

Soil and groundwater assessments performed during site investigations

Petroleum Remediation Program

This document describes the requirements for completing soil and groundwater assessments during a site investigation. All site investigations begin as a limited site investigation (LSI) but may proceed to a remedial investigation (RI). The LSI evaluates risk based on a quick assessment of current site conditions. An objective of the LSI is to identify low-risk sites where further investigation or corrective action is not necessary. The information collected during the LSI helps determine whether an RI is necessary. An RI measures groundwater contaminant concentrations in monitoring wells over time to establish plume stability.

The Minnesota Pollution Control Agency (MPCA) encourages completing the receptor surveys described in [Risk evaluation and site management decision at petroleum release sites](#) prior to initiating the soil and groundwater assessments. Identifying receptors and potential exposure pathways supports effective planning of soil and groundwater assessment activities. Risk is evaluated by measuring the extent and magnitude of contamination with respect to identified receptors. Therefore, it is important to identify receptors ahead of any subsurface investigation.

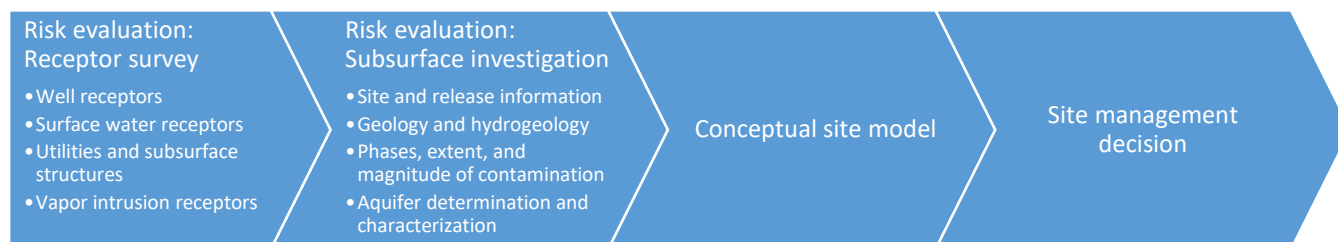
Vapor intrusion assessment

A vapor intrusion assessment is also required during the site investigation. It is discussed in [Vapor intrusion assessments performed during site investigations](#).

I. Conceptual site model

The site investigation involves development of a conceptual site model (CSM). Soil, groundwater, and vapor intrusion assessment data, in conjunction with receptor survey results, are critical for developing the CSM. The following discussion provides the context for planning, completing, and evaluating results from a risk evaluation.

A CSM provides the framework for evaluating site-specific exposure pathways upon which site management decisions are based. The CSM integrates the various elements of the risk evaluation (subsurface investigation and receptor surveys) to assess potential exposure pathways in accordance with the Petroleum Remediation Program's risk-based approach. Site management decisions are often based on multiple risks that must be considered collectively prior to making a comprehensive site management decision. Site management decisions may lead to additional investigation or corrective action that subsequently alters the CSM by addressing one or more of its elements. The [Investigation report](#) is structured to facilitate development of the CSM. The elements outlined in the [Investigation report](#) that need to be considered in developing the CSM are illustrated below.



The focus of the CSM should lead towards identifying any additional investigation, monitoring, or corrective action necessary to address exposure pathways, or towards justifying site closure. The CSM should not summarize or reiterate the various elements of the risk evaluation. A successful CSM focuses on the relationship between identified risks and the investigation results to identify site-specific exposure pathways. The CSM must demonstrate that all exposure pathways have been adequately investigated, and any high risks have been addressed if site closure is recommended.

At the time the [Investigation report](#) is submitted, it may not be possible to create a complete CSM based on the available data. The CSM is still necessary at this stage to identify additional data needs and to focus the investigation. As the site investigation progresses and corrective actions are implemented, update and re-evaluate the CSM to support subsequent site management decisions.

The [Investigation report](#) figures, particularly the cross sections, are essential for illustrating the pathway evaluation discussed in the CSM. Figures should depict significant relationships between risk evaluation elements.

An accurate CSM requires an understanding of the three-dimensional distribution and behavior of each of the four basic subsurface petroleum contaminant phases:

1. Light non-aqueous phase liquid
2. Aqueous phase
3. Vapor or gaseous phase
4. Adsorbed or solid phase

Within a relatively short time after a significant petroleum release, all four petroleum contaminant phases are usually present in the subsurface. The four phases exhibit different subsurface behaviors due to their differing physical and chemical properties. The subsurface behavior of the various phases is also affected by site-specific geology. Identifying exposure pathways for the various phases is fundamental to developing the CSM. Exposure pathway evaluation begins with receptor identification and delineating the extent and magnitude of contamination in relation to receptors.

Natural attenuation of petroleum releases is an important consideration of CSM development. Not all petroleum compounds behave similarly in the environment. Some compounds are resistant to an important natural attenuation process. Leaded gasoline additives, particularly 1,2-dibromoethane (EDB) and 1,2-dichloroethane (DCA), and the oxygenate methyl tertiary-butyl ether (MTBE) are synthetic, non-readily biodegradable compounds. They have higher aqueous solubility limits than naturally occurring, readily biodegradable petroleum compounds such as benzene. Releases of these synthetic compounds present an additional risk. They can travel farther and may persist in the environment longer than naturally occurring hydrocarbons. If these compounds are present, consider their behavior in the CSM and when making the site management decision.

II. Soil contamination assessment

A. Drilling methods

Preferred drilling methods include hollow-stem auger and sonic, or, for LSIs where conditions are appropriate, direct push. Do not use direct push when conditions at the site are likely to result in not meeting, or the technology had previously failed to meet, the drilling depth requirements. Do not use solid-stem flight augers for soil borings unless approved by the MPCA. Perform continuous soil sampling unless the MPCA approves an alternative approach. For all borings, follow the procedures listed below:

1. Completely clean all down-hole equipment and tools prior to each use to avoid cross-contamination. Cleaning methods include power spray wash, brushing with appropriate cleaning solution, and clean water rinse.
2. Boreholes not completed as monitoring wells should be sealed in accordance with the Minnesota Department of Health well code ([Minn. R. ch. 4725](#)).

3. Complete a drilling log for every soil boring advanced. When monitoring wells are completed in a boring, provide well construction diagrams as described in [Section III.B](#) below. At a minimum, information in the logs should include:
- Depth to start and finish of each attempted soil sample interval (feet)
 - Recovery for each attempted soil sample interval (feet)
 - Soil classification in accordance with the 1952 Unified Soil Classification System (USCS) or with [American Society for Testing Materials \(ASTM\)](#) test methods [D2487](#) or [D2488](#)
 - Further description of soil (grain size, sorting, color, geologic origin, etc.)
 - Depth of significant changes in material (feet)
 - Approximate depth to water below grade (feet); include date and time of measurement
 - Soil headspace screening results in parts per million by volume (ppmv)
 - Comments regarding significant geologic and hydrogeologic features, visual and olfactory evidence of contamination, and petroleum sheen test results
 - Depth to top and bottom of open hole or exposed screen if collecting water samples from an open boring or temporary well
 - Date and time boring started and completed
 - Date and time boring sealed
 - Name of driller and consultant, as well as others present during drilling
 - Drilling method
 - Boring identification number
 - Penetration test records, if applicable
 - Ground surface elevation (feet, relative to identified datum). To establish ground surface elevation, survey all boring locations

B. Drilling locations

1. Magnitude of soil contamination and source identification

Advance a soil boring in or immediately adjacent to all tank basins and tank components regardless if there is a known release associated with them. These include underground storage tank basins, aboveground storage tank basins, product transfer areas, piping, dispensers, remote fill pipes, valves, known release areas not previously assessed, and visibly stained areas.

2. Horizontal extent

Drill a sufficient number of soil borings to define the horizontal extent of soil contamination, keeping in mind that the most extensive soil contamination may not be near the ground surface. In general, do not drill the initial borings used to define the horizontal extent more than 50 feet from a source area. The number of borings will vary depending on site conditions, extent of contamination, and locations of receptors. Horizontal extent is considered defined in the field if there is no visual evidence of contamination, there are no petroleum odors, and soil headspace screening results (i.e., photoionization detector (PID) readings) are less than 10 ppmv. In addition to field-based evidence, extent is also defined by a soil analytical level of 100 mg/kg gasoline range organics (GRO) or diesel range organics (DRO). If subsequent laboratory analysis indicates the extent has not been defined, complete additional borings.

3. Vertical extent

Drill soil borings to five feet below the water table or, if contamination extends below the water table, to 10 feet below the deepest measurable contamination, whichever is deeper. If the water table is very deep and you have drilled 10 feet below the deepest measurable contamination in the unsaturated zone, discontinue drilling. Vertical extent is considered defined in the field if there is no visual evidence of contamination, there are no petroleum odors, and PID readings are less than 10 ppmv. If bedrock is encountered, contact the MPCA to discuss whether bedrock monitoring wells are necessary.

Examples:

- If contamination extends to 10 feet and the water table is at 20 feet, advance the boring to 25 feet.
- If contamination extends to 20 feet and the water table is at 15 feet, advance the boring to 30 feet.
- If contamination extends to 20 feet and the boring has been advanced to 30 feet without encountering the water table, end the boring at 30 feet.

4. Site stratigraphy

To evaluate site stratigraphy, complete at least one soil boring to 20 feet below the deepest site contamination. If the water table is encountered, at least one boring a minimum of 20 feet below the water table is necessary. If the water table is very deep and you have drilled 20 feet below the deepest site contamination in the unsaturated zone, contact the MPCA for approval to discontinue drilling deeper. Locate the soil boring near the suspected release point but not within an area of light non-aqueous phase liquid (LNAPL). If there is a risk of cross-contamination by piercing a confining unit, complete the boring in an uncontaminated area. If additional site stratigraphy data are available, the MPCA may waive this requirement with prior approval.

Examples:

- If contamination extends to 10 feet and the water table is at 20 feet, advance the boring to 40 feet.
- If contamination extends to 25 feet and the water table is at 20 feet, advance the boring to 45 feet.
- If contamination extends to 20 feet and the boring has been advanced to 40 feet without encountering the water table, then call the MPCA staff for approval to discontinue drilling deeper.

5. Utility backfill investigation

Advance hand-driven or hand-augured soil borings in the utility backfill if underground utilities (sanitary and storm sewer lines, water distribution lines, etc.) appear to intercept contaminated soil or groundwater. The purposes of these soil borings are to investigate potential migration of LNAPL and contaminated groundwater within the backfill and to assess the potential for water line permeation. The backfill investigation is especially important when low permeability soil (e.g., clay) occurs near the surface.

C. Soil sampling

1. Stratigraphy

Record geologic descriptions for all soil samples collected and note changing drilling conditions that provide relevant geologic and stratigraphic information. Be sure to note the presence and thickness of sand and gravel lenses within less permeable soils.

