracking and security procedures is essential to maintain the integrity and legal validity of your samples. Sample and shipper security measures ensure that the samples were not tampered with before analysis. This can be very important if sample analytical results come under legal scrutiny. Remember, any project and its data can face legal challenge.

Chain of Custody

Chain of custody records document a sample from collection, through handling, storage and shipment, to final analysis. Such records and documentation include: labeling to prevent sample mixup; container and shipper seals to prevent unauthorized tampering; and documenting who has custody of the samples and when. Accurate records provide a legal record of sample handling, possession and security. If a case is under enforcement action, failure to follow proper chain of custody procedures may cause irreparable damage to a legal case.

A chain of custody record must be completed for each sampling event. Each time a sample, a set of samples, or a sample shipper changes possession, the person relinquishing and the person receiving the samples or shipper must sign, date and record the time on the chain of custody record. Appendix A and B of the *Groundwater Sampling Field Manual, PUBL- WR-168-96* include sample chain of custody forms; however, many laboratories prefer to provide their own forms. Check with the WDNR program, project manager and laboratory regarding proper chain of custody procedures and required records or forms.

> **Note:** If you place the chain of custody record in a sealed shipper, the courier (e.g., UPS) does not need to sign, date and time the record beforehand; however, couriers should keep records of when they pick up samples and where they send them.

Sample Identification

Label samples to avoid misidentification. Use waterproof ink and securely attach labels to bottles, as ice used to cool samples can smear ink and cause labels to detach. Storing samples in plastic bags will help prevent these problems. Labels should include: 1) a unique sample number and Wisconsin Unique Well Number (WUWN) if available; 2) site or facility name; 3) date and time sample was collected; 4) sample collector's initials; 5) preservative added to the sample; and 6) the analysis required.

Sample Seals

Some projects require sealed samples to prevent unauthorized tampering. Sample seals are usually required for enforcement samples. (See the following section, "Samples Requiring Strict Custody.")

Affix the seal to the sample container so that it has to be broken to open the container. The seal should include the initials of the person sealing the container and the date and time the sample is sealed.

Shipping Custody Seals

Some projects require that the sample shipper, which is typically a cooler, be secured to prevent unauthorized access and tampering of samples. If you use a lock, make sure that only authorized personnel have access to the keys. If you use security tape, make sure that the tape must be cut or ripped to open the shipper. Use nylon-reinforced or equivalent tape that cannot be tampered with unnoticed. The tape should include the initials of the person sealing the container and the date and time of sealing. Shipping seals are usually necessary when you are collecting samples requiring strict chain of custody procedures. (See the following paragraph.)

Samples Requiring Strict Custody

Certain samples require strict chain of custody procedures (e.g., those collected as part of a WDNR enforcement case) to ensure legal validity. Refer to Appendix C of the *Groundwater Sampling Field Manual, PUBL-DG-038-96*, regarding strict chain of custody for enforcement and similar samples.

3.0 SAMPLING PROCEDURES FOR WATER SUPPLY WELLS

3.1 OBJECTIVES, PLANS, PREPARATIONS and DOCUMENTATION

Although preparations required for sampling groundwater from water supply wells may not be as rigorous as those required for sampling groundwater monitoring wells, careful planning will help avoid many of the common problems, errors and delays that can occur when sampling groundwater from water supply wells.

3.1.1 Data Objectives

Section 3 of this document and the accompanying *Groundwater Sampling Field Manual, PUBL-DG-038 96* focus on collecting *raw, untreated groundwater* samples from both public and private water supply wells. In the broadest sense, raw, untreated groundwater samples are collected from water supply wells to ensure compliance with ch. NR 140, Wis. Adm. Code., preventive action limits (PAL) and enforcement standards (ES); to define the nature and extent of groundwater problems in Wisconsin; and to define and sample potable wells at-risk from groundwater contamination.

The collection of water supply well samples to ensure compliance with ch. NR 809, Wis. Adm. Code and the federal Safe Drinking Water Act (SDWA) *are beyond the scope and intent of this document and accompanying field manual.* A water supply specialist or investigator from the Bureau of Drinking Water and Groundwater in either the central office or one of the regional offices should be contacted in respect to requirements, procedures and training necessary for collecting ch. NR 809 or SDWA water supply well samples.

Regulatory Objectives and Requirements

The regulatory objectives of monitoring raw, untreated groundwater quality from water supply systems fall under four broad categories: 1) management practice monitoring; 2) problem assessment monitoring; 3) at-risk monitoring and 4) regulatory monitoring.

Management Practice Monitoring

Management practice monitoring activities are designed to evaluate the effects of management practices (e.g., land use practices) that may cause groundwater contamination and ch. NR 140 groundwater standard exceedances. The primary goal is to monitor and evaluate management practices that may cause groundwater contamination and to provide effective management solutions to groundwater quality problems.

Problem Assessment Monitoring

Problem assessment monitoring is intended to define the nature and extent of groundwater quality problems in Wisconsin. It is monitoring to detect substances in groundwater and to assess their significance in terms of type, concentration, movement and extent.

Because it is so expensive to construct wells for the sole purpose of problem assessment monitoring (i.e., monitoring wells), problem assessment monitoring focuses on sampling existing water supply wells and preferably existing, nearby monitoring wells. Construction and sampling of monitoring wells is primarily left to "management practice monitoring" and "regulatory monitoring," through which more resources can be focused on groundwater contamination associated with a particular site, facility or practice.

At-risk Monitoring

At-risk monitoring is intended to define and sample at-risk potable wells in areas where substances have been detected, have a reasonable probability of entering groundwater (such as near a landfill) and in areas where PALs or ESs have been attained or exceeded. Because at-risk monitoring and problem assessment monitoring focus on drinking water wells in affected areas, it is difficult to discern when problem assessment monitoring ends and at-risk monitoring begins. One of the obligations of WDNR's groundwater monitoring program is to provide resources for sampling private domestic wells where there is a legitimate demonstrated concern that a domestic well is at risk. This monitoring is used to evaluate whether contamination is significant enough to warrant an investigation and, where possible, to trace the contamination back to its source and clean up the problem if necessary or required.

Large water supply wells (see Section 3.3.1) have large diameters (e.g., 6 to 12 inch and greater) and are typically open or screened over tens or hundreds of feet of aquifer. For this reason, groundwater samples collected from large water supply wells represent an average concentration of contaminants (or groundwater quality) over a large area of the aquifer. By the time a groundwater quality problem is detected at a large water supply well, it may mean that a very large area of the aquifer has been contaminated. Therefore, as an "early warning" and preventive measure, at-risk monitoring of large water supply wells should be supplemented with monitoring nearby small water supply wells (see Section 3.3.2) and preferably, nearby monitoring wells hydraulically connected to the large water supply well.

Regulatory Monitoring

Regulatory monitoring is done to determine if PALs or ESs have been attained or exceeded and to obtain information necessary to respond to contamination at a specific facility or site. Regulated facilities and sites must monitor groundwater to determine if they are affecting groundwater quality. Many monitoring requirements are contained in permits or administrative rules and apply to solid waste sites, hazardous waste sites and wastewater treatment/disposal facilities. Specific monitoring requirements are dictated by the WDNR programs that regulate these sites and facilities.

WDNR's Bureau of Drinking Water and Groundwater monitors public water systems for bacteriological, chemical and radiological groundwater quality problems. Samples are taken

from public water supplies that rely on groundwater. Bureau staff also conduct special projects to monitor private wells for chemical or radiological groundwater quality problems. Bureau staff often collect samples near regulated facilities in order to define problem areas and advise well owners of potential contamination risks. These activities fall under "problem assessment monitoring" and "at-risk monitoring."

WDNR's Bureaus of Air and Waste Management and Remediation and Redevelopment monitor groundwater quality surrounding regulated waste disposal facilities to determine their potential effects on groundwater quality. This "regulatory monitoring" includes monitoring for both organic and inorganic contaminants. It also includes monitoring at environmental repair sites, hazardous waste sites, spill sites, LUST sites and Superfund sites.

3.1.2 Sampling Plans

To monitor the quality of raw, untreated groundwater, the Bureau of Drinking Water and Groundwater recommends that private wells, non-community wells and public water supply wells be sampled as close to the well's pump as possible, before the water passes through any water softener, water heater, storage or pressure system, or tank. This provides data on groundwater quality before it may be affected by any treatment, distribution, or other water system.

To collect meaningful and valid raw, untreated groundwater data from water supply wells, in general, a sampling plan should be created and consistently followed. Although WDNR does not require that a sampling plan be created before collecting raw, untreated groundwater samples from water supply wells, creating and following a sampling plan makes sense in many cases. A sampling plan is especially important if a water supply well is to be sampled more than once or on a regular basis (e.g., quarterly sampling a private well near a landfill). Section 2.1.2 specifies many of the items which may be included in a sampling plan.

3.1.3 Advance Preparations

Pre-field Work Procedures Checklist - Water Supply Wells

The following checklist should help you conduct a smooth, effectively prepared water supply well sampling program for your project. This checklist, in abbreviated form, is also included in Appendix B of the *Groundwater Sampling Field Manual, PUBL-DG-038 96*

All of the following procedures may not be necessary for each sampling event. Use those procedures applicable to your sampling plan or customize this list as appropriate:

Logistics

1.   Contact the well owner or operator to confirm the sampling date and time and to discuss any site access issues (e.g., keys to a gate, location of sample tap). Remember to explain

the procedures you will be following and ask permission to chlorinate the well after taking measurements.

2.   Determine if the well has been inventoried. If not, obtain a WDNR well inventory number (Wisconsin Unique Well Number - WUWN).

3.   Locate the nearest post office, UPS office, Fedex drop off spot, etc., if you will need to mail the samples from the field. (UPS has a 70 pound weight restriction per container.) Make sure you have proper shipping materials (e.g., sufficient ice to cool samples to$^\circ$C throughout the shipping process).

Laboratory Arrangements

1.   Select a laboratory to perform the sample analysis. Pay careful attention to the laboratory selection process. Selection based on price and turn-around alone may doom the project. Evaluate quality objectives for the project and laboratory analyses. Evaluate reporting requirements and other considerations specific to the project. Check that the laboratory (and subcontracted laboratory) is certified or registered under ch. NR 149 to perform the required sample analysis. Check that the laboratory will follow the proper analytical methods and can meet required limits of detection.

2.   Discuss with the laboratory who will supply what sample containers. If the laboratory will supply some or all of the containers, make arrangements for delivery of the number and type needed - **get extras!** Don't forget QA/QC sample containers and trip blanks if VOC samples will be collected. Appendix C of the *Groundwater Sampling Field Manual,* specifies container types and provides recommendations on the minimum sample volumes for a variety of analytical parameters.

3.   Discuss sample preservation, holding time and shipping requirements with the laboratory. Some laboratories provide preservative already in sample containers, or in other containers (e.g., ampules) that you can later dispense into the sample containers. Discuss QA/QC expectations and the type of information that should accompany analytical results (e.g., LOD and LOQ data).

