Solid Waste Permitting Sampling and Analysis Plan Guidance

Appendix A: Groundwater Monitoring Well Sample Collection

This document defines the recommended minimum standard of care for groundwater quality measurements and for collecting and handling groundwater samples obtained from monitoring wells at permitted landfills as required by Minn. R. 7035.2815, subp. 10 and 14 and at other solid waste activities where groundwater monitoring is required. An outline of the sequence of field sampling activities is provided in Section 7 solely as an organizational tool. Actual sampling must follow the facility's Minnesota Pollution Control Agency (MPCA) approved site sampling and analysis plan (SAP) and permit requirements, which should meet or exceed methods described in this document.

1. Pre-mobilization preparation for sampling

1.1. Permitted analytical parameters

Samples must be collected for analysis of the parameters in the effective facility permit or MPCA-approved SAP. Parameters pending addition to or removal from your permit via minor modification, major modification, or reissuance should be added to or removed from your SAP ahead of the permit activity to maintain an up-to-date document with sampling requirements.

1.2. Quality assurance for laboratory analysis

The MPCA requires analytical laboratory certification and accreditation (see Section 8, reference 11, the MPCA Science and data webpage, and Minnesota Department of Health (MDH) Environmental Laboratory Accreditation Program – MnELAP). Laboratories reporting data to the MPCA are required to include the name of the accreditation body on analytical reports. The facility's contracted analytical laboratory's Quality Assurance Manual (QAM) and/or laboratory standard operating procedures (SOPs) should include specific requirements for the following: sample containers, sample testing, temperature blanks, sample labeling and storage, sample preparation, and addition of preservatives to samples. Sampling contractors must coordinate directly with the laboratories on their requirements. A copy of the most up-to-date laboratory QAM and/or relevant SOPs must be included as attachment(s) in the SAP. When substantial changes are made to either document, the facility should submit an updated SAP to the MPCA within 30 days.

1.2.1. Intervention limits (ILs)

Intervention limits are one quarter (1/4) the concentration of the most conservative and current state and federal drinking water limit. ILs calculated at the time of issuance are listed in the effective permit; however, ILs should be calculated using the most up-to-date state and federal drinking water limits for reviewing data in the annual and quarterly reports. The ILs in the SAP should be updated when changes to drinking water limits occur.

Intervention limits (ILs) listed in the effective facility permit are calculated at the time of permit issuance.

However, ILs must continue to be reviewed and calculated by the permittee based on the most conservative and current state and federal drinking water limits.

The reference for current federal and state values is maintained by MDH at Comparison of State Water Guidance and Federal Drinking Water Standards.

In all cases, except where unachievable via available technology, laboratory analytical methods used must achieve reporting limits that are equal to or below the IL. Reporting limits that are greater than the IL for a given parameter should be discussed in the quarterly and/or annual report.

1.2.2. Alternative intervention limits

In limited cases, alternatives ILs may be proposed by the facility if the conditions described by Minn. R. 7035.2815, subp. 4 (H) are met. If alternative ILs are approved in the permit, the SAP must be updated accordingly.

1.3. Quality assurance for field procedures

Sample collection must be done by trained personnel (Minn. R. 7035.2815, subp. 14(F)). The following field procedures are best industry practices as detailed in the references at the end of this document. During sample collection, care should be exercised to prevent cross-contamination of sampling equipment, sampling containers, or anything else that could potentially compromise the integrity of samples. Field personnel should work under the assumption that contamination exists in land surface soils and vegetation, near sampling points, in wash water, etc.

Exposure to these media should be minimized by taking at least the following precautions:

- Minimizing the amount of rinse water left on washed materials.
- Minimizing the time sampling containers are exposed to airborne dust or volatile contaminants in ambient air.
- Placing equipment on clean, surface-covering materials instead of on unprepared/potentially contaminated surfaces.

Special care should be taken to avoid:

- Improper storage or transportation of equipment.
- Contaminating the equipment or sample containers on site by setting them on or near potential contamination sources such as uncovered ground, a contaminated vehicle, or vehicle exhaust.
- Handling containers or equipment with dirty hands or gloves.
- Inadequate cleaning of well purging or sampling devices.

Clean gloves made of appropriately inert material, for example disposable powderless gloves, must be worn by all field crew. Gloves must be kept clean while handling sampling-related materials and must be replaced by a new pair when soiled and replaced again between each sampling point.

1.3.1. Decontamination, storage and transport of equipment

Before mobilizing for fieldwork or performing any decontamination, a source of control water of known chemistry for decontamination should be selected and evaluated for use as rinse water.

Equipment used during purging or sampling should be thoroughly cleaned prior to use in each individual well, even when the wells are located close to each other. Decontaminate all sampling-related equipment that will be reused, including pumps, filtration devices, personal protection gear, etc. The need for decontamination can be avoided by use of new disposable equipment that is certified as clean or by the installation of dedicated equipment. Thoroughly decontaminate non-dedicated pump tubing or use new or dedicated tubing at each well. Use dedicated pumps or decontaminate by circulating decontamination fluids through the pump as described below.

At minimum, equipment should be decontaminated in the following manner:

1. Clean inside and out with a laboratory-grade detergent (Liquinox or equivalent) or clean-water solution, applied with a scrub brush where practical.