2. Grain-size analysis

Grain-size analysis is required at all sites to verify field classification of soils. In saturated conditions, grain-size analysis is required to estimate hydraulic conductivity. Collect a minimum of three soil samples from different locations/horizons. If groundwater is encountered, collect at least two of the samples below the water table from horizons that appear to have the highest hydraulic conductivity. If a confining layer is encountered, collect an additional grain-size sample to characterize the soil. Record the depth of collected samples on the boring logs. Analyze samples using American Society for Testing Materials (ASTM) test methods [D6913 / D6913M](#) and [D7928](#).

If installing deep monitoring wells during an RI, collect additional soil samples for grain-size analysis to estimate the hydraulic conductivity at the depth of the screened interval.

3. Soil headspace screening

Collect and evaluate soil samples for organic vapors with a PID at least every 5 feet in uncontaminated soil, at changes in material, and at least every 2.5 feet in contaminated soil. Record the depth of collected samples and the PID readings on the boring logs. Soil headspace screening procedures are described in [Soil sample collection and analysis procedures](#).

4. Petroleum-saturated soil screening

Use the petroleum sheen test described in [Soil sample collection and analysis procedures](#) to determine if soil is petroleum saturated. Collect and evaluate soil samples for petroleum sheen in contaminated soil with a PID reading of 10 ppmv or greater. Additionally, evaluate soil samples where other field evidence, such as staining, suggests residual LNAPL may be present. Record the depth of collected samples and the results on the boring logs.

5. Laboratory analysis

Select soil samples for laboratory analysis according to the guidelines in Table 1, and record the sampling depth on the boring logs. The objective of discrete soil sampling is to sample the interval that represents the most impacted horizon. Collect and analyze soil samples following the procedures and analytical requirements described in [Soil sample collection and analysis procedures](#).

Table 1. Soil analytical sampling depths based on groundwater and contamination occurrence.

	No contamination	Contamination
No groundwater	Boring terminus	Highest PID reading <u>and</u> boring terminus
Groundwater	Water table	Water table <u>and</u> highest PID reading if not at the water table ^{1,2}

¹If contamination extends more than ten (10) feet below the water table, collect groundwater samples below the water table according to Section III.A.1.

²If the highest PID reading occurs at the water table, only one soil sample is required.

6. Surface soil assessment

The surface soil assessment is supplemental to standard soil headspace screening, petroleum-saturated soil screening, and laboratory analysis sampling described above. For soil borings completed in areas without an impervious surface, assess surface soil according to the following protocols:

- Screen soil using soil headspace screening (PID readings), the petroleum sheen test, and visual observation of stained soil from the applicable depth interval(s) according to current land use: 0-2 feet for commercial and industrial, or 0-2 and 2-4 feet for residential.
- Collect a soil sample for laboratory analysis from each interval where the PID reading is at or above the screening level (Table 2) or the soil is visibly stained. The sample should represent the most contaminated soil within the screened depth interval. When the petroleum sheen test result is positive a soil sample is not required, regardless of PID reading or staining. Analyze samples for GRO and/or DRO according to Table 3.

Table 2. Surface soil headspace screening levels (PID readings).

Petroleum product	Screening level (ppm)
Gasoline, ethanol-blended fuel, and aviation gasoline	40
Diesel fuel, fuel oil, used or waste oils, jet fuel, kerosene	10

Table 3. Surface soil analytical requirements.

Petroleum product	Required analysis
Gasoline and aviation gasoline	GRO
Diesel fuel, fuel oil, used or waste oils, jet fuel, kerosene	DRO
Unknown petroleum or hydrocarbons mixture	GRO and DRO

Surface soil sampling results are reported in the [Investigation report](#). See [Risk evaluation and site management decision at petroleum release sites](#) for the criteria used to define surface soil as contaminated. When you identify contaminated surface soil during the site investigation, provide recommendations for delineating the extent of surface soil contamination in the [Investigation report](#).

Prior to approving a corrective action, the extent of contaminated surface soil must be delineated after the site investigation. Delineation after the site investigation is completed using the same procedures and criteria described above. Base sampling locations on a grid pattern with 20-foot node spacing in areas where contaminated surface soil was identified during the site investigation. Additional laboratory analyses may be required for soil treatment or disposal as described in [Soil sample collection and analysis procedures](#).

7. Water levels

Measure the water level in all borings and compute groundwater elevations. Record the time when measurements are made. Inspect soils for evidence of a fluctuating water table and a seasonal high water table (i.e., mottling). Record on the boring log the amount of time the boring was left open to allow measurement of the water level. Borings may be left open up to 72 hours to facilitate accurate water level measurements and collection of groundwater samples.

8. LNAPL

If mobile LNAPL is found during boring advancement, notify the Minnesota duty officer (651-649-5451 or 800-422-0798) within 24 hours and immediately begin LNAPL recovery. Install permanent monitoring wells as soon as possible to define the extent of mobile LNAPL. If there are questions about whether to convert a boring to a monitoring well when mobile LNAPL is discovered or appears likely to be present, contact the MPCA to discuss. Refer to [Light non-aqueous phase liquid management strategy](#) for additional information.

III. Groundwater contamination assessment

A. Limited site investigations

At sites where contaminated soil is in contact with groundwater, or groundwater contamination appears likely, a groundwater contamination assessment is necessary as part of the LSI. The objectives of the assessment are to determine whether groundwater is, or likely to be, impacted; whether the impacted hydrogeologic unit is considered an aquifer; and, if groundwater is impacted, the magnitude and horizontal extent of the impacts. Horizontal extent is considered defined when contamination at the plume edge does not exceed any drinking water standard or 1 mg/L GRO or DRO. In addition, assessing potential vertical contaminant migration may be required, but defining the vertical extent of groundwater impacts is not required at this point.

1. Groundwater sampling

- Collect groundwater samples from all soil borings (temporary wells) where groundwater is encountered.
- Set temporary well screens to intersect the water table. Provide well construction diagrams for each temporary monitoring well. See [Section III.B.2](#) below for well construction diagram requirements.
- If contamination extends 10 or more feet below the water table, collect additional groundwater samples below the water table.
- Collect and analyze groundwater samples following the procedures and analytical requirements described in [Groundwater sample collection and analysis procedures](#).

2. Aquifer determination

Aquifer determination is based primarily on the transmissivity of the impacted hydrogeologic unit.

Transmissivity is a function of hydraulic conductivity and saturated unit thickness. Hydrogeologic units with a transmissivity greater than 50 ft²/day are considered aquifers. In addition, any unit that produces water to a supply well or spring is considered an aquifer, regardless of the estimated transmissivity.

Hydraulic conductivity: Use an empirical formula to estimate hydraulic conductivity from the grain-size analysis results of samples collected within the saturated zone ([Section II.C.2](#)). Select a formula that is applicable to the grain-size analysis results. For example, do not use a formula if a sample's effective grain diameter or coefficient of uniformity does not fall within the formula's applicable range. If no empirical formulas are applicable, use the value listed in Table 4 for the appropriate soil type. If using Table 4, use the soil type designation from the grain-size analysis results, not the in-field soil type designation.

Table 4. Referenced hydraulic conductivity values.¹

Soil type	Hydraulic conductivity (cm/s)	Hydraulic conductivity (ft/d)
Clay	10 ⁻⁶	0.002835
Silt, sandy silts, clayey sands, till	10 ⁻⁴	0.2835
Silty sands, fine sands	10 ⁻³	2.835
Well-sorted sands, glacial outwash	10 ⁻¹	283.5
Well-sorted gravel	1	2835

¹Fetter, C.W. 2001. Applied Hydrogeology. 4th ed. Prentice-Hall, Inc., Upper Saddle River, NJ. Values represent the higher end of hydraulic conductivity ranges from Fetter (2001).

Hydrogeologic unit thickness: Determine the saturated unit thickness according to what each grain-size sample represents and soil boring data, nearby well records, or other published information. If the sample represents a single impacted unit, use the saturated thickness of that unit. If the sample represents a thinner, more conductive layer within a thicker, less conductive unit, use the thickness of the more conductive layer. Note, however, that the thicker, less conductive unit may also meet the definition of an aquifer. Thickness is not limited to the vertical extent reached in soil borings if other information indicates the unit extends beyond the maximum drilling depth.

Final aquifer determination: If any grain-size sample's transmissivity is greater than 50 ft²/day, it is considered an aquifer. Justify the aquifer determination in the [Investigation report](#) by explaining the rationale for the selected grain-size sample locations, hydraulic conductivity estimates, and unit thicknesses.

3. RI determination

An RI is required if the LSI determines one of the following, conditions exist:

- An aquifer has been (or is likely to be) contaminated by petroleum compounds at concentrations above drinking water standards or above 1 mg/L GRO or DRO.
- Surface water has been (or is likely to be) contaminated by petroleum compounds at concentrations above applicable surface water standards or above 1 mg/L GRO or DRO.
- Mobile LNAPL is encountered.

An RI may be necessary if certain other site-specific conditions are present. If an RI is not necessary, submit the LSI.

B. Remedial investigations

Remedial investigations measure groundwater contaminant concentrations in monitoring wells over time to determine whether a plume is stable. Monitoring well data also are used to calculate travel times within an impacted aquifer to evaluate risk to groundwater receptors. The following section explains monitoring well placement and construction, aquifer characterization, and monitoring well data evaluation.

1. Monitoring well placement

Worst-case monitoring wells: Place monitoring wells within or close to any confirmed or likely source area (e.g., underground storage tank basins, aboveground storage tank areas, product transfer areas, buried lines, pump islands, remote fill pipes, and known spill areas). Install monitoring wells to define mobile LNAPL (if present).

Lateral and downgradient monitoring wells: Place monitoring wells to define plume width and length. Place monitoring wells in an arrangement that defines the downgradient extent of the groundwater contaminant plume (any contamination exceeding drinking water standards or 1 mg/L GRO or DRO). At least one downgradient monitoring well must be located within 20 degrees of the longitudinal axis of the plume. The longitudinal axis is determined using hydraulic gradient measurements. If hydraulic gradient measurements are inconsistent between monitoring events or inconsistent with the plume's geometry, use plume geometry to determine the groundwater flow direction.

Deep monitoring wells: A deep monitoring well has its screen set entirely below the water table. Consideration needs to be given to the design of deep monitoring wells, including screen length and placement. There are several situations when deep monitoring wells may be needed:

- If soil borings show, that contamination has migrated more than 10 feet below the water table
- If an evaluation of hydrogeologic data indicate downward contaminant migration is likely
- If the impacted aquifer is a drinking water aquifer, or hydraulically connected to a deeper aquifer, with an active water supply well within 500 feet

A network of deep monitoring wells may be necessary to determine the three-dimensional extent of the plume, calculate flow direction, and estimate travel time.

Contact the MPCA before installing a deep monitoring well. Be prepared to discuss site stratigraphy, well receptors, and monitoring well construction.

Legal access for off-site monitoring wells: Legal access for off-site monitoring well locations may prove difficult in some locations. If legal access is not obtained after two written attempts, contact the MPCA for assistance.