4.   Inform the laboratory of the date and number of samples you will send. This will help the laboratory prepare for analyzing your samples and meet sample holding times.

5.   Familiarize yourself with chain of custody and other sample tracking procedures.

6.   Discuss any other procedures required by the laboratory (e.g., noting gross sample contamination, field turbidity readings if metal samples are to be analyzed). Some laboratories request previous analytical results for each well to help them determine appropriate sample dilutions up front.

Site History

1.   Review past water quality and sampling data. This will help you determine the well sampling order, which should be least-to-most contaminated, and what types and concentrations of contaminants to expect in each well.

2.   Review the site's hydrogeology and any information available on the well such as its exact location, depth, top of casing elevation, casing diameter and other construction specifications. Previous WSFSs may already have this information recorded.

> **Note:** Copies of most well logs are available from the Wisconsin Geologic and Natural History Survey, 3817 Mineral Point Road, Madison, WI 53705-5100. For well constructor's reports call (608) 262-7430; for geologic logs call (608) 263-7387. At a minimum they will need township, range, section and quarter section location for the well. Order well logs, well constructor's reports and geologic logs<u>far</u> in advance of sampling the well.

<u>Equipment and Field Preparation</u>

1.   Review the sampling plan if required or appropriate.

2.   Organize equipment at least one day before the scheduled sampling day. Refer to Appendix B of the *Groundwater Sampling Field Manual* and use the "Equipment Checklist - Water Supply Well Sampling," or customize your own equipment checklist.

3.   Check that sampling equipment is in good working condition:

> ✓   Test and recharge/replace batteries as necessary.
> ✓   Test the equipment with tap water or calibration standards.
> ✓   Inspect the equipment for defects, loose bolts, frayed wiring, etc.
> ✓   Check the instruments' ability to calibrate and function properly.

4.   Check that all equipment is properly decontaminated and stored for transport (see Section 2.10).

Equipment Checklist - Water Supply Well Sampling

A complete water supply well sampling equipment checklist is included in Appendix B of the *Groundwater Sampling Field Manual, PUBL-DG-038 96* All items included in the checklist may not be necessary for each sampling event. Modify and customize this list as necessary and appropriate.

Coordination with the Well Owner

Inform well owners or operators at least 24 hours in advance of your plans to collect measurements and samples from their wells. If you are sampling a private or domestic well, call the well owner at least one week in advance. Explain what you plan to do and why and the basic procedures you will follow to collect measurements and samples.

> **Note:** If it is necessary to pull a well owner's pump, arrange to have this done far in advance. A licensed well driller should remove and replace the pump. Pulling a

well's pump is an expensive, disruptive and time consuming process and should be considered as a last resort for obtaining information and measurements on a well.

When requesting permission to sample a domestic (private) well, remember that the well owner may hesitate to grant you permission and may view your actions as an invasion of privacy. A clear, non-technical explanation of what you are doing and why can usually put a well owner at ease. WDNR has many brochures on VOCs, nitrate, lead, radon, etc., that can help the well owner/operator better understand why samples are being collected.

Whenever possible, try to work around a well owner's schedule if you need to enter a home or facility to collect samples. Be sure to ask the well owner or operator if it is all right to add chlorine to the well for disinfection after taking measurements. Explain why disinfection is essential and describe the disinfection method you propose to use. If the owner rejects having the well disinfected, do *not* take any measurements; however, you may still collect samples if the owner gives you permission. If measurements on a well are crucial, ask your program supervisor and/or someone in the Water Supply program to talk to the well owner to further explain the necessity of the measurements and of proper disinfection.

If the well owner/operator agrees to allow you to sample, ask for the exact location of the well and sampling tap. Arrange with the well owner or operator for access to the property, well and sampling tap.

It is often much easier to coordinate the sampling of municipal wells versus private wells because municipal wells are usually sampled fairly regularly. These wells typically have taps for collecting water quality samples.

Coordination for sampling irrigation or industrial supply wells may be easy or difficult depending on the well's pumping schedule, access, and whether a sampling tap exists. Coordinate with the well owner or operator far in advance of sampling to avoid problems, misunderstandings and delays.

Initial Coliform Bacteria Testing

Before performing *any* tasks on a water supply well, collect a water sample from the well for coliform bacteria analysis using proper sampling procedures. This sample will indicate whether coliform bacteria were present in the well before measuring.

Wisconsin Unique Well Number (WUWN) Labeling Procedures

Since January 1, 1988, WDNR and other state agencies have been assigning Wisconsin Unique Well Numbers (WUWN) to private water supply wells. Assigning WUWNs allows WDNR to provide well owners with water quality information over the life of an individual well. The WUWNs are assigned during sampling and inspection of wells or automatically at the time of well construction for which the driller fills out a Well Construction Report form. If the private well owner consents, wells with WUWNs are labeled at the fuse box and sampling tap.

WDNR maintains a consolidated list of wells with assigned WUWNs. It is absolutely imperative to ensure that each well has only one WUWN assigned to it! This well inventory list consists of pre-1988 constructed wells that have been inventoried and is maintained by the Bureau of

Drinking Water and Groundwater. Also included are records from the Well Construction Report file (WCR), which the bureau also maintains and which includes wells constructed on or after January 1, 1988. This consolidated list, which includes those wells with assigned WUWNs, is available from the Bureau of Drinking Water and Groundwater in Madison by calling (608) 266-0821, or by calling a water supply specialist/investigator in one of WDNR's regional offices. Be sure to request a current list.

There are three types of WUWN labels. **Printronix labels** are computer-generated WUWN labels assigned to wells constructed on or after January 1, 1988. The assigned number comes from the WCR form the well driller sends to WDNR. After the label is generated, it is sent to the well owner, who then decides if he or she wants to put the label on the fuse box and sampling tap. Because this is a voluntary program, some wells with a WUWN are not labeled.

Blank labels are used for wells with an assigned WUWN when no labels have been affixed. A waterproof marker is used to write in the assigned WUWN. All wells constructed on or after January 1, 1988 have an assigned number. Some older wells sampled by WDNR or others may also have a WUWN. The well owner may have a copy of the WCR or sample report form listing this number.

Preprinted labels come in sheets of six and resemble a license plate sticker. They are used only if no WUWN has been assigned. Check the consolidated inventory list and try to determine if the well was previously assigned a number before using a preprinted label. If you assign a new WUWN, you must fill out a *Groundwater Monitoring Inventory* form. These forms can be obtained from the Bureau of Drinking Water and Groundwater and are included in Appendix B of the *Groundwater Sampling Field Manual*. Unless specifically directed to send them elsewhere, return completed forms to the bureau at P.O. Box 7921, Madison, WI 53707-7921.

3.1.4 Documentation

Carefully documenting a project's monitoring and sampling data and procedures is essential. Documentation provides a permanent record of data collected, equipment and procedures used, sampling personnel, and problems that have occurred at a site. This information will help ensure that water quality data has been consistently collected and that deviations in monitoring and sampling procedures are noted for later data evaluation. Careful documentation also helps protect a project's data from legal scrutiny.

1. **Sampling Plan.** This plan should document the equipment and procedures used during a sampling event. All sampling personnel should read it before heading out to the field and should bring it to each sampling event. Document any deviations from the plan on the "Groundwater Sampling Field Procedures Documentation" sheet included in Appendix B of the *Groundwater Sampling Field Manual, PUBL-DG-038 96*

2. **Well Specific Field Sheet - Water Supply Wells** Document general well information, purging and sampling information, and measurement and samples collected from a well on the "Well-specific Field Sheet - Water Supply Wells." Or, customize your own data sheet.

3. **Groundwater Sampling Field Procedures Documentation**. If you do not have a sampling plan to document your procedures, you may use the "Groundwater Sampling Field Procedures Documentation" sheet included in Appendix B of the *Groundwater Sampling Field Manual*. Customize this sheet to meet your specific needs.

4. **Groundwater Monitoring Inventory Form**. Complete this form if a well has not previously been monitored to document information to be entered into WDNR's computerized data base.

5. **Assigning a Wisconsin Unique Well Number (WUWN) and Well Labeling**. All water supply wells must be documented by having a WUWN assigned to them. Every well must have only **one** WUWN. Water supply specialists/investigators at WDNR regional offices should be able to tell you which water supply wells already have WUWNs.

6. **Chain of Custody Form**. Document the possession of samples collected from water supply wells by completing a chain of custody form and documenting every time the samples change possession.

3.2 MEASURING WATER LEVEL, CASING DEPTH AND WELL DEPTH

Measure the water level, well casing depth and total well depth after receiving training from someone with experience in proper procedures. If available, use a well constructor's log to obtain casing depth and total well depth information. If this information is not available, you may need to remove the well's pump, if the well owner permits, before attempting any measurements. Use **extreme care** so as not to damage or contaminate the well or pump. A licensed well driller, arranged for far in advance, should remove and replace the pump.

Before taking any measurements on a well, ask the well owner/operator to turn off the pump. This is for your personal safety and to protect the pump from any equipment lowered into the well. Make sure the well and wiring are not damaged when taking measurements.

3.2.1 Disinfection Procedures

Properly disinfecting the well before and after collecting measurements is essential to avoid contaminating the well.

Pre-disinfection Procedures for Measuring Equipment

Before placing *any* equipment into a well, properly disinfect the equipment. This will help prevent coliform bacteria, iron bacteria and other contamination from entering the well. Rinse all

equipment parts inside and out with a dilute chlorine solution; use two capfuls of liquid chlorine bleach, with no additives, to one gallon of water.

If there are no inside parts that may become contaminated (e.g., water level indicator, weighted magnetic tape, etc.,), a clean cloth or paper towels soaked in a dilute chlorine solution is acceptable to sterilize the equipment. Do not use towels more than once. You may also use a clean plant spray bottle or laboratory squirt bottle filled with chlorine solution to disinfect equipment.

Decontaminate equipment each time you place it into a different well. In addition, if you insert a measuring device into a well, take it out, and then want to reinsert it back into the same well, disinfect it again first.

Post Disinfection of a Well after Measurements are Taken

Properly disinfect a well after any piece of equipment enters it. Remember to inform the well owner of which disinfection method(s) you will use.

There are no formal standards for determining proper concentrations of chlorine solution to use for chlorinating wells as a preventive measure. A 50 parts per million (ppm) chlorine solution should be adequate for chlorinating wells as a preventive assurance method. One gallon of liquid chlorine bleach, with no additives, mixed with 1,000 gallons of water approximately equals a 50 ppm chlorine solution. Use a sodium or calcium hypochlorite solution. You may use chlorine bleach in a pure state, provided it does not contain any additives such as "fresh scent."

Well Disinfection after Water Level Measurements

Measuring a well's water level usually only affects the first few feet of water. Therefore, disinfection procedures are designed to decontaminate only the upper portion of the water column. Refer to Section 3.3 of the *Groundwater Sampling Field Manual.*

Well Disinfection after Casing Depth and Total Well Depth Measurements

If you measure the well casing depth, the disinfection method you use will depend upon how far you lower the magnet below the water level. Use your professional judgement. If you are unsure how much of the well to disinfect, disinfect the entire well.