2. Rinse with tap water followed by a final rinse with rinse water.
3. Inspect for remaining particles or surface film and repeat cleaning and rinse procedures if necessary.
4. Sampling equipment that contacts free product or heavily contaminated areas may require use of a desorbing agent, a dilute solution of water and isopropanol or methanol, followed by a thorough tap water rinse and a final rinse with rinse water.
5. If inspection continues to reveal that decontamination was insufficient, additional measures should be implemented as needed and documented.

The internal surfaces of pumps and tubing that cannot be adequately cleaned by the above methods alone will also be cleaned by circulating decontamination fluids through them. Exercise special care to ensure that the rinse fluids are circulated in sufficient quantities to completely flush out contaminants, detergents, and desorbing agents.

1.4. Selection of purging and sampling equipment

Well purging and sampling equipment may include the following:

- Submersible, positive displacement bladder pumps;
- Submersible low-flow, electric centrifugal pumps (i.e., Grundfos, Redi-Flo2, etc.);
- Peristaltic suction lift pumps with a maximum working depth of 20-25 feet;
- Conventional submersible and electric centrifugal pumps (if they are permanently installed in the well);
- Piston pumps;
- Following federal and state guidance, bailers are only acceptable for use when other equipment has failed. Use of bailers is further discouraged by references 3, 4, and 9 (see Section 8). If bailers are used in place of pumps for purging or sampling, you must follow MPCA guidance document Groundwater Sample Collection and Analysis Procedures – Petroleum Remediation Program. You must also discuss appropriate sampling approaches/solutions at the affected location(s) with the MPCA hydrologist, include a discussion in the quarterly or annual report, and perform any necessary corrective actions prior to the next sampling event;
- For groundwater samples that will be analyzed for volatile organic compounds, do not attempt to sample with an internal pump/tubing and check valve method. The check valve method is known to produce poor quality groundwater samples due to removal of volatiles from the water column through agitation; and
- Additional equipment considerations are required for per- and polyfluoroalkyl (PFAS) sampling (see section 4.3.2).

Additional equipment considerations and documentation are required for PFAS sampling following MPCA Guidance for per- and polyfluoroalkyl substances (PFAS): Sampling

Equipment description, specification details, inspection, and maintenance schedules should be detailed in the SAP.

1.5. Determination of sampling order

Where water quality data are available, purging and sampling of wells should begin with the least contaminated wells and proceed to increasingly contaminated wells. Where the distribution of contaminants is not known, purging and sampling activities should begin with wells considered upgradient from sources of contamination. Upon completion of upgradient wells, begin sampling downgradient wells furthest away from the suspected source area and finish with downgradient wells closest to suspected contamination. Where the term "upgradient" may not apply and previous water quality data are not available, purging and sampling of wells should begin at wells considered to be background wells. Both the purging and the sampling should be completed without removing the pump or tubing before beginning purging at subsequent wells. Sampling order

may be flexible at facilities where dedicated sampling equipment is installed in all wells. Include the established sampling sequence as an attachment to the SAP.

2. Field work and documentation prior to sample collection

2.1. Field inspections and decisions

Upon arrival at each well, inspect the well to verify that the annular seal is intact at the surface. Put on protective gloves before removing the inner riser cap and set the cap in a clean storage spot. Note missing parts, missing labeling, missing locks, well damage, and/or tampering. The MPCA hydrologist should be notified of damage with the potential to impact data quality, and repairs must be made as soon as possible. The well must be resurveyed after repairs have been made, and an updated SAP must be submitted.

Record field conditions according to section 5.4. Field conditions such as wind direction may affect sampling station setup. Position any running vehicle or field generator downwind of the sampling station. Inspect the surrounding soil and vegetation or other objects in the immediate vicinity of the well. Record any unusual conditions or odors on the field sampling form and note details in the quarterly and annual reports along with the planned actions to correct the issue. If any condition that may interfere with obtaining representative analytical results is discovered, note the condition, and rectify (if possible) before collecting a groundwater sample.

Field decisions to make minor changes to the SAP may be made by the project manager during a sampling event. For significant or recurring changes to the SAP, obtain approval in advance from the MPCA hydrologist. The MPCA hydrologist will review any changes to the plan that may adversely affect results, and approved changes should be included in an updated SAP.

2.2. Water level measurements

Measure and record initial static water levels and total well depths at each well prior to any well evacuation or sampling. This is done to facilitate selection of the proper pump intake depths for purging and sampling, calculating well volume for the purging process, and for calculation of the groundwater flow direction.

Decontaminate water level probes following methods in section 1.3. Measurements should be made with an electric water level probe that has been calibrated within the last month and recorded to the nearest 0.01 feet. Reference for the depth-to-water should be made from the measuring point marked at the top of the innermost well casing. If a measuring point has not been marked, assume the measuring point to be at the top of the innermost casing on the north side, and mark a new measuring point to maintain consistency of future measurements.

During initial static water level measurement, a minimum of two water level measurements should be made at each well. If there is poor agreement between the first and second static water level measurements (a difference of more than 0.01 feet), data should be re-evaluated for measurement errors, unsuspected pumping that may be causing transient changes in gradient, water level indicator sensitivity calibration, etc. If the disagreement cannot be rectified, a third static water level measurement should be made at each questionable sampling point to assess the true water level, verify non-steady state conditions, etc.