Screen placement:

- Install water table monitoring wells so the water table intersects the screen. Document and justify any exceptions in the [Investigation report](#).
- Deep monitoring well screens do not intersect the water table. Screen placement depends on the purpose of the well. If the well is installed to measure vertical gradient, the top of the screen should be at least twenty feet below the water table (but within the same aquifer). If the well is installed to monitor water quality in a deeper aquifer, place the screen entirely within that aquifer, typically using a five-foot screen.
- During monitoring well construction at sites where geologic conditions make it difficult to determine the actual depth to water, allow the borehole to remain open at least 24 hours prior to monitoring well completion to let the water level to stabilize.
- Consider using a slightly longer well screen (15-20 feet) to compensate for water table fluctuations.
- Phased well installation may be appropriate. This allows for determination of the approximate water table depth in one or two wells, and then the remaining wells can be installed with proper screen placement.

2. Monitoring well construction

- Construct monitoring wells in accordance with the Minnesota Department of Health water well construction code [Minn. R. ch. 4725](#). However, it is recommended that monitoring wells not be installed in borings that extend more than 10 feet beyond the bottom of the screen.
- Properly clean all monitoring well materials prior to installation.
- In general, avoid the use of liquid drilling fluids. However, they may be approved by the MPCA on a site-specific basis.
- Properly develop all wells to ensure adequate hydraulic connection with the aquifer and to remove any drilling fluid if used. Document the development procedures and results.

Complete monitoring well construction diagrams for every monitoring well. The minimum information required includes, but is not limited to:

- Diagram of major well features, including borehole annulus, top and bottom of screen, casing/riser, top and bottom of sand pack, top and bottom of pack seal, grout, surface seal, protective casing, etc.
- Depth from ground surface to all major well features including top of casing (feet)
- Well screen slot size (inches)
- Sand pack size (inches)
- Inner diameters of riser casing, screen, protective casing, and borehole (inches)
- Well development information, including date, start/end times, methods used, gallons pumped, turbidity, recharge, etc.
- Well construction materials
- Unique well number and project identification number
- Date well begun and completed
- Driller and consultant names
- Elevation of ground surface and measurement point, i.e., top of riser casing (feet, relative to identified datum)

3. Aquifer characterization

Aquifer characterization involves calculating groundwater velocity and travel time.

Groundwater velocity: The velocity at which groundwater is moving in the aquifer, or seepage velocity, is calculated using the hydraulic conductivity (K), the hydraulic gradient (dh/dl), and the effective porosity of the aquifer (n_e).

$$v = -\frac{Kdh}{n_e dl}$$

Hydraulic conductivity is determined using grain-size analysis results as described in [Section III.A.2](#) above. Select a hydraulic conductivity that represents the contamination's primary flow path, which will typically be the highest conductivity. Measure the hydraulic gradient in monitoring wells during the RI; use an average gradient when multiple measurements are available. If deep wells are installed, separately measure the hydraulic gradient in the deep well network. Estimate effective porosity using a referenced value based on the aquifer material. Calculate the velocity for the water table aquifer. If deep wells are installed, also calculate the velocity at depth.

Estimated travel time: Using the groundwater velocity described above, calculate the distance groundwater will travel in five years. Evaluate whether a receptor exists within the estimated five-year travel time of the plume edge. If there are no receptors within a five-year travel time, the aquifer characterization is complete for submitting the [Investigation report](#).

Measured travel time: When a groundwater receptor is within the estimated five-year travel time of the downgradient plume edge, the MPCA may require a more robust travel-time calculation to further evaluate risk. This travel-time calculation is referred to as a measured travel time. One option is to complete a pump test to determine the hydraulic conductivity. In general, a single-well pump test is completed following the standards in [Minn. R. 4720.5530](#). Use the hydraulic conductivity determined from the pump test to recalculate groundwater velocity and travel time. Other options may also be proposed to measure travel time.

Deep monitoring wells: When deep monitoring wells are installed to evaluate vertical contaminant migration, calculate vertical hydraulic gradients for all nested well pairs. Determine groundwater flow direction using the measured hydraulic gradient in the deeper well network and the plume's geometry.

4. Data evaluation

Investigation report submittal: Submit the [Investigation report](#) after two quarters of groundwater sampling. Continue quarterly sampling from all monitoring wells until site closure or until the MPCA approves a different sampling schedule.

For the [Investigation report](#), consider the following questions when evaluating monitoring well data.

- Has the plume extent been adequately delineated with monitoring wells?
- Is there an adequate downgradient monitoring well along the longitudinal axis of the plume?
- Is groundwater flow direction certain?
- If mobile LNAPL is present, has it been delineated with monitoring wells?
- Is there a need to evaluate the vertical extent of groundwater contamination?

Post-investigation report submittal: In addition to the questions listed above, consider the following questions for monitoring data collected after the [Investigation report](#):

- Is the groundwater plume stable, expanding, or is stability not apparent?
- Are contaminant concentration trends apparent in all wells? Are the trends consistent or inconsistent between wells?
- Have water levels shown seasonal or other significant fluctuations? Are contaminant concentrations correlated to water level fluctuations?
- Is the monitoring well network still adequate to evaluate plume stability?
- Is there evidence of migrating LNAPL?

Plume stability: Multiply lines of evidence should be used to evaluate plume stability. Creating time series plots to show contaminant concentrations over time is one line of evidence that is useful for visualizing data and qualitatively evaluating trends. Plot water levels on the secondary y-axis to look for correlations between water level and concentration. At least six quarters of groundwater monitoring data are required to complete a qualitative trend analysis.

Another way to evaluate plume stability is by monitoring for natural attenuation. Various natural processes can control the movement of a petroleum plume and act to limit the risks. Additional parameters can be collected during groundwater sampling events in order to assess for natural attenuation. See [Assessment of natural biodegradation at petroleum release sites](#).

In addition to natural attenuation, natural source zone depletion (NSZD) is a combination of processes that can reduce the mass of LNAPL in the subsurface. These processes include dissolution of LNAPL constituents into groundwater and volatilization of LNAPL constituents into the vadose zone. Additional information on NSZD can be found in the following publication:

ITRC (Interstate Technology & Regulatory Council). 2009. Evaluating Natural Source Zone Depletion at Sites with LNAPL. The Interstate Technology & Regulatory Council LNAPLs Team
<https://www.itrcweb.org/GuidanceDocuments/LNAPL-1.pdf>.

For sites with nearby receptors, expanding plumes, impacts to a drinking water aquifer, or impacts to water supply wells below drinking water standards, groundwater monitoring is likely to extend beyond six quarters.

For sites with sensitive groundwater conditions, groundwater monitoring is required for a minimum of three years as described in [Assessment of sensitive groundwater conditions](#). When at least 10 sampling events have been completed, a statistical trend analysis such as Mann-Kendall, the Ricker Method, or another approved analysis can be used as another line of evidence to evaluate plume stability. Statistical analyses may have specific data collection and analysis requirements to obtain valid results, so it is important to consider test requirements at the start of the investigation.

Additional information regarding statistical analysis for groundwater monitoring data can be found in the following publications:

ITRC (Interstate Technology & Regulatory Council). 2013. Groundwater Statistics and Monitoring Compliance, Statistical Tools for the Project Life Cycle. GSMC-1. Washington, D.C.: Interstate Technology & Regulatory Council, Groundwater Statistics and Monitoring Compliance Team.
<http://www.itrcweb.org/gsmc-1/>.

Ground Water Monitoring and Remediation. 2008. A Practical Method to Evaluate Ground Water Contaminant Plume Stability by Joseph A. Ricker. Ground Water Monitoring & Remediation 28, no. 4: 85–94.

Other considerations when evaluating groundwater data include:

- Evaluate concentration trends both within the plume and at the plume edge. Are consistent trends seen across the plume, or is there an increasing trend within a part of the plume?
- Data from worst-case monitoring wells may not be suitable for assessing trends if located in areas of residual LNAPL because of the potential for significant concentration fluctuations between sampling events.
- Monitoring wells located beyond the plume edge with non-detectable concentrations should not be used as the only line of evidence to indicate a stable plume.

Before implementing any of these plume stability tools, please contact your MPCA project team to discuss. It is up to the MPCA to determine site closure; therefore, additional work may be requested to reinforce site decisions.

Vapor intrusion assessments performed during site investigations

Petroleum Remediation Program

I. Introduction

This document describes the methodology for completing a vapor intrusion (VI) assessment at a site in the Minnesota Pollution Control Agency's (MPCA) Petroleum Remediation Program (PRP). Vapor intrusion is the migration of volatile organic compounds (VOCs) from an underground source through soil or other pathways into buildings. A VI assessment is required when completing a site investigation within PRP.

The goal of a VI assessment is to evaluate the VI pathway associated with a petroleum release. The VI pathway has three elements: receptor, vapor source, and subsurface migration route. A receptor is a person potentially affected by VI, generally an occupant of a building. A vapor source is the supply of VOCs, such as contaminated soil or groundwater or light non-aqueous phase liquids (LNAPL). A subsurface migration route is the path that vapors travel through soil or other pathways in the unsaturated zone. The VI assessment uses field-based methods to evaluate the VI pathway, including a receptor survey, soil gas sampling, sub-slab sampling, and indoor air sampling. For additional background information, see [Technical Guide For Addressing Petroleum Vapor Intrusion At Leaking Underground Storage Tank Sites](#) (EPA 2015) and [Petroleum Vapor Intrusion Fundamentals of Screening, Investigation, and Management](#) (ITRC 2014).

II. Step 1 - Soil gas assessment

Complete a soil gas assessment while defining the extent and magnitude of soil and groundwater impacts. There are limited situations in which the MPCA may preapprove a different scope of work than what is described here. This may include waiving specific requirements, expediting an investigation, or adjusting the assessment to site-specific conditions.

A. Receptor survey

Start the soil gas assessment by identifying VI receptors within a 100-foot radius of the source area(s), or the area(s) of highest known or suspected petroleum contamination. If there are no receptors within 100 feet of the source area(s), contact the MPCA to determine if a soil gas assessment is required. If it is not required, provide sufficient information in the [Investigation report](#) to document that receptors are not present.

B. Soil gas sampling

Once you have identified receptors and source area(s), collect soil gas samples and submit them for analysis by EPA Method TO-15 for compounds on the Minnesota Soil Gas List and EPA Method 3C for fixed gases (methane, oxygen, carbon dioxide, and carbon monoxide). Collect soil gas samples from the following locations using the procedures in Section V:

- A. **Source area(s):** Collect one soil gas sample from a direct push boring advanced close to the source area(s) to the required depth (Table 1). The highest contamination is often found at the source

Soil gas monitoring points

Permanent soil gas monitoring points to monitor contaminant concentrations over time may be required in certain situations. These may include recent releases, unstable groundwater plumes, migrating LNAPL, and highly fluctuating water tables. See Section V for construction details.

of the release (e.g., tank basin), but other situations may exist and should be assessed to ensure that soil gas associated with the most heavily contaminated soil or groundwater is sampled.

If a source area is adjacent to, or underneath, a receptor, you may need to collect seasonal sub-slab samples with, or instead of, an exterior soil gas sample. If your site fits this situation, contact the MPCA for approval before collecting samples.