If you measure total well depth, disinfect the entire well. The amount of chlorine solution added to the well will depend upon the inside casing diameter, well depth, and amount of water in the well. If you do not know the amount of water in the well, add a minimum of 100 gallons of chlorine solution.

Drive Point Wells

If you need to measure the water level or well depth in a driven point well, hire a registered pump installer to disconnect and reconnect the piping. After collecting the necessary measurements, disinfect the well according to the procedures described above.

Discharge of Chlorinated Water

Unfortunately, there really isn't a good place to discharge the chlorine solution that comes out of the well and faucets. Probably the best place is onto a driveway or other paved area, preferably on a hot, sunny day so the solution can evaporate. Do not discharge chlorinated solution directly into a lake, stream, wetland, lawn, garden, septic system, or sanitary or storm sewer.

3.2.2 Measuring Water Level

Water level measurements taken from water supply wells can provide valuable information on groundwater flow directions and hydraulic head data. However, for water level measurements to be comparable among wells, the wells should be of similar construction and be open to or screened in hydrogeologically-connected and similar geologic units and formations. If the hydrogeology, stratigraphy and well construction for wells in an area are unknown, correlating water levels and hydraulic head measurements among these wells can be misleading and incorrect.

Figure 25 illustrates a lineshaft turbine pump, common for municipal water supply wells, equipped with a water level measuring gauge. If a municipal well pump is not equipped with a water level measuring device (e.g., gauge), then it may be impossible to take a water level measurement on the well.

For domestic wells, you may have to lower a water level measuring device into the well to collect measurements. Exercise caution when removing the well cap and lowering measuring equipment to guard against damaging the well and well cap and contaminating the well. **Figure 26** illustrates some typical examples of sanitary well seals. If the well has a pitless adaptor (see **Figure 27**), it may be impossible to get the water level measuring equipment past it.

Section 2.2 discusses a variety of water level measuring devices, their accuracy, and how to use them.

General Water Level Measurement Procedures

Take a series of water level measurements to determine if the well is still recovering. Take at least three consecutive readings separated by one or more minute intervals and make sure your readings are within ± 0.01 foot (± 0.25 cm) of each other.

If taking a water level measurement to determine groundwater elevations, mark the side of the casing where the water level was measured to provide a reference point for surveying the well.

3.2.3 Measuring Well Casing Depth

If well casing depth or total well depth measurements are required, it is advisable to coordinate pump removal far in advance. Make sure the owner grants permission before you attempt to remove the well's pump. If the owner does not agree or the pump cannot be removed, obtain a copy of the well construction and geologic log, if available, to obtain this information. Copies of well logs for most wells constructed in Wisconsin are available from the Wisconsin Geologic
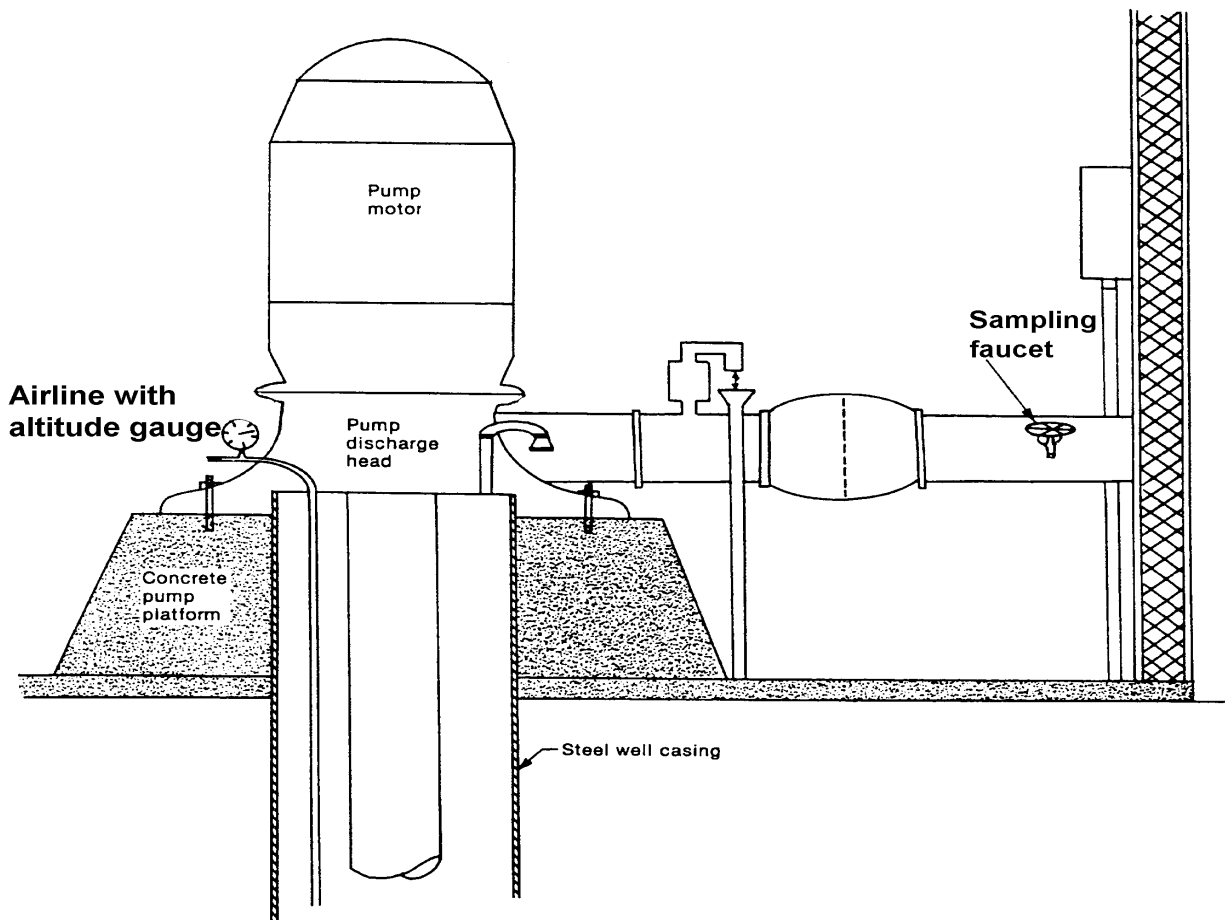
Figure 25: Line-shaft turbine pump (s. NR 812.33, figure 39 - modified, p. 213, 1994).

Screened Well Vent

Compressible Gasket

12" min.

Screened Well Vent (¼" min. dia.)

Conduled box

Pipe Nipple

Expandable Rubber gasket

Electrical Conduit Pipe

12" Minimum

Ground Surface

Well Casing

Compressible Gasket

12" min.

113
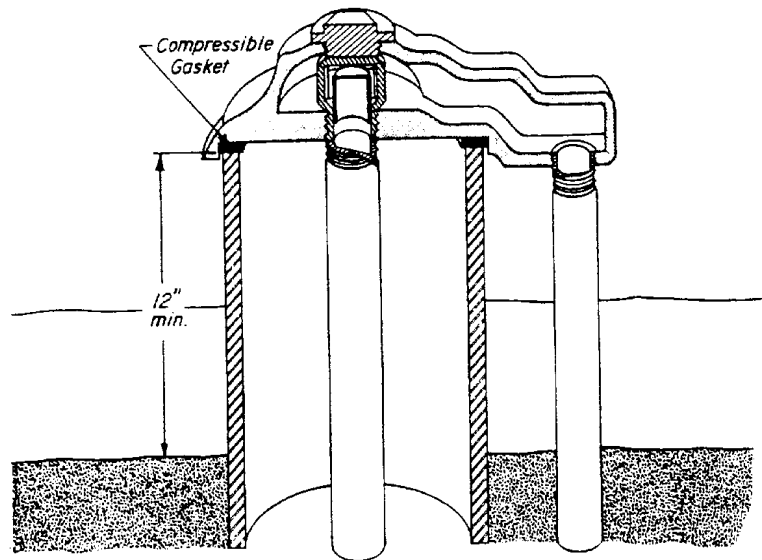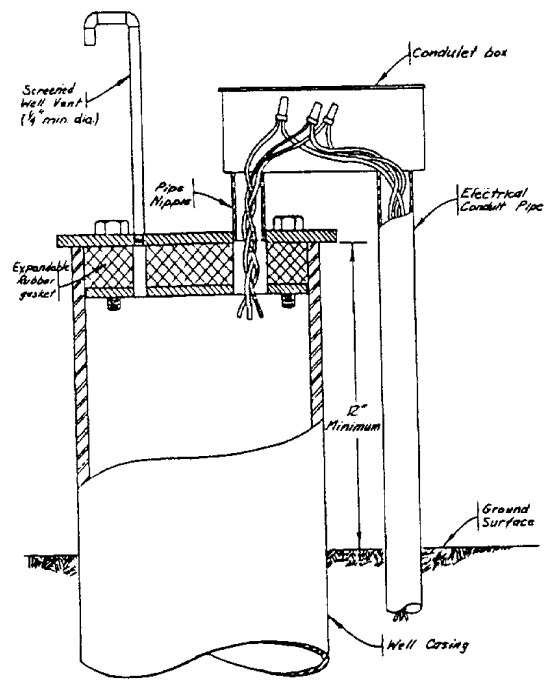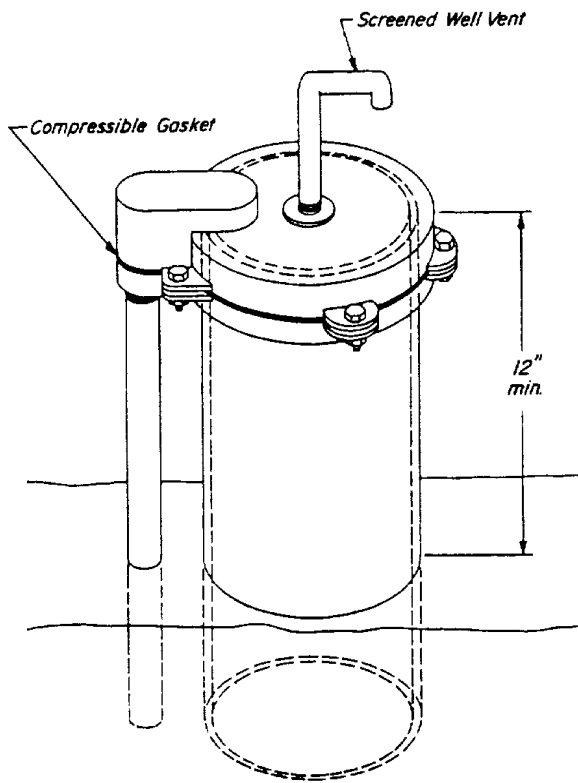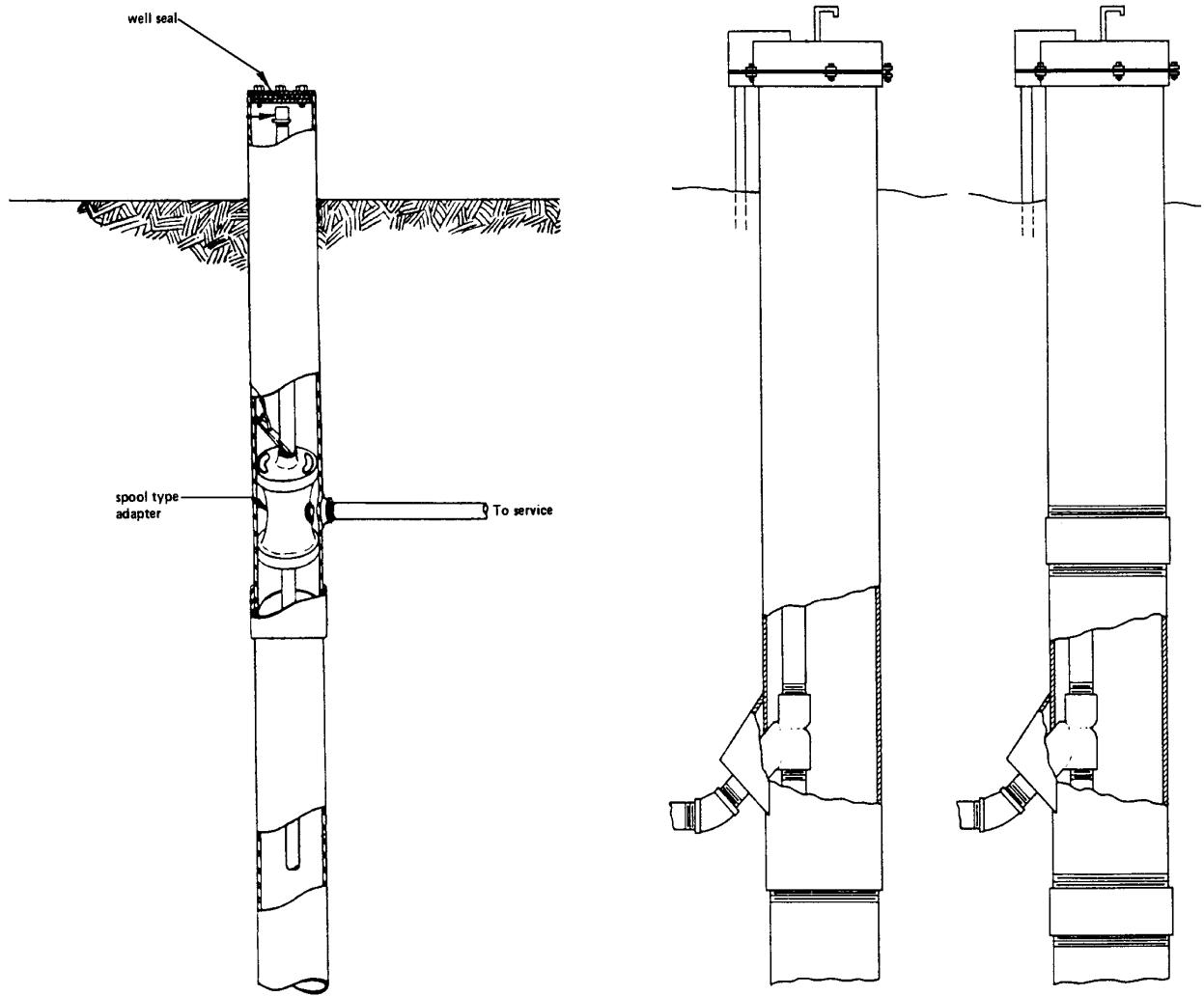
Figure 27: Pitless units: a) factory-assembled spool pitless unit installation, left; and b) two non-spool type pitless units, right (s. NR 812.31, figure 26, modified, and 27, p. 195, 1994).