The field personnel should make water-level measurements at all applicable site wells within a twelve-hour time interval to provide comparable data by which to calculate the groundwater gradient. An additional water level measurement should be taken immediately before purging at each well, and a final measurement should be taken immediately after sampling is completed. Record these water levels on the field sampling form.

3. Well purging and stabilization

Prior to sampling, purging and stabilization of the monitoring well is performed to remove stagnant water from within the well and to stabilize the well to allow for representative groundwater sample collection. A well is

considered stabilized after the field water quality measurements are within acceptable limits for three consecutive readings.

3.1. Field water quality measurements

Field water quality measurements are required. These parameters are only required to be collected/measured in the field and must be submitted via an EDGE_MN EDD (see Solid Waste Permitting SOP Guidance - Appendix B). **Laboratory analysis for these parameters is not required by the MPCA Solid Waste Permitting Program.**

Field water quality parameters include:

- Specific conductance (µmhos/cm);
- Oxidation-reduction potential (ORP, mV);
- pH;
- Temperature (C);
- Turbidity (NTU); and
- Dissolved oxygen (mg/L).

These parameters must be measured in the field during stabilization and immediately before sample collection.

Calibration information and all measurements should be recorded on the field sampling form. Measurement conditions and the steady-state value for each field water-quality parameter should also be noted on the field sampling form (see Section 3.2).

Measurements should primarily be taken within a closed flow cell designed to allow measurement of these parameters while minimizing changes in temperature, pressure, and dissolved gases from the in-situ aquifer environment.

A closed flow cell fulfilling the following specifications is acceptable for use:

- Airtight fittings for installation of all probes;
- Intake connected directly to the pump discharge line;
- Probes reside in a water bath kept at a temperature representative of the in-situ groundwater temperature;
- A minimum cell volume of 250 ml to provide enough thermal mass to minimize external temperature effects;
- Cell and lines are shielded from strong winds and from direct sunlight;
- A discharge line approximately three feet long that is connected to the flow cell with an airtight connection;
- A maximum volume of no greater than five times the per minute volumetric rate of inflow to the cell to maintain measurement sensitivity to temporal changes in water quality;
- The operation of the probes should be done in the following manner:
    - the flow of sample water through the cell should be maintained as continuous and steady as practical throughout the measurement period
    - discharge velocities through the flow cell are kept low to prevent problems of streaming potential with probes;
    - all probes must be fully immersed without touching the sides of the airtight, non-metallic flow cell; for monitoring wells with sufficient yield, all probes should be allowed to equilibrate with fresh well water for five minutes before beginning to record measurements.

General care, maintenance, calibration procedures, and operation of each measurement device must follow the manufacturer's specifications.

3.2. Criteria for stabilization

Field parameters will be measured for stabilization after each water-column volume is purged (for stabilization by well volume) or after each timed interval during stabilization by low-flow sampling methods (See sections 3.3.1 and 3.3.2).

The following target criteria for three consecutive measurements, after the initial readings, should be used to demonstrate stabilization:

- pH +/- 0.1 units
- Temperature +/- 3%
- Specific conductance +/- 3%
- Dissolved oxygen +/- 10% (> 0.5 mg/L)
  - Note: three consecutive readings ≤ 0.5 mg/L can be considered stabilized.
- ORP +/- 10 mV
  - Note: three consecutive readings ≤ 0.5 mV can be considered stabilized.
- Turbidity +/- 10% (> 5 nephelometric turbidity units - NTU)
  - Notes:
    - three consecutive readings ≤ 5 NTU can be considered stabilized.
    - If all other parameters have stabilized apart from turbidity, stabilization may be considered achieved.
    - A range of expected turbidity for each groundwater sampling location should be included in the approved SAP. If turbidity remains higher than the established range during stabilization, or has demonstrated increasing trends in NTUs, an assessment should be made to determine whether the turbidity is a function of the aquifer properties or issues associated with the well. If issues with elevated turbidity cannot be ascribed to the screened formation, the well may require redevelopment or replacement if redevelopment efforts are unsuccessful.
    - A qualitative/visual determination of turbidity should also be noted (e.g., clear, cloudy, very cloudy, etc.). The data should be submitted in the EDGE_MN EDD under "water color" on the SampleParameter_v1 tab.

If field parameters do not stabilize after approximately five water-column volumes have been removed or after 2 hours under low flow conditions, then field staff will review operator procedures, the functionality of equipment, and well construction information for potential problems. If no instrumental or monitoring well issues are identified, samples may then be collected even if field measurements have not stabilized. It should be clearly documented that stabilization was not achieved on the field sampling form and in the quarterly/annual report. If this issue is persistent for a given groundwater monitoring well, separate stabilization criteria should be submitted in an updated SAP. This includes wells where stabilization is achieved while turbidity remains high.

Low-flow stabilization and sampling methods are distinct from well stabilization and sampling by fixed volume. The benefits of low-flow sampling include prevention of water column aeration and potentially expediting the well sampling process by minimizing the quantity of water required to be purged.