- B. **Receptor-specific:** Collect up to four soil gas samples near receptors that are within 100 feet of the source area sample(s). Use Table 1 to determine the required depth. Collect receptor-specific samples under the following scenarios:
- Fewer than four receptors: If four or fewer receptors, including onsite receptors, are located within 100 feet of the source area sample, collect one soil gas sample near each receptor.
 - More than four receptors: If more than four receptors, including onsite receptors, are within 100 feet of the source area sample, collect samples that are evenly distributed near receptors.

Table 1. Soil gas sample collection depths

Sample location	Sample collection depth
Source area(s)	8–10 feet below grade, at least 2 feet above the water table and at a minimum depth of 3 feet. If the water table or bedrock prevent sample collection below 3 feet, the sample does not need to be collected at this time, but the MPCA may request other means of assessing VI.
Receptor-specific	Buildings with basements: 8–10 feet below grade. Buildings with slab-on-grade or crawl space: 3–5 feet below grade. All samples must be at a minimum depth of 3 feet. If the water table or bedrock prevent sample collection below 3 feet, the sample does not need to be collected and the MPCA may request other means of assessing VI.

If contaminated groundwater or LNAPL extends 100 feet beyond the source area, you may need to collect additional soil gas samples near receptors within 100 feet of the groundwater plume or LNAPL body.

Use professional judgment to decide if a receptor-specific soil gas sample is needed. For example, consider not sampling a building with low human exposure, such as a storage garage. Conversely, consider sampling near subsurface structures such as utility corridors, utility service lines, fractured bedrock, or other subsurface anomalies because they may be preferential migration routes for soil gas if they are close to buildings.

C. Data evaluation

Data comparison

For VOCs, compare soil gas results to the applicable vapor screening levels based on the receptor type (i.e., residential versus commercial/industrial buildings). For a soil gas sample, the vapor screening level is the intrusion screening value (ISV) divided by the U. S. Environmental Protection Agency's (EPA's) default VI attenuation factor of 0.03, or 33X ISV for short. ISVs are found in the MPCA's [Intrusion screening values \(ISVs\) for vapor intrusion risk evaluation](#) document. Derivation of 33X ISVs and supporting information are in the MPCA's [Intrusion screening values technical support document](#).

For fixed gases, if the results show a high methane concentration in soil gas, contact the MPCA. A high methane concentration exceeds 10% of the lower explosive limit, or 0.5% methane by volume (5000 ppmv), within 100 feet of a receptor.

Receptor type examples

Residential: Single-family homes, multi-family homes, long-term care facilities, correctional housing, hospitals, childcare centers, churches, schools

Commercial/industrial: Restaurants, retail stores, shopping malls, hotels, non-retail businesses, manufacturing facilities, warehouses, public utilities

Pathway evaluation

Determine if additional pathway evaluation is required based on the following conditions:

- If a contaminant concentration from a receptor-specific sample exceeds a 33X ISV and/or there is a high methane concentration, a building-specific investigation or additional soil gas sampling closer to the receptor is required. See Section III for more information on conducting a building-specific investigation.
- If no 33X ISVs are exceeded and there are no high methane concentration(s), no further pathway evaluation is required.

Please note that these requirements apply to PRP and may differ from other MPCA programs such as the Superfund or Voluntary Investigation and Cleanup Programs.

Conceptual site model

Integrate the results of the soil gas assessment into the conceptual site model (CSM) in the [Investigation report](#). For the VI pathway, describe how quantitative and qualitative factors affect the fate and transport of subsurface vapors and their relationship to identified receptors. Information on developing a CSM is in [Soil and groundwater assessments performed during site investigations](#).

For [Investigation report](#) submittal, do not complete any additional VI assessment beyond the soil gas assessment without preapproval from the MPCA.

III. Step 2 - Building-specific investigation

A building-specific investigation further characterizes the VI pathway and provides direct evidence regarding the risk associated with petroleum vapors. A building-specific investigation is required if the pathway evaluation completed during the initial soil gas assessment shows a contaminant concentration from a receptor-specific sample above a 33X ISV and/or there is a high methane concentration (See Section II subsection C). The building-specific investigation includes completing a VI building survey and sub-slab sampling.

A. Vapor intrusion building survey

Complete a [Vapor intrusion building survey form](#) before sub-slab sampling. The survey provides information on general building characteristics, points where soil gas may enter the building, and potential indoor contaminant sources. Inspect the building floor and document penetrations (e.g., cracks, floor drains, utility perforations, sumps, other preferential pathways) where soil gas may enter the building. Survey results determine the location and number of sub-slab sampling points (Table 2) and whether the default VI attenuation factor is valid (See the Data comparison part of Section III subsection C).

B. Sub-slab sampling

Collect sub-slab samples in a location away from foundation footings and submit them for analysis following the procedures in Section V. Install sampling points at locations where indoor air is unlikely to infiltrate through floor penetrations. If a significant floor penetration is near a sampling location, temporarily seal the penetration to avoid short-circuiting during sample collection.

Complete two sub-slab sampling events, at least 30 days apart, in the following seasonal conditions:

- One sampling event in the heating season (November 1 through March 31)
- One sampling event in the non-heating season (April 1 through October 31)

Two sub-slab sampling events are needed to evaluate risk because seasonal variability (e.g., soil moisture levels, depth to groundwater, changes in the building's heating and cooling system) can lead to fluctuating vapor concentrations and distribution in the vadose zone. The MPCA recommends completing sub-slab sampling points as permanent points to facilitate multiple sampling events.

Sub-slab sampling alternatives

Sub-slab sampling may not be feasible due to physical access, a dirt floor, or a highly deteriorated slab or foundation. See Section III subsection D for alternative investigation methods.

The number of sub-slab sampling locations is dependent on the area of the building foundation and/or slab-on-grade (Table 2).

Table 2. Number of sub-slab sample locations

Building foundation area and/or slab-on-grade (square feet)	Minimum number of sub-slab samples¹
Up to 500	1
501 to 1,000	2
1,001 – 2,500	3
2,501 – 5,000	4
5,001 – 10,000	5
10,001 – 20,000	6
20,001 – 30,000	8
30,001 – 40,000	10
40,001 – 50,000	12
50,001 – 60,000	14
60,001 – 70,000	16
70,001 – 80,000	18
80,001 – 90,000	20
90,001 – 100,000	22
>100,000	22 + 2 samples for every 10,000 square feet above 100,000

¹Includes sub-slab samples within an existing building. Building conditions that may affect the total number of sub-slab samples include the following:

- If the sub-surface or at-grade slab is divided by a footing or foundation structure, collect at least one sub-slab sample on both sides of the slab divide.
- If a building addition is present, collect sub-slab samples from the original building floor slab and the addition's floor slab.

C. Data evaluation

Data comparison

Compare sub-slab sampling results to the applicable vapor screening levels based on the following conditions:

1. Receptor type: Compare to the applicable residential or commercial/industrial or ISV. See Section II subsection C.
2. Building integrity: Determine if the 33X ISV is valid for the building's construction and condition.

To determine if the attenuation factor is valid, refer to the VI building survey. The attenuation factor may not be valid if the building is susceptible to soil gas entry, including, but not limited to, the following situations:

- Buildings with significant openings to the subsurface (e.g., sumps, unlined crawl spaces, dirt floors) other than typical utility penetrations.
- Buildings with deteriorating foundation walls or slabs.

When comparing sub-slab sampling results, pay attention to whether any contaminant concentration exceeds 33 times an expedited intrusion screening value (33X EISV). An exceedance of 33X EISVs for sub-slab sampling requires expedited action, see Section III subsection E.

Pathway evaluation

Use Table 3 or Table 4 depending on whether or not the attenuation factor is valid to determine if corrective action or further pathway evaluation is required.

Note that two seasonal sampling rounds are required for sub-slab sampling (See Section III subsection B). If a 33X ISV or EISV is exceeded in the first sampling event, you can go directly to corrective action. If there was a 33X ISV or EISV exceedance in the second sampling round but not the first, corrective action is necessary.

Table 3. 33X ISV is valid¹

Pathway evaluation decisions based on sub-slab sampling results – when 33X ISV is valid.

Sub-slab Contaminant Concentration (CC)	Action
CC from both seasonal sampling events < 33X ISV	Corrective action is not necessary. Additional sampling is not necessary unless site conditions change ² .
CC from one or both seasonal sampling event(s) > 33X ISV and < 33X EISV	Corrective action is necessary.
CC from one seasonal sampling event > 33X EISV	Corrective action is necessary—contact the MPCA to determine the need for expedited action.

¹Based on building conditions evaluated while completing the Vapor Intrusion Building Survey Form. See the Data comparison part of Section III subsection C.

²Examples of changed site conditions include, but are not limited to: migration of a plume, changed building conditions (e.g., cracks in floor, building additions, HVAC changes).

If a completed VI pathway is identified, corrective action is required (see Section IV). In certain situations, you may need to complete concurrent sub-slab and indoor air sampling to provide a line of evidence for pathway evaluation. Do not complete any additional VI assessment or corrective action without preapproval from the MPCA.

D. Alternative building-specific investigation methods

For buildings where sub-slab sampling is not possible or the attenuation factor is not valid, pathway evaluation is completed by soil gas beneath a building or indoor air and outdoor air sampling.

Sampling requirements

There are two sampling scenarios for an alternative building investigation:

1. Soil gas sampling below the building is feasible.

Collect soil gas samples from a depth of three feet below the building floor level following the procedures in Section V. The number of soil gas samples depends on the area of the building foundation (Table 2).

2. Soil gas sampling below the building is not feasible.

If collecting soil gas samples from a depth of three feet is not feasible due to groundwater, bedrock, or other restrictions, collect concurrent 24-hour indoor air and outdoor air samples to evaluate risk as described below and following the procedures described below and in Section V.

In both scenarios, at least two seasonal sampling events are required as described in Section III subsection B.

Indoor air sampling

Before sampling, complete a [Vapor intrusion building survey form](#) with assistance from the building owner or other designated representative to evaluate building layout and conditions. Identify conditions that may affect sampling and require temporary mitigation. Complete the survey at least **two weeks** before sampling to allow building occupants time to change building use or behaviors that could compromise sample results. Refer to Appendix A for instructions that building occupants should follow before and during indoor air sampling. Include the survey form with all indoor air sampling results, documenting all modifications that building occupants were requested to make and to what extent they complied.

Collect samples over a 24-hour period using a special low-flow precision regulator. There may be sites where a grab sample is appropriate, but contact the MPCA for approval before collecting a grab sample.

Select a representative sampling location following these guidelines:

1. Place the canister in the breathing zone, approximately three to five feet from the floor.
2. Collect samples from the basement or lowest level near suspected vapor entry points to assess the worst-case exposure.
3. Collect samples away from windows or other sources of exterior air leakage.
4. If direct preferential pathways are identified (e.g., earthen floors, unsealed crawl spaces, sumps), collect samples from those areas.

Collect samples under conditions that represent the building use (e.g., doors open or closed depending on their typical condition and if heating system is in use). In summer months, close windows at least 24 hours before sampling to minimize the contribution of outside air.