and Natural History Survey, 3817 Mineral Point Road, Madison, WI 53705-5100. For well constructor's reports call (608) 262-7430; for geologic logs call (608) 263-7387. Be ready to provide the township, range, section and quarter section location for the well.

Typically, casing depth is measured by lowering a weighted magnet attached to a tape down the well's steel casing. When the magnet slips off the end of the casing, this indicates the length of the casing. You can also measure well casing depth with a caliper log or a television camera. However, this equipment is expensive and normally not designed for small diameter wells. Refer to equipment manufacturers' instructions regarding the use and limitation of their devices.

3.2.4 Measuring Total Well Depth

Measure total well depth with a weighted steel tape or weighted synthetic cord calibrated and marked to tenths of a foot. Any tape or cord should have very little or no stretch under tension. D**not** use cotton or cloth cords; they stretch too much and cannot be properly decontaminated.

3.2.5 Post Disinfection Coliform Testing Procedures

Use post disinfection coliform testing for testing the success of the disinfection procedures used on the equipment and well. After the system is*completely* free of any chlorine smell and taste and after waiting several days to a week, collect a post disinfection coliform sample to check for the presence of bacteria. You may need to use a thiosulfate sample bottle because there may be a chlorine residual in the well. Properly-trained well owners, WDNR staff, local health staff, or other trained professionals may collect these samples.

If the post disinfection test for coliform bacteria is positive, a "batch chlorination" may be necessary. Batch chlorination consists of a chlorine solution with a chlorine concentration of approximately 100 ppm or greater. If either the initial coliform test or the post disinfection coliform test is positive for bacteria, *immediately* contact a WDNR drinking water specialist/investigator for further instructions.

3.3   PURGING AND SAMPLING PROCEDURES

Potable water supply systems typically include public water supplies and their distribution systems and private water supplies with single unit plumbing. Non-potable water supply wells include irrigation wells and industrial wells. Potable and non-potable water supply well construction and pump installation are regulated under ch. NR 812, Wis. Adm. Code.

The reasons for purging a water supply well before sampling are the same as those for purging monitoring wells before sampling (see Section 2.5.1); however, the procedures for purging a water supply well are different because you usually do not have direct access to the well. Purging a water supply well before sampling will remove the stagnant water that has been in contact with the well material, pump, plumbing and distribution system.

3.3.1 Large Water Supply Systems (i.e., public water supplies with distribution systems)

Large water supply systems usually service a community or municipality and commonly have an extensive distribution system. To collect raw, untreated groundwater samples from large water supply systems, collect samples from the sample tap or faucet nearest the pump (Figure 25) and located before any treatment, storage or pressure systems.

Make sure the pump is running and water is flowing from the sampling tap for at least one minute, preferably for five or more minutes, before collecting any samples. Record how long the pump was running and how long water was flowing from the sample tap before collecting your samples. Draw a diagram showing where the sample tap is located with respect to the well and any treatment, storage or pressure system.

3.3.2 Small Water Supply Systems (i.e., private water supply and distribution systems)

Sample private and non-community wells as close to the well's pump as possible; preferably before the water passes through any softener, heater, storage or pressure system, or tank. A sample tap is usually located just before the pressure tank. Remove any aerators, filters or other devices from the tap before collecting samples. If you must collect the sample from an outside tap, remove any hoses.

Sampling Tap Located Before the Pressure Tank

If you collect the sample from the well side of the pressure tank and treatment systems, make sure the pump is running and flowing from the sample tap for at least two minutes before collecting any samples. Draw a general diagram of where you collected the samples if appropriate.

If it is difficult or impossible to purge the system from the sampling tap before the pressure tank, choose a sample tap after the pressure tank but still closest to the well, such as a laundry sink faucet.

Sampling Tap Located After the Pressure Tank

If the sampling tap is located after the pressure tank, allow the water to run for at least five minutes and to become cold before collecting any samples. This should allow the stagnant water to be flushed out of the pressure tank and be replaced by freshly pumped water. For large pressure tanks, a longer waiting period may be necessary. Either calculate the necessary flushing time based on the pressure tank volume and purging flow rate, or allow the pump to cycle at least two or three times and wait until the water is cold before collecting your samples.

Document that you collected samples located after the pressure tanks. Record the purging time, tap location, and time of collection. Draw a diagram of where you collected the samples.

3.4 FIELD WATER QUALITY MEASUREMENTS

Perform in-field water quality measurements on unfiltered samples according to the procedures

specified in Section 2.7 of this document and Section 2.6 of the *Groundwater Sampling Field Manual, PUBL-DG-038 96*. For discussion of calcium carbonate saturation indices, see below.

Calcium Carbonate Saturation Indices

You can use calcium carbonate ($CaCO_3$) saturation indices to estimate the scale-forming (precipitate) and scale-dissolving tendencies of water. Estimating this ability of water can be useful for preventing scaling in water heaters or exchanger pipes and for corrosion control. Saturation indices represent the dividing line between "scaling likely" and "scaling not likely." According to Standard Methods, 19th Ed., 1995, the minimum parameters that must be measured to accurately calculate $CaCO_3$ saturation indices include total alkalinity, total calcium, pH, temperature and ionic strength by conductivity or total dissolved solids measurements. Standard Methods, 19th Ed., 1995, recommends that alkalinity samples not be filtered, diluted, concentrated or altered. Refer to the most recent version of Standard Methods for the calculation, interpretation and limitations of saturation indices.

Case Study

Shaver (1993) provides a detailed discussion on the differences in results of field versus laboratory alkalinity and pH and their effects on ion balance and calcite saturation indices. Shaver concluded that laboratory results can provide positive- and negative-biased results for alkalinity and pH that significantly distort the true distribution of calcite saturation indices found in an aquifer. Shaver indicates that he used a field alkalinity method using a sulfuric acid titration to a pH end-point of 4.5 that provides field bicarbonate results accuracy estimated at ± 10 mg/L. Besides titration methods, alkalinity can also be measured in the field by sensor measuring equipment.

3.5 SAMPLE FILTRATION

Do **not** filter samples collected from water supply wells; however, filtration may be appropriate if the samples are being used to model the geochemistry of an aquifer or when you are performing problem assessment monitoring.

3.6 SAMPLE COLLECTION, PRESERVATION AND HANDLING

Section 2.6 details recommendations for collecting groundwater samples. Most of the principles and procedures discussed apply to the collection of groundwater samples collected from water supply wells.

As when collecting groundwater samples from monitoring wells, collect samples and fill sample containers in a manner that minimizes sample alteration. Unless project objectives or regulatory

requirements require otherwise, remove aerators, filters or other devices from a sampling tap before collecting water supply well samples.

3.6.1 Volatile Organic Compounds (VOCs)

Refer to Section 2.6.3 for details on the properties of volatile organic compounds (VOCs) and precautions related to their collection.

Filling VOC Containers

When practical, store empty VOC containers on ice until you use them; this will minimize the loss of VOCs when you fill the containers. Open only one container or one set of containers at a time to minimize exposure of VOC samples to extraneous VOC contamination. After you open a VOC container, add preservative to the empty container, if you haven't already done so. The acid preservative inhibits biodegradation of the VOCs in the sample.