3.3. Methods of purging and stabilization

Within the SAP, define the use of one of the following stabilization methods for facility wells. For most facilities, low-flow sampling is required to obtain representative volatile samples.

For any method, the time purging begins must be recorded on the field sampling log. Any final rinse water remaining in any portion of the sampling pump or discharge lines should be completely purged with well water before measurement of field water quality parameters. While the well is being purged, water quality parameters described in Section 3.1, the quantity of water purged, and the flow-through cell volume should be recorded on the field sample form.

3.3.1. Stabilization by low-flow methods

This method should be used for the majority of wells at the majority of facilities and any well where samples for volatile analytes are being collected. Dedicated equipment is strongly recommended to minimize disturbance in the water column which decreases time needed for stabilization, expedites sampling set up, and minimizes equipment decontamination needs. If used, non-dedicated tubing and/or pumps should be slowly lowered into the well to minimize water column disturbance. The intake port for the pump being used should be placed at a depth near the middle of the well screen interval.

Pumping rates during low-flow purging should be kept at or below 500 mL/min. However, this is dependent on the site-specific hydrogeology and should be lowered as needed to maintain drawdown of no more than 4 inches (0.33 ft or 0.1 m). Stabilization parameters listed in Section 3.1 should be monitored at a frequency of five-minute purge intervals or greater. During the first purge interval, a purge rate will be established for each monitoring well. Samplers should attempt to maintain the same purge rate for the duration of the purge.

The pump's flow rate must be able to fill and replace at least one flow-through cell volume between purge intervals.

- Example 1: flow rate = 50 mL/min, flow-through cell volume = 250 mL -> collect stabilization parameters at least five minutes apart.
- Example 2: flow rate = 250 mL/min, flow-through cell volume = 750 mL -> collect stabilization parameters at least five minutes apart. While the cell was replenished in three minutes, the minimum time between readings should remain five minutes.
- Example 3: flow rate = 100 mL/min, flow through cell volume = 1000 mL -> collect stabilization parameters at least ten minutes apart.

Well stabilization parameters for low-flow sampling include those listed in section 3.2 (pH, temp, SC, DO, ORP, and turbidity). Turbidity is usually the last parameter to stabilize. If unstable turbidity is a known issue at site wells, plan accordingly to assure representative samples are collected.

After three consecutive readings within acceptable limits outlined in section 3.2, groundwater samples may be collected.

Further information regarding the use of low-flow sampling is provided by the Environmental Protection Agency (EPA) Guidance Document on Low-Flow Sampling Procedures.

3.3.2. Stabilization by fixed well volume purge

This method is only applicable for wells where samples for volatile compounds are not being collected.

A well volume is measured as the volume of water present inside a well screen and casing prior to stabilization and sampling. Field water quality measurements should be recorded after the purging of each well volume with the pumping rate set to the lowest practicable setting. Stabilization criteria include those listed in section 3.2 (pH, temperature, specific conductance, ORP, DO, and turbidity).

After three consecutive readings within acceptable limits outlined in Section 3.2 have been collected, groundwater samples may be collected while maintaining the pumping rate used for stabilization.

3.3.3. Low-yield wells

Pumping a well dry/drawing the water level below the top of well screen should be avoided. The time required for sufficient recovery, increased hydraulic gradient in materials surrounding the well, cascading and aeration of formation water entering the screen, entrapment of air in the filter pack, and the potential for insufficient recovery are introduced when a well is pumped dry and will reduce sample quality. However, for some screened materials and aquifer settings, low-yield wells may purge dry prior to stabilization requiring other purge and sample methods.

A well is considered a low-yield well when it purges dry at pumping rates between 100 – 200 mL/min and cannot be sampled by the low-flow methods described in 3.3.1. Identify these wells in the facility SAP and quarterly/annual reports and notify the MPCA hydrologist. If a well purges dry that has not done so during previous sampling events, evaluate and discuss the need for well redevelopment in quarterly/annual reports and in separate timely communication with the MPCA hydrologist. Low-yield wells may be sampled following

the methods described in the sections below. If a monitoring well purges dry over multiple sampling events, additional corrective actions may be needed (such as redevelopment or replacement).

3.3.3.1 Pumping to near dryness

A low-yield well may be pumped to near dryness and allowed to recover to at least 80 percent of its static water level one time prior to sampling. The sample should be collected between 2 and 14 hours of recovery. Recovery must last a minimum of 20 minutes and no longer than overnight for representative sample collection. If the well recovers to 80 percent of the static water level within 20 minutes, low flow sampling methods should be attempted at the well prior to pumping to near dryness (see Section 3.3.1). If 80 percent recovery overnight is unrealistic for a well (or wells) on site, include an alternative recovery volume along with supporting information in the facility SAP for approval.

If there is insufficient sample volume for the required analyses after appropriate recovery and sampling attempts, contact:

1. The contracted analytical laboratory to determine if reduced sample volumes may be submitted for analysis.
2. The MPCA hydrologist to determine if sampling should be carried out with a reduced and prioritized list of analytes.

Agreed upon procedures and data collected should be clearly documented on the field sampling form.