Site-specific, high-risk situations identified during the site investigation may warrant indoor air sampling to assess indoor air conditions before characterizing soil gas, with or without concurrent sub-slab sampling. Notify the MPCA before initiating immediate indoor air sampling. Examples may include, but are not limited to, the following situations:

- Measurable organic vapors observed in a building when screening with a field meter (e.g., photoionization detector (PID), explosimeter) and the source is unknown.
- Soil or groundwater contamination is beneath the building, the building is prone to groundwater intrusion or flooding (e.g., sump pit overflows), and sub-slab sampling is not feasible.
- Residents complain of being able to smell petroleum vapors frequently but field meters do not show detections. Please note that this may be an emergency situation that should be reported to the Minnesota Duty Officer.

Outdoor air sampling

Outdoor air samples are collected to characterize site-specific outdoor air conditions. Concurrent indoor and outdoor sampling results with the findings of the building survey are used to distinguish indoor air contaminants from VI versus those originating from background contaminant sources.

Collect outdoor air samples concurrently with indoor air samples over a 24-hour period using a special low-flow precision regulator.

Select a representative sampling location following these guidelines:

1. Place the canister in the breathing zone, approximately three to five feet from the ground.
2. Collect outdoor air samples from a representative upwind location, away from obstructions (e.g., trees, buildings).
3. Avoid locations near localized sources (e.g., running single-cylinder engines, oil storage tanks) that may influence the sample.

Document the following items to help with data evaluation:

- The building site, area street, outdoor air sample locations, location of potential interferences (e.g., gasoline stations, factories, lawn mowers), and compass orientation on outdoor plot sketches.
- Weather conditions (e.g., precipitation, indoor and outdoor temperature, barometric pressure) and ventilation conditions (e.g., heating system active and windows closed).
- Any relevant observations such as odors, field meter readings, and significant activities in the vicinity (e.g., heavy equipment operation or dry cleaners nearby).

Data comparison

Compare soil gas or indoor air results directly to the appropriate ISVs and EISVs to determine the need for corrective action.

Pathway evaluation

If soil gas samples beneath the building are collected, use Table 4 to determine the need for corrective action. If soil gas samples beneath the building cannot be collected, corrective action is necessary if sampling results show an ISV exceedance in indoor air that cannot be attributed to an indoor or outdoor ambient source. If an ISV is exceeded in the first sampling event, corrective action can proceed without a second event. If an EISV is exceeded, contact the MPCA to determine the need for expedited action.

Table 4. 33X ISV is NOT valid¹

Pathway evaluation decisions based on soil gas beneath a building sampling results – when 33X ISV is not valid.

Soil gas beneath a building Contaminant Concentration (CC)	Action
CC from both seasonal sampling events < ISV	Corrective action is not necessary. Additional sampling is not necessary unless site conditions change ² .
CC from one or both seasonal sampling event(s) > ISV and < 33X ISV	Corrective action is necessary. OR Complete concurrent sub-slab (or soil gas below building), indoor air, and outdoor air sampling – contact the MPCA before performing for approval. Report results to the MPCA immediately to determine corrective action need. OR Address building conditions so 33X ISV screening level is valid, then repeat seasonal sub-slab sampling to determine corrective action need.
CC from one seasonal sampling event > 33X ISV and < 33X EISV	Corrective action is necessary—contact the MPCA to determine the need for expedited action ³ .
CC from one seasonal sampling event > 33X EISV	Corrective action is necessary—contact the MPCA to determine the need for expedited action.

¹Based on building conditions evaluated while completing the [Vapor intrusion building survey form](#). See the Data Comparison part of Section III subsection C.

²Examples of changed site conditions include, but are not limited to: migration of a plume, changed building conditions (e.g., cracks in floor, building additions, HVAC changes).

³For residential buildings, contact the MPCA to determine the need for expedited action.

If a completed VI pathway is identified, corrective action is required (see Section IV). **Do not complete any additional VI assessment or corrective action without preapproval from the MPCA.**

E. Expedited action

If expedited action is necessary, it should begin as soon as possible but no later than 30 days after receiving laboratory analytical results. Expedited action options include the following:

- Expedited mitigation: Install a mitigation system as soon as possible but no later than 30 days from receipt of laboratory analytical data. The standard mitigation installation timeframe is generally 60 to 90 days.
- Expedited sampling: Sub-slab or indoor air sampling paired with outdoor air sampling and pressure differential measurements at sub-slab sampling points, if applicable. The expedited sampling timeframe is sample as soon as possible with a rush laboratory analysis (i.e., three-day turnaround time) and results reported to the MPCA immediately upon receipt.

IV. Step 3 - Evaluating corrective actions

If the VI assessment shows direct or significant indirect evidence that a VI pathway is complete, the MPCA will require corrective action to minimize the risk of exposure to building occupants. Corrective action may include remediating the vapor source, interrupting the migration route between the vapor source and the receptor, or a combination of both approaches. Building control technologies, such as sub-slab depressurization systems, can be highly effective at mitigating VI impacts. Building pressurization or heating, ventilating, and air conditioning

modifications at larger commercial or industrial buildings may be appropriate as well. See [Vapor investigation and mitigation decision best management practices](#) for additional information regarding corrective actions.

When corrective action is required, refer to [Corrective action design and implementation](#) for instructions on how to proceed. The first step is to contact the MPCA to discuss corrective action requirements and potential alternatives before completing a [Conceptual corrective action design report](#). When expedited action is needed, the MPCA may modify the approval process to accelerate the mitigation response.

If petroleum vapors have migrated beyond an impacted building(s) toward other receptors, the MPCA may require additional soil gas assessment. You can make recommendations for additional assessment any time in a subsequent investigation or corrective action design report.

In cases where buildings overlie or are adjacent to contaminated groundwater or LNAPL, the MPCA may require soil gas monitoring along with groundwater monitoring to demonstrate stable or declining contaminant concentrations. If you feel this work is necessary, include a recommendation for the specific activities that you will conduct in a monitoring-based corrective action design.

Note for commercial/industrial properties where one or both seasonal sampling events is greater than 33X ISV and less than 33X EISV, the MPCA may approve conducting an interim completed pathway evaluation conditions to determine if sub-surface vapors are migrating into the indoor building air. This interim approach requires collecting paired sub-slab, indoor and outdoor air samples along with evaluating the existing building conditions to determine if sub-surface vapors are migrating into the indoor building air. Completed pathway evaluation is not considered a stand-alone, long-term vapor mitigation approach. However, completed pathway evaluation may be an appropriate interim measure for specific situations. See [Vapor investigation and mitigation decision best management practices](#) for completed pathway evaluation requirements. Contact the MPCA to determine if this approach is appropriate for your site.

V. Recommended sampling methods, procedures, and field quality assurance/quality control (QA/QC)

Below are recommended field methods and procedures for soil gas, sub-slab, indoor air, and outdoor air sampling to be included in any sampling protocol. Although you may use various field methods based on experience and available equipment, the MPCA expects that field staff take the utmost care to ensure sample integrity and data quality. You may change the procedures recommended below with MPCA approval depending on site-specific conditions or emerging technologies and methodologies. In all cases, you must thoroughly describe the methods and procedures used in the field in the final report accompanying the sampling results. Use the same methods and procedures at all sampling locations throughout the site investigation.

Collect samples using an evacuated stainless steel canister and analyze them by EPA Method TO-15 for compounds on the [Minnesota soil gas list](#). For the soil gas assessment (Section II), in addition to EPA Method TO-15, also analyze samples by EPA Method 3C for fixed gases (methane, oxygen, carbon dioxide, and carbon monoxide). Fixed gases will require a separate analysis, but a single canister will supply enough sample volume to complete the Method TO-15 and fixed gases analyses. Laboratory QA/QC requirements for Method TO-15 and fixed gases are provided in Section VI. Contact the MPCA to determine if fixed gas analysis is required for the building-specific investigation (Section III) or the alternative building-specific investigation (Section IV) require fixed gases analysis.

A. Temporary soil gas sampling point installation

1. Advance the soil gas sampling point to the necessary depth (Table 1) using direct push technology or manual probes as site conditions permit.
2. Place an appropriate sealing material (e.g., bentonite slurry) at the ground surface around the probe rod to avoid the sample short-circuiting to the atmosphere.
3. Fit the soil gas sampling point with appropriately sized inert tubing (e.g., polyethylene, stainless steel, Teflon®).

B. Permanent soil gas monitoring point installation

Single sampling point

1. Advance the soil gas monitoring point to the necessary depth (Table 1) using direct push technology or manual probes as site conditions permit.
2. Fit soil gas monitoring point with appropriately sized inert tubing (e.g., polyethylene, stainless steel, Teflon®) and a screen approximately six inches long comprised of stainless steel, slotted polyethylene, or polyethylene mesh.
3. Install an airtight check valve or cap on the surface end of the tubing. The valve must not allow ambient air to enter the tubing.
4. Place an artificial filter pack in the annular space between two to four inches below the screen tip to six inches above the screened interval.
5. Grout the remaining annular space to the surface using bentonite or other appropriate material.
6. Fit the soil gas monitoring point with an at-grade cover or above-grade protective casing grouted in place to minimize infiltration of water or atmospheric air and prevent accidental damage. Proper construction will ensure the sampling interval is adequately sealed off from casing and atmospheric air.
7. If you are collecting a sample the same day as the installation, wait a minimum of 30 to 60 minutes before purging and sampling.

Nested sampling point

1. Complete steps 1 through 4 listed in the single sampling point instructions above.
2. Seal the space between individual screened intervals with at least two feet of bentonite.
3. Complete step 4 above to set the second sampling screen in filter pack.
4. Repeat steps 2 and 3 in this section as needed for the number of nested points required.
5. Cut the protruding tubing shorter so that the deepest screened interval has the longest tubing length, with shallower intervals becoming progressively shorter. Label each tube clearly upon completion. Varying the tubing length is a safeguard to prevent misidentification of the sampling interval.
6. Install an airtight check valve or cap on the surface end of each tube. The valve must not allow atmospheric air to enter the tubing.
7. Fit the soil gas monitoring point with an at-grade cover or above-grade protective casing grouted in place to minimize infiltration of water or atmospheric air and prevent accidental damage. Proper construction will ensure the sampling intervals are adequately sealed off from casing and atmospheric air.
8. If you are collecting a sample the same day as the installation, wait a minimum of 30 to 60 minutes before purging and sampling.

C. Sub-slab sampling point installation

1. Advance a boring into the sub-slab material using a rotary hammer drill or other device.
2. Fit soil gas sampling points with appropriately sized inert tubing (e.g., polyethylene, stainless steel, Teflon®).
3. Insert a vapor sampling point into the material immediately below the slab.
4. Add coarse sand or glass beads to cover the point tip.
5. Seal the boring at the surface with grout, cement, or other non-VOC containing and non-shrinking product to prevent air infiltrating from above the slab.