If the sampling tap has an aerator, filter or other device, remove it before sampling. These devices can cause significant aeration and loss of VOC samples. If there is a device on the sampling tap that cannot be removed, be sure to document this. Purge the well as described under Section 3.3 before collecting VOC samples.

When filling VOC containers, tip the container at a slight angle and allow a slow steady stream of water to run down the inner wall of the sample container. This will minimize the agitation, aeration and volatilization of VOCs during filling. Fill VOC containers until a positive meniscus forms at the top of the container (see Figure 21); this should leave no headspace, or airspace, in the container. If airspace remains, VOCs in the water can volatilize to this space and be lost when the container is opened before analysis.

After filling a VOC container and replacing the cap, invert the sample and tap it lightly to check for bubbles. If bubbles are present, discard this sample and fill additional vials. If bubbles are unavoidable, collect numerous samples and save the ones with the fewest bubbles. Remember, one trip blank is required per VOC sample batch (cooler).

3.6.2 Semi-volatiles and Pesticides

Refer to Section 2.6.4.

3.6.3 Other Sample Parameters

Refer to Section 2.6 regarding collection procedures for inorganics (i.e., dissolved metals), major and minor ions, and other sample parameters. One procedural exception is that water supply samples are **not** filtered; therefore, do not filter dissolved metal samples collected from water supply wells.

3.6.4 Sample Containers and Preservation

Refer to Section 2.9.1 for information on sample containers and preservatives for a variety of common parameters and substances.

3.6.5 Sample Handling and Storage

Refer to Section 2.9.2 for information on handling, storing and transporting samples.

3.7 QUALITY ASSURANCE/QUALITY CONTROL

Use the quality assurance and quality control procedures and requirements described in Section 2.10 to ensure the integrity of the samples you collect. Consult with a WDNR water supply specialist if different QA/QC procedures are required or requested.

4.0 VADOSE ZONE SOIL-WATER MONITORING

4.1 INTRODUCTION

The vadose zone, commonly referred to as the unsaturated zone, is the subsurface area that extends from the ground surface to the water table surface. The vadose zone includes the capillary fringe where the soil and geologic material may be saturated; this is why the term vadose zone is preferred over unsaturated zone. In addition, perched groundwater may also exist within the vadose zone.

In Wisconsin, the thickness of the vadose zone is commonly less than 50 feet (15 meters). In the western United States, the vadose zone may extend to several hundred feet deep. A complete discussion of vadose zone monitoring is beyond this document's scope; however, some of the more salient aspects are covered.

Soil water samples are commonly collected to monitor the performance of a facility (e.g., landfill). These samples can act as an early warning system that contamination is moving through the vadose zone and may intersect and affect groundwater quality. WDNR may require vadose zone monitoring beneath a regulated facility, commonly a landfill, to provide early detection of contamination before it reaches groundwater. The advantages of early contaminant detection are both environmental and financial. Operational systems may be modified to prevent or minimize further releases of the contaminant to the soil, thus preventing or minimizing extra compliance monitoring and the potential expense of remediating contaminated groundwater.

When a contaminant leaks from a landfill or is spilled on the land surface, it migrates downward through the vadose zone under the forces of gravity, surface tension and capillary action. To determine the chemical composition and monitor the soil-water quality in the vadose zone, a soil-water sample must be collected. However, soil-water is held in the vadose zone under tension between the soil and water and therefore, a suction or vacuum must be applied to the soil-water to extract a sample.

4.2 LYSIMETERS AND FREE DRAINAGE SAMPLERS

Suction or vacuum lysimeters are devices commonly used for collecting soil-water contained in the vadose zone. Collection basin lysimeters or percolation lysimeters allow the free drainage of soil-water into a collection basin from which a sample may be recovered.

4.2.1 Technical Considerations

Choosing appropriate soil-water sampling equipment for a particular project and site conditions depends on many factors. Some include:

- Type, characteristics and constraints of the soil from which soil-water samples are collected.
- Chemistry and stability of the soil-water being sampled.
- Depth below the ground surface from which samples are collected.
- Soil-water flow regimes in the vadose zone.
- Volume of the samples required.
- Reliability, durability, availability and cost of the equipment.
- Installation requirements of the sampler and associated site constraints.
- Ease of operating and repairing the equipment under field conditions.
- Equipment operation limitations and difficulties due to climate.
- Degree of sample alteration due to sampler operation.

4.2.2 Suction (or Vacuum) Lysimeters

Suction or vacuum lysimeters consist of a hollow porous cup typically located at the end of a hollow tube. When you operate them, a suction or vacuum draws soil-water into the cup. After a sufficient volume of soil-water has entered the lysimeter, you either apply a suction or a positive pressure to bring the sample to the surface through the tubing.

In theory, an applied suction should be able to lift water up to 32 feet (10 meters); however, in practice anywhere from 15 to 25 feet (4.5 to 8 meters) is the upper limit of a suction lysimeter's effectiveness. **Figure 28** illustrates a simple, easy to operate, low pressure-vacuum lysimeter. This device commonly has a maximum operational depth of approximately 50 feet (15 meters). Pressure-vacuum lysimeters that have a low bubbling pressure porous section (made of PTFE such as Teflon®) have a maximum operational depth of approximately 150 feet (45 meters). High pressure-vacuum lysimeters have a maximum operational depth of approximately 300 feet (90 meters). High pressure vacuum lysimeters have a check-valve in a transfer tube (see **Figure 29**) or a separate chamber between the porous section and sampler casing.

Collecting Soil-water Instead of Sucking Air

When you use a suction or vacuum lysimeter, make sure the device is collecting soil-water, not just sucking air. The maximum suction pressure that a saturated porous section of a sampler can withstand before air enters is a function of the pore configuration and pore size and the degree of hydrophilicity (water-loving) and hydrophobicity (water-hating) of the porous section. The maximum suction pressure for a sampler is commonly measured by its "bubbling pressure." Bubbling pressure is commonly measured by saturating the porous section of the sampler, immersing it in water and applying positive air pressure to the inside of the porous section. The pressure at which air starts bubbling out of the section and into the water is its "bubbling pressure." The bubbling pressure is a good indicator of a sampler's ability to collect a soil-water sample under various soil conditions (ASTM Method D 4696 - 92).

Soil-water tension will also have a profound effect on the ability of a suction lysimeter to collect a soil-water sample. The dryer the soil and the lower its hydraulic conductivity, the more slowly soil-water will flow into a sampler. Soil-water tension above approximately 60 centimeters of barometric pressure (cbar) for coarse-grained soils and above approximately 80 cbar for fine-grained soils will not allow soil-water to enter a suction lysimeter (ASTM Method D 4696 - 92).

VACUUM OR PRESSURE TUBE

SAMPLE DISCHARGE TUBE

BENTONITE SEAL

PLUG

BACKFILLED "NATIVE SOIL"

PVC OR PTFE CASING (2" DIAMETER)

POWDERED QUARTZ

POROUS CERAMIC TIP

BENTONITE
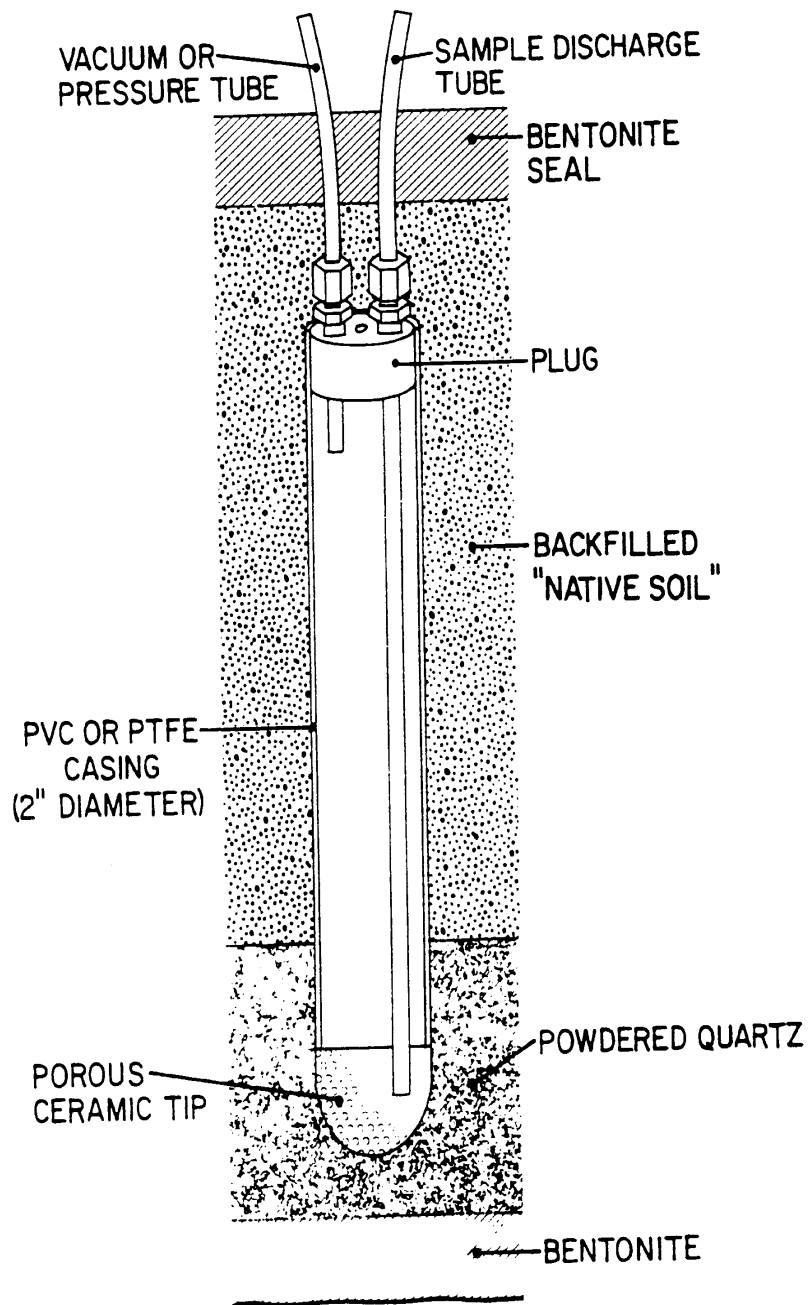
Figure 28: Suction or vacuum lysimeter and installation.
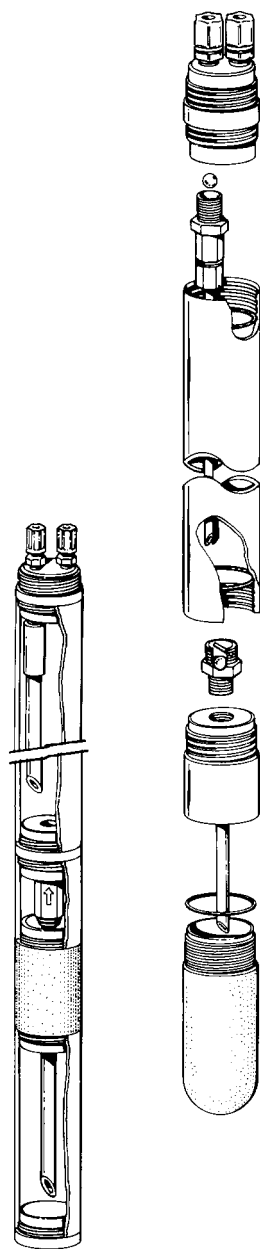
Figure 29:   Deep sampling lysimeters (Courtesy of TIMCO[TM]).