3.3.3.2 Micro-purge sampling

A low-yield well may be micro-purged if a permanent dedicated pump has been installed. The dedicated pump intake must be set within the well screen, at least two feet from well bottom. During micro-purging the well must be pumped at a rate equal to aquifer yield to minimize drawdown. The water level must not drop below the top of screen during sampling and purging. If there is sufficient yield, field water quality measurements should be taken after one pump-tubing volume is displaced and after each ½ water column volume is purged. A minimum of one water column plus one pump-tubing volume should be purged before sample collection.

4. Sample collection

This section describes procedures for setting the sampling pump and collecting groundwater samples. Field data for these items will be recorded on the field sampling form for each sampling point.

4.1. Pumping rate for sampling

The sample collection pumping rate should be less than or equal to the purging rate. The field sampling form should show what type of pump was used to sample each well even if dedicated tubing and/or pumps are in place, the approximate depth of the pump intake setting, and sampling time. The same pump should be used for sampling as was used for purging. Pumping should be continuous; if pumping is not continuous it should be noted on the field sampling form. Sampling, with the exception of low-yield wells, must immediately follow purging. For wells without dedicated equipment, the pump should be pulled immediately after sampling and the water level measured immediately after removal of the pump.

4.2. Sample filtration

Unless otherwise specified in the approved SAP or if there have been three consecutive turbidity measurements of < 5 NTU (see section 4.3.3), samples collected for metals analysis must be field filtered (representing the dissolved fraction). The Laboratory QAM/SOPs will dictate which other sample containers must be filled with sample water that has been filtered in the field. Sample filtration will be completed as follows:

1. The new filters must be flushed with fresh sample water before collecting samples.

2. The filter may be connected directly to the well sampling pump discharge line using positive pressure to force the sample through the filter.
3. From the filter, the flow should be routed directly into the sample collection container.
4. A 0.45-micron pore size filter should be used unless otherwise specified.
5. The flow rate should not exceed 500 mL per minute.
6. Agitation and aeration of the sample should be minimized.
7. Inert tubing must be used for the pump and filter discharge lines when collecting filtered samples for organic compounds.

4.3. Filling sample containers

General guidance for the manner in which containers should be filled is described below in subsections of 4.3. However, the Laboratory QAM/SOPs should detail the analytical method, sample container type, filling method, preservation method and holding time for each analytical parameter. The Laboratory QAM/SOPs supersede recommendations made here.

Individually prepared containers will not be opened until they are to be filled with water samples. At minimum follow the procedures below:

1. The area surrounding the wellhead should be kept as clean as practical to minimize the potential for contamination of samples.
2. Care should be exercised to minimize the potential for airborne contamination of sample water during collection. If vehicles or generators are left running during sample collection, containers should be filled upwind from engine exhaust sources. If conditions are dusty, an effort should be made to shield the sample collection area from windborne contamination.
3. A sheet of inert and uncontaminated material should be placed on the working surface in the wellhead area. If materials used in the sampling process must be put down, they should be placed on a clean portion of the sheet instead of an uncovered surface.
4. A clean pair of powderless nitrile gloves should be put on at the onset of sampling activities at each new sampling point.
5. Sampling personnel should keep their hands as clean as practical and must replace gloves if they become soiled while performing sampling activities.
6. Sampling personnel must not touch the inside of sampling containers, container caps, or rim of sample containers. If contact occurs, sample containers must be replaced.

Containers should be labeled at the sampling point at the time of sample collection. Select information may be pre-populated on labels by the laboratory (parameter names, preservation method, unique container ID). Additional pre-population may be considered if care is taken to avoid transposing labels and/or sample containers. The Chain-of-Custody (COC) sections should be filled out by the field personnel according to procedures described below in Section 5. COC information must be recorded on the field sampling form or the COC itself before leaving the sampling point. Laboratory prepared containers must be used to assure quality control.

The order of filling containers with water to be analyzed should be as follows:

1. Volatile organic compounds (VOCs)
2. Per- and polyfluoroalkyl substances (or collect during another event as a single parameter)
3. Inorganics
4. Nitrogen series
5. General parameters

Duplicate samples will be collected sequentially as described in section 4.4. Methods for filling sample containers for individual analyses are described below.

The sample water discharge point at the end of the tube should be held as close as possible to the sample container without allowing the sample tubing to contact the container. The exception to this rule is for dissolved oxygen and chemical oxygen demand samples where the container is filled from the bottom up by inserting the tube into the bottom of the container. At a minimum, sampling personnel will use their body to shield the sampling container from wind and airborne dust while filling. When strong winds, heavy rain, or dusty conditions are present, additional measures will be implemented to guard against background interference, such as use of a portable shelter at the well head. A final water level measurement should be made immediately after sample collection is finished.

After sampling containers have been filled, those used for the collection of temperature-sensitive analytes should be placed on ice immediately.

4.3.1. Volatile organics

The 40-ml purge and trap vials should be filled in a manner that minimizes turbulence, entrapment of air, and overfilling. They should not be rinsed in the field but should be completely filled in a manner that leaves a positive meniscus at the top of the vial. Acidic preservatives prepared specifically for volatile organics analysis by the laboratory should be used to preserve samples. The acid may be added to vials at the laboratory in advance of sampling, **with extra caution exercised to minimize overfilling in the field.** Alternatively, the acid may be added immediately after filling the vials in the field. Field personnel should add the number of drops specified by the sampling SOPs and immediately cap the vials.