D. Soil gas and sub-slab sampling

1. Before collecting the sample, purge a minimum of two volumes (i.e., total volume of the sampling point and tube) using a graduated syringe for volume accuracy. This ensures the sample is representative of sub-surface vapors.
2. Install an in-line particulates filter to prevent particulates and moisture from entering the canister.
3. Collect a sample by attaching the top end of the tubing to a canister equipped with a vacuum gauge.
4. Record the initial vacuum gauge reading on a sampling form.
5. Open the canister valve and monitor the vacuum gauge to check progress of canister filling. Avoid pulling groundwater into the tubing. If groundwater is pulled into the tubing, make note of it on the sampling form.
6. Close the canister valve after collecting an adequate volume of air or the vacuum gauge indicates the canister is full. Use a vacuum gauge on each sampling canister to ensure an adequate sample volume was collected. Make sure that the vacuum readings on the canister do not go all the way down to zero. Final vacuum readings should be between five and one inches of Hg. Without an adequate sample volume, the laboratory may not be able to meet the reporting limits necessary to compare to compound-specific ISVs. **If reporting limits are consistently higher than the ISVs, a decision regarding VI risk may not be possible and resampling may be required.** Consult with the laboratory supplying the canisters to obtain the vacuum gauge readings corresponding to an acceptable canister volume.
7. Record the required sampling time and final vacuum gauge reading on the sampling and chain-of-custody forms.
8. After disconnecting the canister, connect the sampling point tubing to a field meter (e.g., PID) and measure the organic vapor concentration. Record the PID reading on the sampling and chain-of-custody forms.
9. Submit the canister for laboratory analysis.

Sub-slab sampling methodology. For more information on the steps to collect a representative sub-slab sample, check out the MPCA's methodology video:

<https://www.youtube.com/watch?v=ub7m6KknVtU&feature=youtu.be>

For sub-slab sampling only:

10. Use a certified clean canister.
11. For permanent monitoring points, seal the monitoring point tight with a hex wrench to allow for follow up sampling.
12. After sampling activities are completed, properly seal the slab hole opening.

Fixed gas analysis note: If your site has permanent soil gas monitoring points for long-term monitoring, you may use a direct reading methane field instrument (e.g., landfill gas meter) instead of laboratory analysis for fixed gases if there is a good correlation between two consecutive laboratory and field measurement events. The MPCA recommends quantifying methane using the required lab analysis and a methane field instrument during the investigation.

E. Indoor and outdoor air sampling

1. Affix a flow controller to a canister equipped with a vacuum gauge. The flow controller must be pre-set by the laboratory to collect the sample over a 24-hour period.
2. Install an in-line particulates filter to prevent particulates and moisture from entering the canister.
3. Record the initial vacuum gauge reading.
4. Open the canister valve to begin sample collection.
5. After approximately 24 hours, close the canister valve. Record the sampling time and final vacuum gauge reading on the sampling and chain-of-custody forms.
6. Submit the canister for laboratory analysis.

7. If the MPCA requires a grab sample, follow the same procedure without the use of a flow controller.

F. Field QA/QC

Take extreme care during all aspects of sample collection to minimize sampling error. Sampling team members should avoid actions that can cause sample interference such as fueling/idling vehicles, using permanent marking pens, smoking, and wearing fragrances or freshly dry-cleaned clothing. Follow appropriate QA/QC protocols for sample collection and laboratory analysis, such as using certified clean sample devices, meeting sample holding times and temperatures, and proper completion of the chain-of-custody form. Deliver samples to the analytical laboratory as soon as possible after collection.

Follow laboratory procedures for field documentation (sample collection information/locations), chain-of-custody form, field blanks, and field sample duplicates and laboratory duplicates, as appropriate.

Field sampling personnel must maintain a field sampling log summarizing the following information (**Note:** the field logs are required to be submitted as an appendix of the final report):

- Sample identification
- Sample location
- Date and time of sample collection
- Sampling depth interval (soil gas or sub-slab)
- Sampling height (indoor or outdoor)
- Name(s) of samplers
- Sampling methods and devices
- Purge volumes and devices used
- The vacuum (pressure) of the canister before and after sample collection and PID measurements must be recorded on chain-of-custody and sampling forms
- Apparent moisture content (e.g., dry, moist, saturated) of the sampling zone
- Type of soil present in the sampling zone (e.g., clay, sand, gravel)
- Chain-of-custody records to track samples from sampling point to analysis

G. Supplemental sampling QA/QC

Use the following methods to provide further QA/QC when conducting soil gas or sub-slab sampling.

Flow rate and vacuum

To minimize the potential for short-circuiting air flow from the surface and desorption of contaminants from the soil under saturated conditions, use techniques to control and minimize the flow and vacuum applied to the soil. In these cases, use an in-line flow controller set at a flow of 200 mL/minute and vacuum less than 15% of atmosphere (\approx five inches of Hg). The MPCA may require flow controllers for soil gas samples based on data quality objectives and site conditions.

Leak check compounds

To determine if atmospheric breakthrough down the probe rod's annular space has occurred while sampling, use leak check compounds. At this time, the MPCA does not require the use of leak check compounds, but MPCA staff may request their use on a site-by-site basis based on data quality objectives and concerns. The fixed gas analysis serves as a surrogate to a leak check compound because results may indicate whether oxygen levels are near atmospheric levels suggesting that oxygen has entered sampling chain.

Several compounds can be used as leak check compounds during soil gas collection. Gaseous compounds using shrouds or liquids applied to paper towels can be used. Isopropyl alcohol, pentane, isobutene, and helium are some common compounds used in tracer analysis for soil gas samples. For additional information regarding leak check compounds, refer to [Petroleum Vapor Intrusion Fundamentals of Screening, Investigation, and Management](#) (ITRC 2014).

Soil gas samples with concentrations of the leak check compound greater than 5% of the initial concentration (equal to 100% for gaseous compounds and to the partial pressure for liquid compounds) are not considered reliable.

VI. Required laboratory QA/QC

A. EPA Method TO-15

Each laboratory analyzing samples by EPA Method TO-15 must follow the method described in the EPA's [Compendium of Methods for the Determination of Toxic Organic Compounds in Ambient Air – Second Edition](#) (EPA 1999), including the following elements:

1. The laboratory must supply the following analysis with each report:
 - a. Method blank (Zero canister): All results from analysis of the method blank should be less than the reporting limits. If concentrations are reported above the reporting limits, the laboratory will document this occurrence within the narrative and flag any concentration reported above the reporting limit for this compound up to 10 times the level measured in the blank. The area responses for the internal standards (IS) must be within $\pm 50\%$ of the area response of the ISs in the mid-point standard of the most recent initial calibration. The retention time for each IS must be within ± 0.33 minutes between the blank and the most recent calibration. Method blanks shall be run every 20 environmental samples or once per day, whichever is more frequent.
 - b. Laboratory Control Sample (LCS): The laboratory will report the percent recoveries from all analytes spiked into the LCS. One LCS will be run within each 24-hour period of TO-15 samples analyzed.
 - c. The narrative of the laboratory report will define if the initial calibration curve, continuing calibration check sample (when appropriate), and internal quality assurance (such as internal standards, blanks, etc.) met the method requirements for each report.
 - d. The chromatogram for each analysis will be submitted with the data and have the compounds identified in the Minnesota Soil Gas List clearly labeled on the chromatogram.
 - e. The laboratory shall report the results using the field sample ID and the associated laboratory sample number.
 - f. The laboratory shall report all compounds in units of $\mu\text{g}/\text{m}^3$.
 - g. The laboratory report must contain the following information: Coversheet with signature of a laboratory supervisor or designee, a narrative discussing the sample results and any irregularities that were found during the analysis, chain of custody and sample condition upon receipt forms, tables containing the VOC compounds, Chemical Abstract Service number of each reported compound, measured concentration in $\mu\text{g}/\text{m}^3$, reporting limit, date of analysis, labeled sample chromatograms, method blank data for the batch, and a summary of applicable quality control.
2. The laboratory is required to maintain the data for a minimum of 10 years with the ability to reconstruct the data either via a computer or paper.
3. Laboratories must verify their reporting limits by running a standard at the reporting limit once every month. The recovery of the reporting limit shall be $\pm 40\%$ of the true value.
4. Laboratories shall verify their calibration curve a minimum of every 24 hours. The 24 hour clock will begin at the injection of a standard for tuning the instrument (bromofluorobenzene is the suggested tuning standard). The calibration verification standard must be at the midpoint (or lower) of the calibration curve.

The standard must meet TO-15 or laboratory generated limits for the compounds of interest/target compounds (as identified on the chain of custody), not a set of continuing calibration check compounds. If no direction is given to the laboratory for check compounds, then the laboratory Standard Operating Procedure (SOP) shall be followed.

5. Laboratories should run 10% laboratory duplicates. Duplicate samples should have less than or equal to 25% relative percent difference or corrective action should be initiated.
6. The MPCA accepts a holding time of 14 days for the TO-15 analysis.
7. Reporting limits: The MPCA expects that for the following compounds: benzene, toluene, the xylenes, ethylbenzene, the trimethylbenzenes, trichloroethylene, and vinyl chloride will have reporting limits between 0.2-0.4 ppbv (reported as $\mu\text{g}/\text{m}^3$). The other compounds on the Minnesota Soil Gas List should have reporting limits between 0.5-1.0 ppbv (reported as $\mu\text{g}/\text{m}^3$). The MPCA does recognize that some compounds will have issues with chromatography or interferences that will prevent the expected reporting limits from being met. Laboratories should clearly document these cases within their SOPs and on reports as necessary.
8. Canisters: The laboratory providing summa canisters shall verify each batch of 20 canisters by analyzing one container after cleaning. The canister chosen for post-cleaning analysis shall be the canister with the highest recorded VOC concentration from prior analyses. The container shall be verified by charging the canister with clean zero air, analyzing the container by TO-15, and verifying no compounds are found above the reporting limits required by the MPCA. Additionally, the supplier of summa canisters is expected to verify the operability of the canisters. The TO-15 SOP (or equivalent) should describe the preventative maintenance performed on the canisters. 100% certified canisters may be required upon request.
9. Whenever a high concentration sample is analyzed (sample with concentrations outside the calibration curves), a zero canister analysis should be performed to check for carryover. If carry over is detected, column bake out shall be performed.
10. Tentatively identified compounds: The MPCA requires each TO-15 analysis to include the reporting of the top 10 tentatively identified compounds greater than five ppbv that are not attributed to column breakdown, as compared to response of the nearest IS, when using full scan mode of the mass spectrometer. The laboratory will also report within the narrative if a hump is seen within the chromatogram such as is typical for gasoline, fuel oil, mineral spirits, etc.
11. The laboratory is not required to quantify this as part of the analysis, although this may be requested of the laboratory at a later date for an additional cost.
12. Lab certification: At this time, certification is available for the TO-15 method through the Minnesota Department of Health (MDH) Environmental Laboratory Accreditation Program. The MPCA requires that TO-15 analytical results submitted be completed by an MDH accredited laboratory.
13. Method detection limit (MDL) studies must be performed at least annually. The MDLs should be ≤ 0.5 ppbv for all target analytes.
14. Field samples can be analyzed after successfully meeting all criteria established for instrument performance checks, calibrations, and blanks. All target analyte peaks should be within the initial calibration range. The RT for each IS must be within ± 0.33 minutes of the IS in the most recent calibration. The area response for the IS's must be within $\pm 50\%$ of the area response of the ISs in the mid-level standard of the most recent initial calibration.
15. Daily check standard must be analyzed every 24 hours. This standard is at the mid-point of the calibration curve (ten ppbv suggested). The percent D must be within $\pm 30\%$ for each target analyte. Control charts should be maintained for the percent D values.
16. Internal standard: A suggested internal standard mixture of bromochloromethane, chlorobenzene-d5, and 1,4-difluorobenzene will be added to each sample as standard. The resulting concentrations are at ten ppbv (suggested).