Suction lysimeters can be modified so that a vacuum is applied to draw the soil-water sample into the lysimeter and then a positive pressure is applied to force the sample up the sample tubing or discharge line. The type, design, material, installation and operation of pressure-vacuum lysimeters vary greatly. A complete discussion of lysimeters is beyond this document's scope.

Installation, 0peration and Materials

Detailed instructions on the installation, operation and material of specific suction lysimeters and their operation is beyond this document's scope. However, some basic considerations apply to the installation of most types of suction lysimeters. These devices should be installed to a depth that prohibits freezing and damage associated with frost heaving. Line and connection leaks can be minimized by proper sealing and pressure testing before installation. According to Wilson (1991), in order for a suction lysimeter to function properly, it must be carefully constructed and installed.

Before installation, clean the porous ceramic cup section of a suction lysimeter with a 10 percent hydrochloric acid solution followed by a distilled water rinse. This pre-cleaning before installation should remove dust and trace metals that are common artifacts of the manufacturing process.

U.S. EPA (1986b) provides detailed installation instructions for a variety of suction lysimeters. The manufacturer's of these devices should provide detailed instructions related to the installation, operation and limitations of their instruments.

Sample Results

If you collect a sample from a lysimeter over a short period of time (< 1 day), the sample results will represent a grab sample. However, if a suction is applied to the sampler over an extended period of time (days, weeks, etc.), then the results will be more representative of a time-composite sample. Interpretation of lysimeter data is complex and beyond this document's scope; however, lysimeter data's greatest uses are facility performance, early leak detection and contaminant trend analysis.

4.2.3 Free Drainage Samplers

Free drainage samplers are also called collection basin lysimeters, trench lysimeters or percolation lysimeters. For these devices to work, soil-water or leachate must enter the device by force of gravity. Collection basin lysimeter samplers commonly consist of a synthetic material placed horizontally to collect the leachate, a perforated collection pipe and a non-perforated transfer pipe connected to a sampling chamber (see **Figure 30**). The design and installation of gravity style samplers vary greatly – a detailed discussion is beyond this document's scope.
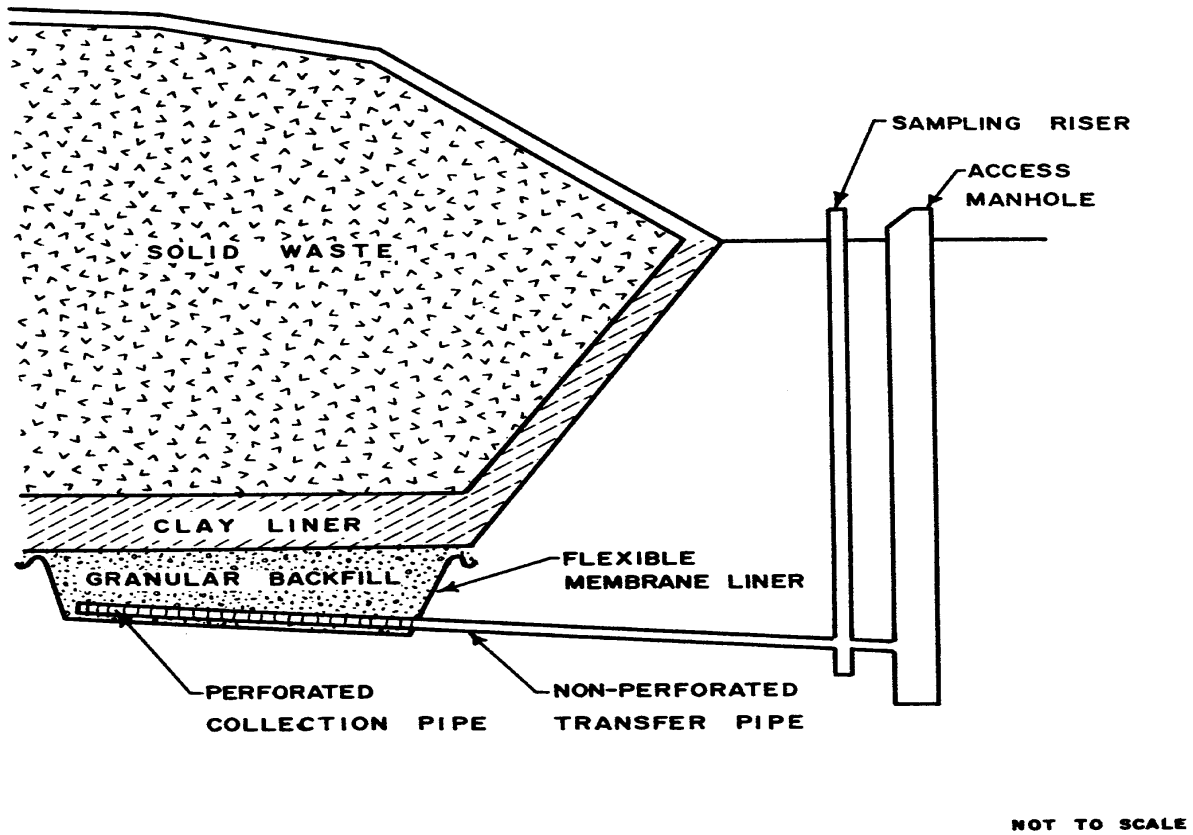
Figure 30: Corss-section of a collection basin lysimeter.

4.2.4 Additional References

American Society for Testing and Materials *Standard Guide for Pore-Liquid Sampling from the Vadose Zone, ASTM Method D 4696-92* provides a detailed and thorough discussion and guidance on the operating principles, descriptions, installations (limited information), operations and limitations for a wide variety of soil-water sampling devices used in vadose zone monitoring. An extensive list of 143 references related to soil-water sampling is also included at the end of this guide.

Other useful publications and articles that discuss soil-water sampling devices and vadose zone monitoring programs include: Wilson L.G., (1981, 1982, 1983 and 1990); Wilson L.G. et al., (1995); Wilson N., (1995); Everett et al., (1982 and 1984); Merry et al., (1986); and Morrison (1983).

APPENDIX A: PURGING AND SAMPLING TECHNIQUES - LITERATURE REVIEW AND EVALUATION

A variety of purging techniques and procedures have been presented in various articles and books. Most authors conclude that the best method for purging a well is often site-, well- and contaminant-specific. No single method appears appropriate for all wells in all hydrogeologic settings or for all contaminants being collected. Well construction, well performance, contaminants being collected, and aquifer hydrogeologic properties should influence your decision on which purging technique is best-suited for a particular well.

Purging a Specified Number of Well Volumes

Historically, WDNR has recommended that wells be purged by removing four well volumes before sampling. A well volume equals the amount of water in the well casing and screened portion of the well at static water level conditions. Water existing in the filter pack is not included.

Although it is impossible to establish a specific number of well volumes that will always remove all stagnant water from all wells, the removal of four well volumes does remove most stagnant water in most wells under most conditions. Maltby and Unwin (1992) conducted several studies of stagnant water removal using different pumps and pump inlet locations in experimental wells. They found that when a peristaltic pump inlet was placed near the static water level and the well purged at 1 L/min, only 1 percent of the original stagnant water remained after four well volumes had been removed. Other authors have concluded anywhere from one to 20 well volumes need to be purged until a well is ready to be sampled; the average number seems to be three to five well volumes.

Advantages of removing a specific number of well volumes

- It is simple, consistent and quick to calculate.
- It may be the only practical means for determining purge volumes when bailers are used.
- Purging four well volumes removes most stagnant water in most wells under most conditions.

Limitations of removing a specific number of well volumes

- There is no guarantee that all the stagnant water has been removed; purging may be overly conservative in some cases, insufficient in others.
- Large purge volumes may be necessary, especially in large diameter and deep wells.
- It may promote continual development and over-development of a well.
- Removing four well volumes is not well-specific or site-specific; it is arbitrary.
- Because high purging rates are typically used, sample turbidity may be artificially high.

Low-Flow Pumping and Monitoring Indicator Parameters for Stability

This approach involves purging the well at a low-flow rate (1 L/min or less) and monitoring indicator parameters such as conductivity, dissolved oxygen (DO), turbidity, pH, temperature and Eh until their measurements have stabilized. Ideally, the well should be purged at a rate at or below the well's recovery rate to simulate the natural flow conditions of the aquifer and minimize sample turbidity.

After the indicator parameters stabilize and purging is completed, the pumping rate is decreased to initiate low-flow sampling (300 ml/min or less). Under most circumstances the decrease in pumping rate during sampling will allow the well to slowly recover, thus further reducing the chance that any remaining stagnant water in the well will be incorporated into the sample. Changing pump placement during sampling or using inflatable packers can also help reduce the chance that any remaining stagnant water will be incorporated into the sample stream.

The following research, studies and articles support the use of low-flow purging and low-flow sampling technique: Gibs and Imbrigiotta (1990), Barcelona et al., (1994, 1988, 1985a), Puls and Powell (1992), Puls and Eychaner (1990), Puls (1994), Panko and Barth (1988), Robin and Gillham (1987), Kearl et al., (1992), Parker (1994), Miller (1993), Bangsund et al., (1994) and USEPA (1992).

Indicator parameters and stability

The tricky part to using this purging method is determining which indicator parameters best "indicate" when the stagnant water in the well has been removed and when fresh formation is the only water entering the sample stream. In addition, determining which ± range or which percent change in indicator parameters represents "stability" is not an easy task.

Barcelona et al., (1994) considered that water quality stability was reached when the following four indicator parameters met the following criteria over one successive bore volume: temperature ± 0.1℃ pH ± 0.10, dissolved oxygen ± 0.2 mg/L and conductivity of ± 10.0 µS/cm. A bore volume equaled the water included in the filter pack, screen and casing of the well. To develop their well stability criteria, the authors looked at various stability criteria recommended in the literature (Gibb et at., 1981, Barcelona et al., 1985 and Gibs and Imbrigiotta, 1990), including hydrogeologic setting, well design and the well's hydraulic performance. Their results indicated that dissolved oxygen and specific conductance were the most useful parameters for indicating stabilization of background water chemistry during purging; while pH and temperature achieved stable values almost immediately and provided little value in determining when purging was adequate. Purging and sampling flow rates were maintained at 1.0 ± 0.1 L/min (sampling flow rates were reduced even more when VOC samples were collected). In almost all cases, indicator parameter stabilization was reached within two bore volumes purged. In addition to considering parameter stability, drawdown was targeted not to exceed 0.5 feet (15 cm) during purging and sampling. The authors used close-fitting dedicated bladder pumps with the pump's intake placed in the middle of the well's short-screened (5 feet or 1.5 meters) interval. They believed that the use of close-fitting dedicated pumps minimized the purge volume required to achieve parameter stabilization.

