

# **Groundwater Sampling Guidance**

# **Guidance Document 12**

Obtaining representative groundwater samples from the formations of concern is a critical goal of any groundwater sampling effort. Appropriately trained and qualified field personnel are necessary to properly collect groundwater samples in conjunction with a well-planned sampling protocol. The sampling protocol should define the procedures used to accurately make field measurements, to purge and withdraw samples from the well, fill sample containers and collect blank and replicate samples. The scope of this guidance document is to provide general guidelines to follow when preparing site specific sampling plans for groundwater sampling. Sampling plans are made after a monitoring scheme has been carefully designed and wells have been installed and properly developed.

The following are summaries of recommended sampling procedures to consider when planning a sampling event:

#### 1. Quality Assurance

#### a. Field Quality Assurance/Quality Control (QA/QC)

There are many potential sources of error in the field that can be difficult to control or assess. In order to minimize the possibility of cross-contamination:

- i. When sampling monitoring wells, begin with the well expected to have the best water quality and end with the well expected to have the worst water quality (i.e., sample from the least- to most-contaminated well). The sampling order for future event(s) may need to be modified depending on the most recent analytical results.
- ii. Use dedicated sampling equipment whenever possible. If dedicated equipment is unavailable or impractical, utilize a separate laboratory-cleaned or a new, prepackaged bailer (stainless steel, Teflon or polyethylene) for each well. Discard any sampling equipment that cannot be properly decontaminated (gloves, string, etc.) before proceeding to the next well.
- iii. Collect field blanks if re-usable sampling equipment is to be utilized for groundwater sampling. Field blanks consist of de-ionized water samples run through the sampling equipment after cleaning. The field blank water samples are handled and analyzed the same way as the well water samples.
- iv. A minimum of 10% duplicate samples (two samples taken sequentially) must also be collected at each sampling event. All blanks and replicate samples must be submitted as "blind" samples to the laboratory.

#### b. Laboratory QA/QC

If the contract laboratory does not have a current quality assurance/quality control plan on file with the Minnesota Department of Agriculture (MDA), the information required in the MDA guidance document GD24 <u>Fixed Base Laboratory</u> Assurance/Quality Control Plans must be provided to the MDA and be reviewed and approved by the MDA laboratory can be utilized for the project. The MDA staff may split samples with any facility todocument the accuracy and reproducibility of the analyses and/or request additional QA/QC information.

#### 2. Hydraulic Conductivity Tests

Slug or plug tests that estimate the horizontal hydraulic conductivity of the screened formation must be performed once on select new monitoring wells. In order to obtain accurate results, slug or plug tests must be conducted on undisturbed wells before water samples are collected. Please include the proposed methodology for conducting slug or plug tests in your Remedial Investigation Work Plan (RI Work Plan).

625 ROBERT STREET NORTH, SAINT PAUL, MN 55155-2538 · 651-201-6000 or 1-800-967-2474 · WWW.MDA.STATE.MN.US In accordance with the Americans with Disabilities Act, this information is available in alternative forms of communication upon request by calling

#### 3. Water Level Determinations

Prior to purging and sampling, measure well water levels in all site monitoring wells to the nearest 0.01 foot from the surveyed reference point (top of well casing).

#### 4. Sampling Procedures

- a. Calibrate all field instruments in the field before collecting samples.
- b. Choose a sampling device based on the following site characteristics: depth to groundwater, parameters of interest, well construction details, and accessibility of the well(s). Ideally, well purging and sampling equipment should be inert, economical, easy to clean, reusable, operable at remote sites and versatile. Care should be taken when reviewing the advantages and disadvantages of a sampling device. It may be appropriate to use different devices for purging and sampling. The most common example of this is to use a submersible pump for purging and a bailer for sampling (see Attachment 4).
- c. Before a representative sample can be withdrawn from a well, the "old" or stagnant water must be completely removed. Monitoring wells are purged of the stagnant water until certain field water quality parameters have been monitored and stabilized. The following criteria are utilized to demonstrate stabilization:
  - i. Measure specific conductance, temperature, and pH in the field after each well volume is purged until three successive readings yield measurements within the following ranges:
  - 1. Specific Conductance: +/- 5%
  - 2. Temperature: +/- 0.1 degrees Celsius
  - 3. pH: +/- 0.1 standard units
  - Dissolved Oxygen (DO): +/- 0.2 mg/L (Note: If DO is measured, a membrane electrode probe in a flow cell or a luminescence-based sensor must be used. Modified Winkler and Colorimetric ampoule methods can also be used under proper field conditions).
  - ii. A stabilization test must be completed on all newly installed monitoring wells during the initial sampling event, after each well volume is purged. The volume of water required to reach stabilization of these parameters should be recorded and used as a minimum purge volume for subsequent groundwater sampling events. Typically, the minimum purge volume is between three and five well volumes.
  - iii. For a well that pumps or bails dry, allow the well to recover prior to sampling. If well recovery is slow, the well may be sampled after purging one well volume. Stabilization parameters should be measured after well recovery if there is sufficient water volume to allow for measurement and sample collection.
  - iv. For Long-Term Monitoring sites, you must propose any stabilization parameter measurement frequency changes to MDA Incident Response Unit project staff for approval prior to implementation in the field.