4.3.2. PFAS

For the most up-to-date and detailed agency sampling guidance please refer to the Guidance for per- and polyfluoroalkyl substances (PFAS): Sampling document on the MPCA website.

4.3.3. Inorganics

Sample containers for general ions and metals analysis should be prepared in advance by the laboratories with HNO3 as a preservative. This will ensure that samples will be acidified as soon as they are collected. Containers should be filled approximately 95% full (up to the neck). Containers should not be rinsed or overfilled at any time in the field.

The sample containers for metals analysis must be clearly labeled as “filtered” or “unfiltered”.

1. Unfiltered samples may be collected after the third consecutive purge interval of turbidity results of 5 NTUs or less.
2. Filtered samples must be taken at wells where turbidity exceeds 5 NTUs after purging and well stabilization. Sample water should be filtered through a 0.45-micron pore size filter unit before filling the laboratory prepared container. New filters should be used for each sample.

Samples for metals analysis should be collected in a manner that minimizes turbulence and aeration and then acidified immediately as described above. Plastic containers should be used for sample collection. The acid will be produced/controlled following the Laboratory QAM/SOPs to ensure that it is pure enough with regard to metals to avoid a false positive analytical result.

4.3.4. Nitrogen series

Sample containers for nitrate/nitrite and ammonia analysis should be prepared in advance by the laboratories with H_2SO_4 as a preservative. The containers should be filled approximately 95% full with unfiltered water. Containers should not be rinsed or overfilled anytime in the field. Samples may be checked with pH paper in the field to verify that the pH has been lowered to less than or equal to pH = 2.

4.3.5. General parameters

The sample containers for laboratory analysis of general parameters, i.e. anions, total dissolved solids, total suspended solids, and alkalinity should not be rinsed in the field or allowed to overflow excessively during sample collection. The containers should be filled completely and capped promptly.

4.4. Trip blanks, equipment blanks, field blanks and duplicate samples

Blanks should be collected to detect background or method contamination. Duplicate samples should also be collected to evaluate analytical precision associated with sample homogeneity, collection, preservation, and storage, as well as lab procedures. Other QA/QC samples (i.e. Matrix Spike and Matrix Spike Duplicates, or Material Checks) may be collected as needed, per the approved SAP. All QA/QC samples should be collected in the same type of container as the corresponding primary samples.

QA/QC sample count should follow:

1. One trip blank for each cooler containing VOC samples. A PFAS trip blank may also be considered.
2. One equipment blank day per day per each field representative conducting independent sampling. At sites where dedicated sampling equipment is installed in all monitoring wells, the equipment blank sample may be eliminated.
3. At least one duplicate sample at a randomized location per event per analysis or one duplicate sample at a randomized location per every 10 samples, whichever is greater. Additional duplicates may need to be taken at other wells to ensure all required parameters are captured in the duplicate evaluation (i.e. if the randomized well selected is not sampled for VOCs, duplicate VOC samples should be collected at an additional randomized location).
4. In cases where cross contamination is suspected, or when PFAS samples are being collected, at least one field blank should be collected each day of the sampling event.

Analytes for each type of QA/QC sample are:

- Trip blanks: VOCs only. Trip blanks for PFAS analysis may also be considered.
- Equipment blank: all permit analytical parameters applicable to the given sampling event.
- Duplicate: all permit analytical parameters applicable to the duplicated well.
- Field blank: all permit analytical parameters applicable to the given sampling event.

4.4.1. Blank sample collection

- **Trip blanks** must be filled and sealed by the analytical laboratory performing the work with laboratory-controlled, analyte-free water. Blank samples should travel in the cooler with the actual sample to and from the field, and to the well head, etc., so that the blanks are exposed to the same conditions as the actual samples. The container blanks should not be opened until they are analyzed in the laboratory along with the primary samples they have accompanied.
- **Field blanks** must be collected in the field. Containers should be opened and placed nearby or held as closely as practical to the point at which actual sample containers are opened and filled. The sample blank containers should be filled with the laboratory-supplied analyte-free water by the same personnel and at approximately the same time as the primary samples are being collected. The sample blank water in each container should be exposed to the air on site for an amount of time equivalent to that for filling and closing a primary sample container.
- **Equipment blanks** are collected in the field. Containers used for each blank should be the same type as for the actual sample. Laboratory-supplied, analyte-free water must be used to fill all blank samples. The same preservatives should be added to both the equipment blank and the primary samples. The equipment blank water should contact all the equipment surfaces, for the chosen piece of equipment being analyzed, that the sample water will contact.

4.4.2. Duplicate sample collection

All containers should be filled as close together in time as practical with a sampling stream that is steady and continuous. Sampling order should follow Section 4.3 (i.e. VOCs for both the primary sample and the duplicate, inorganics for both the primary sample and the duplicate etc.).