Barcelona and Helfrich (1986) considered that water quality stability was reached when pH, Eh, temperature and conductivity were within ± 10 percent over a minimum of 4-5 liters purged at a

purging rate of 0.5 to 1 L/min. No rationale was provided for this criteria. Sample rates were 100 to 500 ml/min. Barcelona et al., (1988) considered stability reached when pH, Eh, temperature and specific conductance stabilized to within ± 10 percent over two successive well volumes pumped. The authors recommended that monitoring indicator parameters for stability be done in conjunction with calculating the purge volume required for the hydraulic performance of the well and considering hydrogeologic conditions.

EPA (1992) recommends that, for most wells, purging should continue until turbidity, Eh and dissolved oxygen have stabilized within approximately 10 percent over at least two successive measurements taken three minutes apart. The EPA recommends using a flow-through cell or downhole measurements. The EPA based these recommendations on the following literature: Puls and Powell (1992), Puls and Eychaner (1990), Puls et al., (1990), Puls and Barcelona (1989) and, Barcelona et al., (1988).

The following literature recommends using monitoring of indicator parameters until stability is reached, based on the hydraulic performance of the well, geochemical and hydrogeologic data from the well and the geologic material in which the well is screened: Barcelona et al., (1988), Miller (1993), Bangsund et al., (1994), Nielsen (1990), Robin and Gillham (1987), Maltby and Unwin (1992), Panko and Barth (1988), Puls (1994), Palmer et al., (1987), Unwin and Maltby (1988), Barcelona and Helfrich (1986), Ross et al., (1992), Gibbs and Imbrigiotta (1990) and Barcelona et al., (1994).

Advantages of low-flow purging and monitoring indicator parameters technique

- This technique greatly reduces the likelihood of mobilizing colloids that are not mobile under natural flow conditions. Sample turbidity may be low enough so that filtering is not required.
- Research has shown that for many wells, purge volumes are usually two casing volumes or less; much less than the four well volumes WDNR has historically required.
- Valuable geochemical and water quality data are collected in the process of monitoring the indicator parameters.
- The criteria to determine when the well is sufficiently purged is well-specific, and relatively easy to collect and evaluate under field conditions.
- Many researchers believe this is the most valid method for determining when a well is adequately purged and that fresh aquifer formation water is being sampled.
- The type and number of parameters monitored and criteria used for determining when stability is reached can be based on analytical data, well-specific hydraulic behavior and other hydrogeologic data.
- This technique does not over-develop the well or damage the filter pack which may occur when a well is purged with a bailer or pumped at high flow rates.
- This technique minimizes agitation and turbidity in the well; especially if a dedicated system is used. It reduces the possibility of VOC volatilization, degassing and redox reactions during purging and sampling.

Limitations of low-flow purging and monitoring indicator parameters technique

- This technique does not work well, if at all, in wells that purge dry because these wells typically purge dry before all indicator parameters stabilize.

- It may take an hour or more before all indicator parameters stabilize. This is more typical of portable rather than dedicated pumping systems.
- As with other purging techniques, there is no guarantee that stabilized indicator parameters signify that all stagnant water has been removed.
- If the well is screened across numerous geologic materials, the indicator parameters may take an excessively long time to stabilize.
- Transport, set-up and decontamination of a portable pumping system and indicator parameter equipment can be time-consuming and burdensome.
- Equipment costs are relatively high compared to bailers.
- It may be complicated, impractical and excessively expensive for small sites/facilities that collect few samples, or non-sensitive samples, or do simple compliance monitoring (e.g., small wastewater treatment facilities, small closed landfills).
- Some skill is required in determining which indicator parameter and stability values represent when a well has been adequately purged of stagnant water.

Purging Based on Well Hydraulics and Aquifer Transmissivity

This purging technique, also known as the time-drawdown method, uses theoretical and actual time-drawdown data (from aquifer pumping tests) to calculate when the stagnant water in the casing of the well has been removed. This method assumes that water is entering the well only when drawdown is occurring. The pumping test data are used to calculate a theoretical draw-down curve that can be used to predict the time at which the effects of stagnant water becomes negligible in respect to groundwater sample quality (Maltby and Unwin, 1992). This drawdown curve serves as a guideline, along with monitoring of indicator parameters, for selecting the appropriate purging rate and casing volumes to be removed before sample collection.

When the National Council of the Paper Industry for Air and Stream Improvement (NCASI) tried to use this method on six monitoring wells at different locations in Illinois, it encountered several difficulties (Maltby and Unwin, 1992). These included 1) the inability to reproduce theoretical drawdown curves under field conditions, and 2) the that stability of indicator parameters directly contradicted pump test data stability information.

Barcelona et al., (1985a) and Barber and Davis (1987) provide a detailed description and examples on how this method can be used to calculate purging of monitoring wells.

Advantages of purging based on well behavior:

- It takes into account the well's specific hydraulic flow characteristics and the characteristics of the geologic materials in which the well is screened.
- Provides data on well hydraulics and aquifer transmissivity.
- If used with monitoring of indicator parameters for stability, it should be adequate under most settings for properly purging the well of stagnant water before sampling.

Limitations of purging based on well behavior:

- It requires pumping test data and/or aquifer transmissivity and well efficiency data.
- Pumping test data and theoretical time-drawdown curves may not match actual field conditions.
- It is a time-consuming, relatively complicated process and is not commonly used.

- It only accounts for stagnant water contributed by drawdown in the well casing.
- There is no guarantee that sufficient stagnant water has been removed before sampling if not done in conjunction with monitoring of indicator parameters.

While this method may provide valuable information on the hydraulic performance of a well and aquifer transmissivity, it is probably too time-consuming and impractical for purging monitoring wells regularly. It may be prudent to use this method on a well at least once; then annually thereafter to test a well's hydraulic performance over time and determine whether well rehabilitation is necessary.

Other Available Literature on Well Purging and Sampling

Many articles and publications have been written on well purging and sampling techniques and experiments. Some that may prove useful include the following:

Maltby and Unwin (1988): A field investigation of commonly-used monitoring well purging techniques and pumps (peristaltic and helical rotor) conducted under different conditions including changing the location of a pump's inlet in a well and the use of packers to isolate stagnant water from the pump inlet.

Svavarsson et al., (1995): Unpublished WDNR study compares low-flow pumping with a helical-rotor pump and bailing in their abilities to collect representative and similar VOC data. Study results indicated little or no difference in VOC analytical results collected from the same well with Keck$^®$low-flow pump and a Teflon$^®$ bailer.

Ostergren and Connelly (1994): Unpublished WDNR study compared levels of metals detected in samples collected with a bailer, then filtered, and samples collected using low-flow pumping and not filtered. Results did not show a significant difference in the levels of metals detected using both methods.

Ross et al., (1992): Evaluates a purging method that significantly reduces the volume of water needed to be purged for a 5-inch diameter, deep well.

Barcelona et al., (1994): Evaluates the use of easily-measured indicator parameters during well purging as consistent criteria for determining stabilization of VOCs before sampling.

Puls (1994): Provides a general discussion and summary of the advantages of low-flow pumping for collecting representative groundwater samples.

Gibs and Imbrigiotta (1990): Compares three purging techniques' abilities to collect representative VOC samples by 1) monitoring indicator parameters until stability is reached, 2) arbitrarily removing three well volumes and 3) purging to achieve hydraulic equilibrium between the well and the aquifer.

Pionke and Urban (1987): Looks at the time required for different purging indicator parameters to stabilize for wells constructed in sandstone, siltstone and shale aquifers.

Palmer et al., (1987): Looks at the potential for contaminants to be retarded by a filter pack and the need to let a newly-constructed well equilibrate with the aquifer before sampling.

Puls and Eychaner (1990): Looks at purging rate, filtration and oxidation effects on samples collected for inorganic parameters.

Robin and Gillham (1987): Non-reactive tracers are used to test the effectiveness of various purging techniques.

Puls and Powell (1992): Looks at low-flow pumping procedures to collect representative samples for metals.

Kearl et al., (1992): A colloidal borescope is used to assess the effects of pump inlet placement (bladder and peristaltic), purging, sampling and filtering on sample turbidity.

Pohlman et al., (1990): Evaluates analytical results for samples collected from wells that had little or no purging done before collecting the samples.

Herzog et al., (1991): Evaluates the advantages and disadvantages of different purging techniques and their abilities to collect representative samples.

Herzog et al., (1988): Evaluates purging slowly-recovering monitoring wells and optimal times to collect a VOC sample after purging these wells.

USEPA (1995): Provides a good summary of talks and discussions related to purging and sampling techniques, groundwater monitoring goals and objectives, colloidal transport, filtration, sample handling and documentation.

Macfarlane et al., (1992): Compares analytical results for tar and PAH samples collected from a manufactured gas plant by slow-flow purging and sampling, and traditional pumping and bailing methods.

Meyer, jr., K.A. (1990) Study concludes that dedicated systems are cost-effective, technically superior, and improve data quality and data assurance for groundwater samples.

Barker and Dickout (1988): Compares sample results for VOCs charged with methane and CO_2 using a bladder pump, momentum-lift pump and peristaltic pump.

Gass (1991): Evaluates the ability of the Grundfos Rediflo $2^{®}$ pump to collect "representative" VOCs and inorganic samples under laboratory and field conditions.

Parker (1994): A critical review of several groundwater purging and sampling techniques and devices.

Barcelona et al., (1984): Laboratory study to identify reliable sampling devices for VOCs and gas-sensitive parameters. Compared 14 devices including positive displacement and suction-lift devices and grab samples. Evaluations included availability, portability, simplicity, purging and sampling rates, depth limitations, etc.

Stolzenburg and Nichols (1985): Laboratory study on chemical changes such as CO_2, pH, oxidation, VOC loss, precipitation reactions and adsorption during purging and sampling, and filtration practices.

Snow et al., (1992): Evaluates a Redi-Flo $2^{®}$, ISCO$^{®}$ bladder pump and Teflon$^{®}$ bladder pump to collect pesticide and nitrate samples.

Imbrigiotta et al., (1988): A good study comparing a bladder, gear, helical-rotor and peristaltic pump, a point-source and open bailer, and syringe sampler in their abilities to collect VOC samples and their effects on VOC analytical results.

American Society for Testing and Materials (1994): "Standard Guide for Sampling Groundwater Monitoring Wells," D4448-85a (reapproved 1992).

Barcelona (1988): *Principles of Environmental Sampling.* Provides a good discussion and overview of the entire sampling process.

Van Ee and Mcmillion (1988): *Ground-Water Contamination: Field Methods.* Good discussion of groundwater sampling procedures and techniques.