<u>Note</u>: Monitoring well construction and development can significantly affect many water quality parameters, including those monitored during well purging. It is normally recommended to wait at least one week after development before collecting the first round of samples. Newly installed monitoring wells should be developed until clear, sediment-free water is obtained. Groundwater sampling plans, provided in the RI Work Plan, should include a schedule of sampling events.

Submit documentation of purging method, purge volume, recovery rate and stabilization test results to the MDA along with the analytical results.

- d. The labels on the water sample bottles must denote:
  - i. Type of analysis;
  - ii. Name of facility;
  - iii. Monitoring point identification;
  - iv. Name of person collecting the sample;
  - v. Time and date the sample was collected and,
  - vi. Whether a preservative was added to the sample or the sample was filtered.

#### e. Sample Collection:

Use a I-liter (amber-colored) glass bottle with Teflon-lined caps for pesticides analysis. <u>Attachment 3</u> lists the containers, preservation techniques and holding times.

Use a plastic bottle for nitrate + nitrite nitrogen analysis (a glass bottle may be used for samples analyzed immediately). Keeping these bottles free of extraneous contamination is imperative. Do not drop the cap or place it on the ground or touch the sample bottle to the tap/sampling device. Allow only water from the sampling point and preservatives, if required, to come in contact with the inside of the sample bottles.

Rinse each unpreserved bottle used for sampling pesticides and nitrate + nitrite nitrogen three times with water from the well before filling. Rinse the bottle caps also. Do not rinse sample bottles that already contain a preservative. To rinse, fill the bottles approximately one-third full, replace cap and shake vigorously. Discard the rinse water after each rinse cycle. Following rinsing, fill the bottles with water from the well, replace the Teflon-lined lid snugly, label and seal the bottles, and place the bottles into a cooler for storage and transport.

f. Chain of Custody:

"Chain-of-custody" tracking is required on all samples. "Chain-of-custody" provides a record of the personnel responsible for handling the samples. An example of a "chain-of-custody" form is included as <u>Attachment 2.</u>

#### 5. Transportation

Store samples, blanks and duplicates at four degrees Celsius until analyzed. Freezer packs are preferable to ice for short time periods. If ice is used, use Ziploc-type bags to contain ice and meltwater and prevent meltwater from loosening bottle caps and labels. Coolers should also be packed with vermiculite or other absorbent packing material to prevent container breakage. Floating sample bottles or bottles with detached labels may be rejected by the laboratory. When any sample is to be shipped by common carrier or sent through the United States Postal Service, it must comply with the Department of Transportation Hazardous Materials Regulation (49CFR Part 172). The person offering such material for transportation is responsible for ensuring such compliance.

#### 6. Reporting

Certain procedures should be followed when submitting groundwater quality data to MDA staff. Please refer to <u>Attachment 1</u> when compiling information for groundwater quality reports.