Blind duplicate samples may be collected if there is uncertainty related to laboratory procedures and sample analysis and should be discussed between the MPCA and the permittee. **This sample type will require additional coordination on the part of the samplers and laboratory performing the work.** Blind duplicates should be assigned identification aliases (i.e. BD-1, BD-2 etc.) on the sample container label and on the COC sheet. To maintain sample anonymity, the date must be included on the sample container label and COC but not the time. After sample analysis has been completed and prior to submitting the final Lab_MN EDD to the MPCA, this information must also be provided to the laboratory, and they must use this information to identify the sample appropriately in the EDD submittal. The identity of the blind duplicate samples and time of collection must also be recorded in the field sampling form.

5. Documentation of sampling event

Field sampling forms should be designed for documentation of field activities and collection of field data and included with quarterly and annual reports. A blank template should be included as an attachment to the SAP. The field sampling forms must be completed before leaving the sampling point and should be used to collect and document:

- well common name and unique ID;
- pre and post purging/sampling water-level data;
- total well depth as measured during the sampling event;
    - if the total well depth at the time of sampling deviates from the total well depth at the time of construction, evaluate and discuss this information in the quarterly/annual report.
    - well obstructions preventing the collection of a representative well sample should be immediately reported to the MPCA hydrologist, and corrective actions should be completed to resolve/remove/repair the obstruction.
- sampling/purging method and equipment used;
- purging and sampling rate calculations and information including start and stop time;
- total groundwater volume purged;
- well purging/stabilization field water quality measurements; and
    - groundwater sample information (including filtration information)
- blank sample identification as necessary.

5.1. Sample identification

Each sample container must be labeled with the following information using a non-VOC permanent ink on firmly affixed, water-resistant labels:

- site name/permit number;
- unique well identification number;
- well common name;
- unique container ID;
- sample collection date;
- sample collection time;
- initials of field personnel collecting the sample;
- parameter names/groups to be analyzed; and
- preservation method.

5.2. Sample custody protocol

A COC must be completed to document all samples collected. The MPCA COC and instructions for use can be found here. A COC should be initiated in the field at the time of sampling, and a copy must accompany each cooler shipped to any laboratory.

5.2.1. COC documentation

The Minnesota Location Identifiers, Minnesota Unique Well Number, or Location Unique Identifier (LUI) must be used to ensure the data are associated with the correct sampling locations. The "Sample Type" must be populated accurately for each sample listed on the COC within the "Sample Type" column. The codes listed below are common sample types:

Sample type code (for use on COC)	Sample type description
Sample	Routine environmental sample
FMO	Field measurement/observation
QC-FR	Field replicate/duplicate
QC-FB	Field blank sample
QC-BD	Blind field replicate sample/duplicate
QC-EB	Equipment blank
QC-TB	Trip blank

For further information and instruction on sample type selection see Appendix B.

5.2.2. COC documentation

All signatures related to sample custody will be made in blue or black ink on the chain-of-custody in a timely fashion. One or more signatures will be entered to identify the person or persons who are collecting the samples. Each time the custody of a sample or group of samples is transferred, a signature, date, and time will be entered to document the transfer. A sample is considered to be in custody if it is in any one of the following states:

- in actual physical possession;
- in plain view of the custodian;
- in physical possession and secured by a lock so that it cannot be tampered with; and
- in an otherwise secured area, restricted to authorized personnel.

A secured area such as a locked storage shed or locked vehicle may be used for temporary storage. After samples are collected under chain-of-custody tracking, a de-briefing will be held in the field to verify the adherence to the chain-of-custody procedures and to determine whether additional samples are required.

5.2.3. COC during shipping and transfer samples

When samples are shipped, the person sealing the shipping container will enter the time, date, and their signature on the chain-of-custody. The laboratory portion of the chain-of-custody will be enclosed in the container. A post office receipt, bill of lading, or similar document from the shipper should be retained as part of the permanent chain-of-custody documentation.

One or more custody seals will be affixed over the opening of the shipping container in a manner that precludes opening the container without breaking the seals. The container seals will be signed by the person sealing the container and with the date and time sealed.

The receiving laboratory will be notified in advance of any unique chain-of-custody procedures that must be followed for a group of samples. The laboratory should be instructed to note whether or not the container seals are intact and sign in the appropriate blank on the chain-of-custody at the time of receipt. They should also be instructed to make a copy and return it to the permittee or their consultant for inclusion in quarterly and annual reports.

5.3. Field log

A daily field log of sampling activities should be kept by the field sampling personnel. This record or log should supplement information entered on the field sampling forms. At a minimum, the log should contain a record of the following items:

- list of field personnel present;
- field conditions as described below in Section 5.4 "Field Conditions";
- meter calibration information;
- summary of how samples were transferred/transported to laboratories; and
- description of exceptions to the approved SAP including specifications of which samples may have been impacted by those exceptions.

Information for each well sampled should include:

- the unique identifier used to label samples;
- well name and unique well number;
- date and time that sampling began and ended;
- list of primary and QA/QC samples sent to each laboratory; and
- if needed, an alias cross-reference list for QA/QC samples.

5.4. Field conditions

Field conditions during the sampling event should be recorded on the field sampling forms. The quarterly and/or annual report should include a statement regarding the likelihood that any unusual field conditions had a significant impact on the integrity of results. Field conditions reported should include but not be limited to the following:

- air temperature;
- wind direction;
- precipitation/moisture;
- ambient odors; and
- airborne dust.