Hergoz et al., (1991): *Practical Handbook of Ground-Water Monitoring.* Covers all aspects of groundwater sampling including factors affecting groundwater sampling, filtration and preservation.

APPENDIX B: REFERENCE MATERIALS

● Substance Potential to Volatilize from a Water Sample

● Equivalency and Conversion Tables

● Bibliography of Selected Groundwater Sampling and Monitoring Topics

Substance Potential to Volatilize from a Water Sample

Substance	CAS Number	Henry's Law Constant (atm-m^3/mole)	Potential for Volatilizing from Water
Acenaphthylene	208-96-8	1.1×10^{-5}	Low
Acetone	67-64-1	3.9×10^{-5}	Low
Aldicarb	116-06-3	1.4×10^{-9}	Low
Ammonia	7664-41-7	3.2×10^{-4}	Moderate
Anthracene	120-12-7	6.5×10^{-5}	Low
Atrazine	1912-24-9	2.6×10^{-13}	Low
Benzene	71-43-2	5.6×10^{-3}	High
Benzo(a)pyrene	50-32-8	1.1×10^{-4}	Moderate
Benzo(b)fluoranthene	205-99-2	1.1×10^{-4}	Moderate
Bromodichloromethane	75-27-4	1.6×10^{-3}	High
Bromoform	75-25-2	5.5×10^{-4}	Moderate
Bromomethane	74-83-9	6.2×10^{-3}	High
Carbaryl	63-25-2	4.4×10^{-9}	Low
Carbofuran	1563-66-2	9.2×10^{-5}	Low
Carbon tetrachloride	56-23-5	3.0×10^{-2}	High
Carbon disulfide	75-15-0	3.0×10^{-2}	High
Chlordane	57-74-9	4.9×10^{-5}	Low
Chloroethane	75-00-3	6.2×10^{-4}	Moderate
Chloroform	67-66-3	2.7×10^{-3}	High
Chloromethane	74-87-3	8.8×10^{-3}	High
Chrysene	218-01-9	9.5×10^{-5}	Low
1,2-Dibromoethane (EDB)	106-93-4	6.7×10^{-4}	Moderate
Dibromochloromethane	124-48-1	8.7×10^{-4}	Moderate
1,2-Dibromo-3-chloropropane	96-12-8	1.5×10^{-4}	Moderate
Dibutyl phthalate	84-74-2	1.8×10^{-6}	Low
Dicamba	1918-00-9	7.9×10^{-9}	Low
1,2-Dichlorobenzene	95-50-1	1.9×10^{-3}	High
1,3-Dichlorobenzene	541-73-1	3.3×10^{-3}	High
1,4-Dichlorobenzene	106-46-7	2.4×10^{-3}	High
Dichlorodifluoromethane	75-71-8	3.4×10^{-1}	High
1,1-Dichloroethane	75-34-3	5.6×10^{-3}	High

Substance	CAS Number	Henry's Law Constant (atm-m^3/mole)	Potential for Volatilizing from Water
1,2-Dichloroethane	107-06-2	9.8 x 10^{-4}	Moderate
1,2-Dichloroethylene (cis)	156-59-2	4.1 x 10^{-3}	High
1,2-Dichloroethylene (trans)	156-60-5	9.4 x 10^{-3}	High
1,1-Dichloroethylene	75-35-4	2.6 x 10^{-2}	High
2,4-Dichlorophenoxyacetic acid	94-75-7	1.0 x 10^{-8}	Low
1,2-Dichloropropane	78-87-5	2.8 x 10^{-3}	High
1,3-Dichloropropene (cis/trans)	542-75-6	1.8 x 10^{-2}	High
Di (2-ethylhexyl) phthalate	117-81-7	3.6 x 10^{-7}	Low
Dimethoate	60-51-5	6.2 x 10^{-11}	Low
2,4-Dinitrotoluene	121-14-2	1.3 x 10^{-7}	Low
2,6-Dinitrotoluene	606-20-2	7.5 x 10^{-7}	Low
Dinoseb	88-85-7	4.6 x 10^{-7}	Low
Dioxins	1746-01-6	5.6 x 10^{-3}	High
Endrin	72-20-8	7.5 x 10^{-6}	Low
Ethylbenzene	100-41-4	8.4 x 10^{-3}	High
Fluoranthene	206-44-0	6.5 x 10^{-6}	Low
Fluorene	86-73-7	1.0 x 10^{-4}	Moderate
Fluoride	16984-48-8	6.0 x 10^{-8}	Low
Fluorotrichloromethane (freon 11)	75-69-4	9.7 x 10^{-2}	High
Formaldehyde	50-00-0	1.7 x 10^{-7}	Low
Heptachlor	76-44-8	1.1 x 10^{-3}	High
Heptachlor epoxide	1024-57-3	3.2 x 10^{-5}	Low
Hexachlorobenzene	118-74-1	1.3 x 10^{-3}	High
Lindane	58-89-9	1.4 x 10^{-5}	Low
Mercury	7439-97-6	1.1 x 10^{-2}	High
Methanol	67-56-1	4.5 x 10^{-6}	Low
Methoxychlor	72-43-5	1.6 x 10^{-5}	Low
Methyl isobutyl ketone	108-10-1	1.4 x 10^{-4}	Moderate
Methyl ethyl ketone (MEK)	78-93-3	2.7 x 10^{-5}	Low
Methylene chloride	75-09-2	2.0 x 10^{-3}	High
Monochlorobenzene	108-90-7	3.8 x 10^{-3}	High
n-Hexane	110-54-3	1.4 x 10^{-2}	High
Naphthalene	91-20-3	4.8 x 10^{-4}	Moderate

Substance	CAS Number	Henry's Law Constant (atm-m³/mole)	Potential for Volatilizing from Water
Pentachlorophenol	87-86-5	2.4×10^{-6}	Low
Phenol	108-95-2	3.3×10^{-7}	Low
Polychlorinated biphenyls	1336-36-3	1.1×10^{-3}	High
Pyrene	129-00-0	1.1×10^{-5}	Low
Pyridine	110-86-1	8.9×10^{-6}	Low
Simazine	122-34-9	2.7×10^{-9}	Low
Styrene	100-42-5	2.8×10^{-3}	High
1,1,1,2-Tetrachloroethane	630-20-6	2.4×10^{-3}	High
1,1,2,2-Tetrachloroethane	79-34-5	4.6×10^{-4}	Moderate
Tetrachloroethylene	127-18-4	1.8×10^{-2}	High
Toluene	108-88-3	6.6×10^{-3}	High
Toxaphene	8001-35-2	6.6×10^{-6}	Low
1,2,4-Trichlorobenzene	120-82-1	1.4×10^{-3}	High
1,1,1-Trichloroethane	71-55-6	1.7×10^{-2}	High
1,1,2-Trichloroethane	79-00-5	9.1×10^{-4}	Moderate
1,2,3-Trichloropropane	96-18-4	3.4×10^{-4}	Moderate
Trichloroethylene	79-01-6	1.0×10^{-2}	High
2,4,5-Trichlorophenoxy-propionic acid (2,4,5-TP)	93-72-1	8.7×10^{-9}	Low
Trifluralin	1582-09-8	2.6×10^{-5}	Low
1,2,4-Trimethylbenzene	95-63-6	5.6×10^{-3}	High
Vinyl chloride	75-01-4	2.7×10^{-2}	High
Xylene (mixed o-, m-, and p-)	1330-20-7	7.0×10^{-3}	High

CAS Number: Chemical Abstract Service (CAS) registry numbers are unique numbers assigned to a chemical substance and are widely used in scientific publications.

Note: Most metals (exception - mercury) and inorganics are not suseptable to volatilizing from a groundwater sample under normal sampling conditions and temperatures.

(Sources: USEPA Superfund Chemical Data Matrix [SCDM] March 1993 data tables. U.S. Environmental Protection Agency (EPA). 1990. *Basics of Pump-and-Treat Ground-Water Remediation Technology*. U.S. Environmental Protection Agency, Washington, D.C. EPA/600/8-90/003.)

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Equivalency and Conversion Tables

Volume Equivalents

unit	cc	in^3	liters	Quarts	Gals	ft^3
cc	1	.06102	.001	.00106	.00026	.00004
in^3	16.387	1	.01639	.01732	.00433	.00058
Pints	473.18	28.875	.47318	.5	.125	.01671
liters	1000	61.023	1	1.0567	.26417	.03531
Quarts	946.36	57.75	.94636	1	.25	.03342
Gallons	3785.4	231	3.7854	4	1	.13368
ft^3	28317.0	1728	28.317	29.922	7.4805	1
meter^3	100000	61023.4	1000	908.08	227.02	35.314

Equivalent Pumping Rate Table

Milliliters per Minute (ml/min)	Liters per Minute (L/min)	Gallons per Minute (gpm)
100	0.1	0.026
200	0.2	0.05
300	0.3	0.08
400	0.4	0.11
500	0.5	0.13
600	0.6	0.16
700	0.7	0.18
800	0.8	0.21
900	0.9	0.24
1000	1	0.26
2000	2	0.53
3000	3	0.79
4000	4	1.06
5000	5	1.32

Conversion formulas for rates not included in this table:
Liters per minute X 0.26417 = gallons per minute

Gallons per minute X 3.7854 = liters per minute

Length

To Convert From	To	Multiply By
inches	centimeters	2.540
inches	feet	0.0833
feet	meters	0.3048
feet	miles	0.0001894
meters	miles	6.214×10^{4}
meters	yards	1.094

1 meter = 10 decimeters = 100 centimeters = 1000 millimeters

Volume

To Convert From	To	Multiply By
cubic centimeters	cubic inches	0.06102
cubic inches	cubic feet	0.00058
cubic inches	liters	0.01639
cubic inches	gallons	0.00433
liters	gallons	0.14546
gallons	cubic feet	0.13368

1 liter = 1 cubic decimeter = 10 deciliters = 100 centiliters = 1000 milliliters = 1000 cubic centimeters

Cubic foot
7.48 gallons
28317 milliliters
28.317 liters
62.428 lbs

Gallon
231 cubic inches
3785 milliliters
3.785 liters
8.345 lbs

Liter
0.2642 gallons
61 cubic inches
2.205 lbs

Cubic meter
1000 liters
264.2 gallons
22.045 lbs

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INDEX

R

S

T

U

V

equipment effects on, 33, 34, 38-44, 47-   51, 54-56, 60
sampling effects on, 33, 34, 65, 69, 79

W

Water level measurements, 19-28, 111
Water quality measurements, 75-84
Water supply well labeling, 107, 108
Water table well, 19, 20, 23, 29, 82
Wax-impregnated graphite (WIG) electrode,
    83
Well constructor's report, 106, 109, 115
Well logs, 106, 111
Well maintenance/rehabilitation, 64, 65
Well-specific field sheet (WSFS), 18, 108
Well volume(s), 65-69, 87, 89, 127
Westbay® sampler, 43
Winkler (titration) method, 81
Wisconsin Unique Well Number (WUWN),   100, 105, 107-109

Z

Zinc, 65, 75, 85