#### ATTACHMENT 1

#### **GROUNDWATER MONITORING REPORTING REQUIREMENTS**

MONITORING REPORTS (QUARTERLY, OR SEMI ANNUALLY)

Information submitted to MDA should include:

- 1. Analytical results for samples including QA samples;
- 2. Stabilization, purge volume and/or recovery rate test forms;
- 3. Copies of "*chain-of-custody*" forms, lab analytical reports, lab QA/QC reports, and MDA Laboratory Data Review Checklist for each lab report (GD29 Attachment);
- 4. Copies of field records;
- 5. Water level measurements to the nearest 0.01 foot from the surveyed point referenced to the National Geodetic Vertical Datum (NGVD) or to a local benchmark if identified;
- 6. A table showing all water level information to date;
- 7. A table showing all analytical results to date. Include numerical information (specify reporting limit) rather than "non detect" for those parameters not detected above reporting limits;
- 8. A detailed site map showing the location of all monitoring wells;
- 9. Groundwater flow maps should be constructed for different depths and elevations of well screens. Use only wells finished at the water table to construct a water table groundwater flow map. Construct other flow maps using wells finished at similar depths and elevations. Do not construct groundwater flow maps using data from wells finished at different depths and elevations. The groundwater flow maps should clearly indicate the elevations of groundwater contour lines and groundwater elevations in each well. The maps should also indicate the direction of groundwater flow with a directional arrow. All maps should have a north arrow and scale.
- 10. A brief description of how the groundwater contour maps were completed (for example, the name of the groundwater model used);
- 11. Groundwater contaminant isoconcentration maps should be provided for different depths and elevations of well screens, similar to the groundwater flow maps. Use only wells finished at the water table to construct an isoconcentration map of contaminants present at the water table. Construct other isoconcentration maps using wells finished at similar depths and elevations. Do not construct groundwater contaminant isoconcentration maps using data from wells finished at different depths and elevations. All maps should have a north arrow and scale.
- 12. A statement explaining the reasons for and ramifications of any deviation in sampling, analytical techniques or equipment from those stated above or in the laboratory quality assurance/quality control plan;
- 13. Hydrographs showing changes in water level elevations over time;
- 14. Provide all calculations needed to determine unionized ammonia concentrations, if applicable;
- 15. Provide all calculations needed to determine the horizontal hydraulic conductivity from slug or plug test data; and
- 16. Provide all calculations needed to determine the vertical hydraulic gradients and directions for all nested well groups.

#### ANNUAL MONITORING REPORT

Once a year, or as agreed to by MDA, a summary and discussion of the monitoring results should be submitted to the MDA. This annual report should:

- 1. Identify recent and long-term trends in the concentrations of monitored constituents and in water elevations;
- Tabulate the analytical results to date and highlight those that exceeded groundwater regulatory standards (such as Health Risk Limits, Health Based Values or Maximum Contaminant Levels). On tables include numerical information such as <0.1 rather than "Not Detected" for those parameters not detected above reporting limits and list the regulatory standards;
- 3. Provide concentration versus time graphs for selected analytical parameters. Use an appropriate scale so that all data are easily seen;
- 4. Provide hydrographs showing changes in water level elevations over time;
- 5. Evaluate the effect the facility is having on groundwater;
- 6. Describe any changes in known or potential receptors during the period, such as abandonment or installation of supply wells;
- 7. Suggest any additions, changes, or maintenance needed in the monitoring program; and
- 8. Provide groundwater flow maps (see #9 above).

MSD					F	PROJECT L	EADER		RE	MARKS												
PROJECT	NAN	/IE/LOC/	ATION																			
ESD SAMP	TER	5 SOIL/SEDIM 7 SLUDGE	ENT			SAMPLEF	र		DAT	A TO: CIRCLE/AE	חו		[	A.N.	ALYS	19				٩	eipt by lab	LAB USE ONLY
2 GROUND IN 3 POTABLE WA 4 WASTEWATE 5 LEACHATE 11 OTHER	TER	8 WASTE 9 AIR 10 FISH							s	parameters list no. of co submitted	desired			· _ /			/		7	intact at la	: upon rece	
STATION NO.	SAMPLETYPE	19 DATE	TIME	COMP	GRAB	STATION LC	OCATION/DESC	CRIPTION	TOTAL CONTAINERS		102	Semino	PEST ON CON	META.	Chan	<del>3</del> 0,		TAG NO	/REMARKS	Custody seals intact at lab	Seals not intact upon receipt by lab	
	S								10			/								Ŭ	0	
relinquishe Print)	ED BY:			DA	TE/	TIME	RECEIVED E (PRINT)	BY:	RELI (PRIN	NQUISHED T)	BY:				DA	TE/TIN	ИE	RECI (PRIN	EIVED BY: T)			
SIGN)							(SIGN)		(SIGN	)								(SIGN	)			
relinquishe Print)	ED BY:			DA	TE/	TIME RECEIVED BY: (PRINT)			RELINQUISHED BY: (PRINT)									RECEIVED BY: (PRINT)				
SIGN)							(SIGN)		(SIGN	\ \								(SIGN	n			