B. Fixed gases analysis

Fixed gases in soil gas: Soil gas samples may be analyzed for methane using a GC/FID. Other fixed gases including oxygen, carbon dioxide, and carbon monoxide may be analyzed using a GC/TCD (Thermal Conductivity Detector) technique based on EPA Method 3C. Laboratories analyzing samples for fixed gases in soil gas must also incorporate the following additional quality control procedures.

1. General considerations: Helium is used to prepare calibration gases. Use sample collection procedures described in EPA Method 3C or 25C. The sample loop must be Teflon or stainless steel tubing of the appropriate diameter. Peak height or peak area can be used for quantitation.

EPA Method 3C requires that each sample must be analyzed in duplicate to calculate the average response. For the purposes of the MPCA PRP, a single analysis will be adequate.

2. Initial calibration: An external standard calibration technique is used. The concentration of the target analyte is calculated from the average response factor or from a standard curve. The initial calibration curves should contain at least five calibration points. The percentage RSD for average response factors must be less than or equal to 30% or the r^2 value for the curve must be greater than or equal to 0.995. The recovery (accuracy) for each point in the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curve shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, a smaller sample volume is injected into the GC and reanalyzed. If the instrument calibration results are outside the acceptance criteria, a number of actions can be taken:
 - a. Check the instrument operating conditions. Instrument maintenance may be required.
 - b. Review the response at each calibration level to insure that the problem is not associated with one standard. If the problem appears to be associated with one of the standards, that standard can be reinjected. If the problem persists, remake the standard and reanalyze it.
 - c. The last alternative is to delete calibration points from the curve. The MPCA will allow the removal of the lowest or the highest calibration point from the curve under the following provisions. If a non-linear calibration model is used in the initial calibration curve, a quadratic (second order) curve will require at least six non-zero standard levels while a polynomial (third order) curve will require at least seven non-zero standard levels. Care must be taken to insure that there are enough remaining calibration points for the initial calibration curve. If the calibration criteria are now met, the analysis can proceed. However, there are ramifications in removing calibration points. If the top point is removed, the need for diluting samples and reanalyzing will occur at a lower concentration level. If the low point in the curve is removed, the sensitivity of the analysis has changed and thus the report level will need to change.
3. Continuing calibration: The initial calibration curves are verified at the beginning and ending of an analytical sequence. The drift must be within 70% to 130%. If the instrument calibration results are outside the acceptance criteria, check the instrument operating conditions and/or perform instrument maintenance. Reanalyze the calibration standard. If the calibration criteria are still not met, a new initial calibration must be performed. All samples that were analyzed since the last passing calibration standard must be reanalyzed. There is one exception allowed for this QC criterion. If the recovery of the calibration verification standard is >130% of the true value and the environmental samples show no detection of the analyte, the "less than" value can be reported without reanalysis.
4. Method validation: The laboratory must perform an initial demonstration of low background for each matrix by analyzing instrument blanks and demonstrating that the analytical system is free of contamination and that the method analytes are not detected above one-half the report levels.

The laboratory must also perform an initial demonstration of capability for the analysis of each matrix. Four to seven LCSs near the mid-range of the calibration curve must be prepared and analyzed. The samples must be processed through the entire preparation and analysis procedure. The average percent recovery of the replicate analyses must be $\geq 70\%$ and $\leq 130\%$ (with a relative standard deviation of $\leq 30\%$).

5. Method detection limit/report level: MDLs and Reporting Levels (RLs) are determined annually or after a major change to the instrument conditions. The RLs should be three to five times the MDLs. The lowest calibration point in the curve shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, new RL standards are chosen and analyzed until the accuracy criteria are met. Contact the MPCA Project Manager for any required report level for each project. RLs depend on program needs. They can change as new information becomes available. RLs are verified after each calibration and at least monthly. For most analytical work for the MPCA, the RLs should be at or below 1% for reported fixed gases. The MPCA requires that final results be reported as a percentage for fixed gases.
6. Batch QC: A batch is defined as up to 20 environmental samples. At a minimum, each batch must contain a method blank and a LCS/Laboratory Control Sample Duplicate (LCSD) pair.

The concentration of methane in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be reprocessed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.

Methane is to be spiked into the LCS and LCSD. The spiking levels should be five to ten times the report levels. The LCS is made from reagent-grade helium that has been demonstrated to be methane-free. In a soil gas matrix, the percent recovery of methane in the LCS or LCSD must be $\geq 70\%$ and $\leq 130\%$. The relative percent difference between the LCS/LCSD pairs in water must be $\leq 30\%$.

Any QC failure that is not remedied by reanalysis or re-extraction/reanalysis must be flagged in the final report.

Appendix A: Instructions for occupants

Follow the instructions below to minimize the detection of background indoor air compounds during indoor air sampling. If possible, begin to follow these instructions at least 48 hours before starting indoor air sampling and during the event. Conduct normal building ventilation for the time of year, except that windows are closed. Following these instructions may not completely eliminate the potential for background indoor air contamination, but may help minimize its effects. Please inform field sampling staff whether these instructions were completed.

Building occupants should comply, to the extent practical, with the following instructions:

- Do not open windows, doors, fireplace dampers, openings, or vents.
- Do not keep doors open.
- Do not use air fresheners, scented candles, or odor eliminators.
- Do not smoke in building.
- Do not use wood stoves, fireplaces, or auxiliary heating equipment (e.g., kerosene heater).
- Do not use paint or varnishes.
- Do not use cleaning products such as bathroom cleaners, furniture polish, appliance cleaners, all-purpose cleaners, floor cleaners.
- Do not store containers of gasoline, oil, or petroleum-based or other solvents within the house.
- Do not operate or store automobiles in an attached garage.
- Do not use cosmetics such as hair spray, nail polish, nail polish remover, perfume, cologne, etc.
- Do not partake in hobbies that use solvents or other volatile chemicals.
- Do not conduct lawn-mowing, snow blowing, or paving with asphalt.
- Do not use caulk, adhesives, or roofing tar.

Risk evaluation and site management decision at petroleum release sites

Petroleum Remediation Program

This document describes the procedures for completing receptor surveys, evaluating risk, and making a site management decision at petroleum release sites. **You are strongly encouraged to complete the surveys prior to starting subsurface investigation activities to optimize site work.**

I. Water supply well receptor survey and risk evaluation

The water supply well receptor survey identifies water wells that may be at risk from the petroleum release and also provides information regarding the geology and groundwater use near the release site. For the water supply well receptor survey, complete the following:

A. Walking survey

Conduct a walking survey of all properties within 500 feet of the source. This survey consists of the following steps:

1. Prepare a base map showing property boundaries and relevant features, such as buildings, roads, and surface water within 500 feet of the source.
2. Identify property ownership. Base maps with property ownership can usually be obtained from the city or county.
3. Contact residents, property owners, and business owners within 500 feet of the source and obtain the following information for each property:
 - Presence of a water supply well(s) or connection to a public water supply. Include a description of how this information was obtained, such as visual observation, personal contact, telephone conversation, returned postcard, or assumed.
 - Type of well usage, such as private, domestic, or irrigation, and the well construction, if applicable
 - Presence of a basement or sump
 - Possible petroleum sources
 - Property-specific comments

The first attempt at contacting residents, property owners, and business owners must be in person. This is usually done during the walking survey. If personal contact is not made, follow up by phone, or leave a stamped, self-addressed postcard or letter at each address to request the information listed above. The request should communicate at a minimum:

- The purpose of the request is to assess potential risk to nearby water supply wells and basements from the nearby property that contains petroleum contamination.
- A statement that if no reply is received by a specified date, an assumption will be made that there is no wells or basements on site.

4. Complete a visual inspection of properties located within the 500-foot radius during the walking survey. This consists of inspecting each property from all accessible property lines or vantage points. Physical limitations to this inspection must be noted in the [Investigation report](#). During the inspection, document and map the following:
 - Water supply wells
 - Subsurface structures, such as basements, utility markers, and manholes
 - Obvious surface water features such as, but not limited to, lakes, creeks, rivers, ponds, and wetlands within the survey area
 - Possible petroleum sources such as underground storage tanks, above ground storage tanks, hydraulic lifts, etc.

B. Public water supply confirmation

Submit a list of the addresses of all properties within 500 feet of the source to the city utility billing department to confirm the status of water supply to those addresses. In addition, request information regarding plans for groundwater development in the impacted aquifer within ½ mile of the site or one mile of the site if the aquifer is fractured bedrock. Document the water supply confirmation and groundwater development information in the [Investigation report](#).

C. Well records search and review

Review the [Minnesota Well Index](#) for wells within ½ mile of the source to gather information on groundwater usage, well construction, aquifers, and geology. Provide this information in the [Investigation report](#). Include copies of the well logs, or well logs for the nearest 25 wells if there are over 25 within ½ mile, and an accurate map depicting the location of the wells. If there are no wells within ½ mile of the source, expand the search to 1 mile.

D. Sensitive groundwater conditions

Sensitive groundwater conditions are determined based on geology and groundwater usage. Sensitive conditions include wellhead protection areas, shallow bedrock, sole source aquifers, and shallow sand and gravel aquifers. When a sensitive groundwater condition exists, additional investigation may be necessary to determine actual risk due to the sensitive condition. See [Assessment of sensitive groundwater conditions](#) for definitions, reporting requirements, and investigation requirements and options.

E. Risk evaluation

Information from the water supply well receptor survey guides the soil and groundwater investigation. For example, the geology data from well logs facilitates planning the depth of subsurface investigations in order to assess the potential for contaminant migration to an aquifer or well. Collect and analyze water samples from water supply wells that may be at risk.

When monitoring wells are installed for remedial investigations, use the monitoring data to evaluate groundwater flow direction, assess plume stability, and calculate the hydraulic gradient within the impacted aquifer. Estimate groundwater travel times in aquifers using grain size-based hydraulic conductivity and hydraulic gradient. Estimated travel times and contaminant distribution can be used to quickly assess risk to nearby water supply wells and other receptors.

Groundwater travel time

Estimated groundwater travel times are used for the initial risk evaluation and as a basis for recommendations. Measured groundwater travel times, as referred to in Section VI, are more robust calculations used to make a site management decision.