6. Sample preservation, handling and transport

This section describes procedures that will be followed between the time samples are collected and the time they are either shipped or delivered to an analytical laboratory.

6.1. Sample preservation

All chemical preservatives added to containers in the laboratory or field must be produced and controlled within the laboratory's QA/QC program as reflected in the Laboratory QAM or SOP. Field supplies of preservatives and sample containers with pre-dosed preservatives will be discarded and replaced with fresh preservatives no later than 14 days after receipt from the laboratory or the time allowed by the Laboratory QAM and/or SOPs.

All samples will be thermally preserved in the field immediately after sample collection by placing the samples in an insulated ice chest containing uncontaminated/securely sealed ice. The use of freezer packs is not acceptable. The ice chest containing volatile organic compound samples will be checked for a temperature that is recorded just before transporting samples and upon receipt at the laboratory to verify whether or not samples are kept refrigerated at 4 $\pm$ 2 degrees C.

6.2. Sample handling and transport

All ice chests shipped will be accompanied by a chain-of-custody and will contain a complete address and return address both inside and outside. The samples will be kept at 4 ± 2 degrees C during transport to laboratories. Before transporting samples, the sampling consultant should:

- Verify that laboratory personnel will be present to receive samples when they arrive;
- Verify that laboratory personnel understand chain-of-custody and sample storage/preservation requirements;
- Check labeling and documentation to ensure sample identity will be clear to laboratory personnel;
- Hand deliver or ship samples in a manner that ensures samples will remain cool, 4 ± 2 degrees Celsius, until received by laboratory personnel; and
    - an exception is made for samples that were collected and placed in the ice chest very shortly before delivery.
- Maintain the chain-of-custody according to procedures described above.

7. Example sequence of field sampling activities

1. Inspect the well for damage, missing parts, labeling, and for evidence of tampering. Document field conditions.
2. Review equipment list; prepare area around well for sampling; don protective gloves.
3. Unlock well and remove inner riser cap to clean storage.
4. Use explosivity meter and/or organic vapor monitor, as appropriate.
5. Calibrate equipment within specified operating limits, and document.
6. Measure static water elevation and well depth; calculate well volume.
7. Document field work in the field logbook and other appropriate forms.
8. Measure field parameters while simultaneously purging the well based on predetermined rates.
9. Consult parameter list; adequately label parameters on the sample container.
10. Collect the sample and field filter as appropriate; add preservatives as specified.
11. Place the samples on ice in a shipment cooler.
12. Prepare and collect quality control samples.
13. Perform additional field analyses if specified.
14. Measure final water level.
15. Complete documentation for the field sampling form.
16. Replace inner riser cap and lock well.
17. Clean any reusable equipment and proceed to the next well.
18. Initiate chain-of-custody controls.
19. Ship the samples to the laboratory for analysis.

8. References and resources

1. Low-Flow (Minimal Drawdown) Ground-Water Sampling Procedures, Environmental Protection Agency, 1996. https://www.epa.gov/remedytech/low-flow-minimal-drawdown-ground-water-sampling-procedures.
2. Sampling Procedures for Ground Water Monitoring Wells, Minnesota Pollution Control Agency – Water Quality Division, Reapproved 2006. https://www.pca.state.mn.us/sites/default/files/wq-gw1-01.pdf.
3. Code of Federal Regulations Title 40: Protection of the Environment, Chapter I: Environmental Protection Agency, Subchapter 1: Solid Wastes, Subpart E – Groundwater Monitoring and Corrective Action, Office of the Federal Register, 2016. https://www.epa.gov/sites/default/files/2016-03/documents/subparte_0.pdf.
4. Standard Guide for Sampling Ground-Water Monitoring Wells D4448-01, ASTM® International, Reapproved 2019.
5. Guidance for Per- and Polyfluoroalkyl Substances (PFAS): Sampling, Minnesota Pollution Control Agency, 2022. https://www.pca.state.mn.us/sites/default/files/p-eao2-27.pdf.
6. Closed Landfill Program Sampling Protocol for Monitoring Wells, Minnesota Pollution Control Agency – Closed Landfill Program, 2022. Available via MPCA information request form.
7. Instructions for filling out the MPCA Chain of Custody form, Minnesota Pollution Control Agency, 2023. https://www.pca.state.mn.us/sites/default/files/c-rem4-49.pdf.
8. Standard Guide for Purging Methods for Wells Used for Groundwater Quality Investigations D6452-18R23, ASTM® International, Reapproved 2023.
9. Groundwater Sample Collection and Analysis Procedures, Minnesota Pollution Control Agency – Petroleum Remediation Program, 2024. https://www.pca.state.mn.us/sites/default/files/c-prp4-05.pdf.
10. Quality Assurance Project Plan Standard, Environmental Protection Agency, 2024. https://www.epa.gov/system/files/documents/2024-04/quality_assurance_project_plan_standard.pdf.
11. Laboratory Quality Control and Data Policy, Minnesota Pollution Control Agency, 2024. https://www.pca.state.mn.us/sites/default/files/p-eao2-09a.pdf.
12. MERLA Groundwater and Soil Investigation Guidance, Minnesota Pollution Control Agency, 2025. https://www.pca.state.mn.us/sites/default/files/c-rem3-34.pdf.