## CHAIN OF CUSTODY RECORD

DISTRIBUTION White and Yellow copies accompany sample shipment to Laboratory; Yellow copy retained by Laboratory White copy is returned to samplers; Pink copy returned by samplers

PAGE OF

MAGRICULTURE

Q

**ATTACHMENT 2** 



## ATTACHMENT 3

## **Containers, Preservation Techniques and Holding Times**

Parameter	Container	Preservative <sup>1</sup>	Maximum Holding Time <sup>2</sup>			
Nitrate + Nitrite	100 ml. poly	Cool 4°C, H <sub>2</sub> SO <sub>4</sub> to pH<2	28 days			
Ammonia	100 ml. poly	Cool 4°C, H2SO4 to pH<2	Record pH and temp. at time of collection 28 days			
Base Neutral Pesticides (MDA List 1)	1000 ml. amber glass	Cool 4°C	Follow applicable method holding times			
Acid Pesticides (MDA List 2)	1000 ml. amber glass	Cool 4°C, H₂SO₄to pH<2	Follow applicable method holding times			
Pentachlorophenol	1000 ml. amber glass	Cool 4°C, H <sub>2</sub> SO <sub>4 to</sub> pH<2	7 days until extraction			

#### NOTES:

<sup>1</sup>Sample preservation should be performed immediately upon sample collection.

<sup>2</sup>Samples should be analyzed as soon as possible after collection. The times listed are the **maximum** holding times that samples may be held before analysis and still be considered valid.



### ATTACHMENT 4

#### Advantages and Disadvantages of Various Groundwater Sampling Devices (modified from EPA/540/P-91/007 January 1991)

Device	Advantages	Disadvantages
Bailer	<ul> <li>The only practical limitations are size and materials</li> <li>No power source needed</li> <li>portable</li> <li>Inexpensive; it can be dedicated and hung in a well reducing the chances of cross-contamination</li> <li>Minimal outgassing of volatile organics while sample is in bailer</li> <li>Readily available</li> <li>Removes stagnant water first</li> <li>Rapid, simple method for removing small volumes of purge water</li> </ul>	<ul> <li>Time consuming, especially for large wells</li> <li>Transfer of sample may cause aeration</li> </ul>
Submersible Pump	<ul> <li>Portable; can be used on an unlimited number of wells</li> <li>Relatively high pumping rate (dependent on depth and size of pump)</li> <li>Generally very reliable; does not require priming</li> </ul>	<ul> <li>Potential for effects on analysis of trace organics</li> <li>Heavy and cumbersome, particularly in deeper wells</li> <li>Expensive</li> <li>Power source needed</li> <li>Susceptible to damage from silt or sediment</li> <li>Impractical in low yielding or shallow wells</li> </ul>
Non-Gas Contact Bladder Pump	<ul> <li>Maintains integrity of sample</li> <li>Easy to use</li> </ul>	<ul> <li>Difficult to clean although dedicated tubing and bladder may be used</li> <li>Only useful to approximately 100 feet in depth</li> <li>Supply of gas for operation (bottled gas and/or compressor) is difficult to obtain and is cumbersome</li> </ul>
Suction Pump	Portable, inexpensive, and readily available	<ul> <li>Only useful to approximately 25 feet or less in depth</li> <li>Vacuum can cause loss of dissolved gases and volatile organics</li> <li>Pump must be primed, and vacuum is often difficult to maintain</li> <li>May cause pH modification</li> </ul>
Inertia Pump	<ul> <li>Portable, inexpensive, and readily available</li> <li>Rapid method for purging relatively shallow wells</li> </ul>	<ul> <li>Only useful to approximately 70 feet or less in depth</li> <li>May be time consuming to use</li> <li>Labor intensive</li> <li>WaTerra pump is only effective in 2-inch diameter wells</li> </ul>

625 ROBERT STREET NORTH, SAINT PAUL, MN 55155-2538 · 651-201-6000 or 1-800-967-2474 · WWW.MDA.STATE.MN.US In accordance with the Americans with Disabilities Act, this information is available in alternative forms of communication upon request by calling

651-201-6000. TTY users can call the Minnesota Relay Service at 711. The MDA is an equal opportunity employer and provider. GD 12 ATT. 4 (03-2022)