II. Water line permeation receptor survey and risk evaluation

Water line permeation is the mass transfer of a chemical into and through the walls of a water line via diffusion. This process has the potential to adversely affect the quality of the water standing in or transmitted by the water line. Data have shown that certain piping, such as polyethylene, polybutylene, polyvinyl chloride, and asbestos cement, and gasket materials such as non-metallic, are subject to permeation by petroleum contaminants. Petroleum contaminants can infiltrate directly through some materials or degrade and weaken the material, allowing permeation to occur. The highest risk scenarios involve:

- Small diameter, permeable pipe, and/or gaskets used for private service lines that have a low flow volume. This allows the contents of the line to remain stagnant for a period of time and, subsequently, contaminant concentrations to increase.
- Instances where high concentrations of petroleum compounds exist in the subsurface adjacent to water distribution lines. However, any permeable piping or gaskets exposed to petroleum contamination may be at risk.

The following receptor survey and risk evaluation must be completed to assess the risk of water distribution line permeation.

A. Water line permeation receptor survey

The construction details of all public and private water line distribution components within the contaminated area must be well documented by collecting the following information. If water line construction details are unknown, it may be necessary to expose the water line(s) by completing a small excavation.

- Piping and gasket materials used
- Pipe diameter(s)
- Approximate daily water usage of a facility; this information may be determined by using past water meter readings
- Flow directions
- Depth
- Backfill materials
- Age (date installed)
- Distance to nearest point of use for each section of pipe
- Length of the pipe within the impacted zone
- Name of person who owns each section of pipe within the survey area

B. Risk evaluation

If permeable piping or gaskets are present within a contaminated area, advance soil borings to determine the magnitude of soil and groundwater contamination in contact with these components and the length of pipe that may be impacted. If light non-aqueous phase liquid (LNAPL) or highly contaminated groundwater is in contact with a pipe, assume permeation is a risk and collect and analyze water samples from the line at the nearest point(s) of use (i.e., water faucet, spigot, etc.). Refer to [Groundwater sample collection and analysis procedures](#) for water line sampling procedures.

III. Surface water receptor survey and risk evaluation

Sites involving spills that flow to surface water generally pose the greatest potential impact to surface water quality and, therefore, should be addressed immediately. The following procedures apply to potential surface water impacts due to discharge of contaminated groundwater.

A. Surface water receptor survey

Identify and prepare a map showing the locations of all surface water features within ¼ mile of the site. Include any features identified during the 500-foot walking survey discussed in Section I.A. Obtain surface water information from a variety of sources, including United States Geological Survey (USGS) topographical maps and in-field surveys. Identify any potential pathways such as ditches, drain tiles, and storm sewers that may lead to an identified surface water feature.

B. Risk evaluation

Use the survey to plan sampling locations for the subsurface investigation. Evaluate the groundwater quality between the site and a surface water feature by drilling a soil boring or installing a monitoring well between the site and the feature. If the boring or well is contaminated, assume contaminated groundwater discharges to surface water. If a discharge is occurring or is assumed to be occurring, determine the discharge rate based on the plume width, plume thickness, hydraulic conductivity, and horizontal gradient. Calculate discharge using the equation provided in the [Investigation report](#).

If contamination may be discharging to surface water via a pathway such as a leaky storm sewer or other conduit, collect samples within the conduit at the nearest downgradient location. Based on initial sample results, it may be necessary to sample additional locations to adequately evaluate risk to the receptor.

The MPCA will evaluate the need for corrective action based on a comparison of contaminant concentrations at the surface water discharge point to applicable standards in Minnesota's surface water rules.

IV. Vapor receptor survey and risk evaluation

This section discusses the assessment of petroleum vapors that may result in explosive conditions in structures and utilities. If the vapor receptor survey and risk evaluation identify structures or utilities intersecting contamination that poses a risk, then perform a vapor survey as described in subsection C below.

A. Vapor receptor survey

To complete a vapor receptor survey, identify the location and type of nearby vapor receptors.

1. Buildings

Vapor receptors include buildings, especially those with basements and sumps. Building location and construction information within 500 feet of the site is obtained as part of the walking survey described in Section 1, therefore no additional work is required for the vapor receptor survey.

Vapor intrusion assessment

Chronic human health risk from low-level indoor vapor impacts is evaluated by a vapor intrusion assessment, which is discussed in [Vapor intrusion assessments performed during site investigations](#).

2. Utilities

Vapor receptors include:

- Manways, fiber optic conduits, sanitary and storm sewers, and other subsurface structures where petroleum vapors could accumulate.
- Water, electric, telephone, gas, and cable television lines, etc. That can act as migration pathways via the backfill or conduits.
- On-site service lines connecting site structures to main lines that can act as conduits or contaminant migration pathways.

Contact public and private utility owners for information about their subsurface structures. Document the available information on their construction, such as material, depth, elevations, and liquid flow direction, and the condition, such as if it's cracked or leaking, and its age.

Identify all utility vapor receptors on site and on adjacent properties, including underneath all roadways. If the risk evaluation identifies contamination that poses a vapor risk beyond these boundaries, or a vapor survey identifies impacts beyond these boundaries, extend the utility receptor survey to include all areas where subsurface structures intersect contamination or impacts have been detected. This may require multiple vapor receptor survey events when additional risk evaluation or vapor survey data are obtained.

Contact the local fire department to ask about petroleum vapor complaints or reports in the vicinity of the site. Ask occupants of potentially impacted buildings whether they have smelled petroleum odors.

Prepare a vapor receptor map(s) showing the location and identity of all vapor receptors and vapor migration pathways. Include the map(s), subsurface structure construction information, and data sources in the [Investigation report](#).

B. Risk evaluation

If there are vapor receptors, use the data to plan the soil and groundwater investigation. Utility backfill investigations are discussed in [Soil and groundwater assessments performed during site investigations](#). Evaluate the data collected from the soil and groundwater investigation relative to the locations and types of subsurface pathways and structures. In making this evaluation, consider the following:

1. The highest vapor risk settings involve:
 - Sites with LNAPL or groundwater with high levels of dissolved volatile petroleum products.
 - Groundwater that intersects contamination and backfilled utility trenches, sewer lines, basements, or other confined spaces.
2. Vapors migrate along pressure gradients, moving from high to low pressure. Enclosed structures can be a low pressure point, particularly when a furnace is operating. Even buildings without basements draw subsurface vapors. Vapors can migrate in backfill of intact sewer lines.
3. The condition and type of storm and sanitary sewer lines can influence vapor risk since clay tile sewers or very old sewers with cracks or gaps can allow inflow of LNAPL and groundwater.
4. Utility trenches or building foundations that are backfilled with more permeable material than the native soil, such as sand or gravel backfill in clay soil.

Discuss the evaluation of vapor risks in the [Investigation report](#). If any of the above conditions exist, then perform a vapor survey as described in subsection C below.

C. Vapor survey

When conducting a building vapor survey for possible emergency conditions:

1. Interview the building owner and/or occupant to determine the frequency and occurrence of petroleum odors.
2. Check buildings and basements which the vapor risk assessment indicates may be impacted, including site basement, using both an explosimeter and photoionization detector (PID) to take vapor readings. Record names, addresses, and telephone numbers of building owners/occupants.
3. Take vapor readings to assess explosive conditions in the basement.
4. Check for vapors near basement sewer drains and near any cracks in the foundation. Carefully check for vapor pockets at covered sumps, building corners, crawl spaces, or in any area of poor air circulation.

When conducting a sewer vapor survey:

1. Only a person with proper training, experience, and equipment should conduct the survey due to the potential hazards of working with sewers and confined spaces.

2. Contact the city utility department. They can provide sewer maps to determine sewer construction, depth, and the direction of sewer flow and assist in locating and opening manholes.
3. Contact the local police department or public works department if traffic control is needed. If the vapor survey is near a State Trunk Highway and traffic control is needed, contact Minnesota Department of Transportation district personnel.
4. Always use an explosimeter before a PID. Unsafe conditions may exist if explosimeter readings are above 10% of the LEL. When it is safe to use a PID, start at the manhole closest to the site. Work upstream and downstream to determine where product or vapors are entering and the extent of the impacted area. "Crack" each cover first and take readings of oxygen, explosimeter, and PID. Repeat measurements at mid-depth and at the waste water level.
5. Check the airflow direction from the manhole to determine if dilution is occurring.
6. Check water flow direction and collect a water or sewage sample (but do not enter the sewer for this sample). Look for rainbow sheen and check for odors. If there is odor but no product, use a PID to conduct a bag headspace analysis on the water or sewage sample. Consider collecting samples for laboratory analysis if it is important to demonstrate whether and where petroleum contamination is entering a leaking sewer.
7. Check all the incoming branches in the sewer, if possible. If odors are detected, continue upstream and downstream even if no product is present. Vapors may travel "upstream" from the source (especially in winter) and therefore may be misleading.
8. Check lift stations near the site.

What to do when vapors are detected during a vapor survey:

Situation	Actions to take
>10% LEL	Do not enter buildings or continue the sewer survey Immediately contact the local fire department (911) and the Minnesota Duty Officer (24 hours) 651-649-5451 or 800-422-0798

B. Risk evaluation

Results from the site investigation are used to evaluate risk. Surface soil contamination is considered a high risk if the soil is petroleum saturated according to the petroleum sheen test or has a gasoline range organics (GRO) or diesel range organics (DRO) concentration of 100 mg/kg or greater.

VI. Site management decision

The decision to complete a corrective action, monitor contaminant trends, or close a site is based on information collected during the site investigation. Site management decisions are based on the rationale described below.

A. Corrective action

When risk is considered high according to the conditions listed below, corrective action will usually be required. When recommending corrective action, contact the MPCA prior to submitting the [Investigation report](#). The process for obtaining corrective action design approval is described in [Corrective action design and implementation](#). When remediation is being considered as the corrective action alternative, the cleanup must focus on targeting the LNAPL body and must be technically feasible.

High-risk conditions:

- Petroleum impacts to a drinking water supply well above a drinking water standard or conditions that indicate impacts above a drinking water standard are imminent.
- Petroleum impacts to a nondrinking water supply well above a beneficial use level.
- Expanding groundwater contaminant plume within a measured five-year groundwater travel time of a water supply well. See [Soil and groundwater assessments performed during site investigations](#) for more information on measuring groundwater travel time.
- Petroleum compounds are present above a drinking water standard in the aquifer associated with a sensitive groundwater condition.
- Petroleum impacts to a drinking water supply line above a drinking water standard or conditions that indicate impacts above a drinking water standard are imminent (water line permeation).
- Contaminant concentration above a surface water standard at the compliance point.
- Petroleum sheen on the surface water.
- Actual or potential for explosive vapor accumulation in structures or utilities.
- Petroleum impacts to a habitable structure above a vapor intrusion screening value (ISV) or conditions that indicate impacts above an ISV are imminent.
- Surface soil that is petroleum saturated or has a GRO or DRO concentration of 100 mg/kg or greater within the uppermost two feet of soil at a commercial or industrial property.
- Surface soil that is petroleum saturated or has a GRO or DRO concentration of 100 mg/kg or greater within the uppermost four feet of soil at a residential property.
- When a recent release has occurred (see [Recent releases at petroleum tank sites](#)).

Drinking water standards

Applicable standards include state Health Risk Limits (HRLs), Health Based Values (HBVs), Risk Assessment Advice (RAA), and federal Maximum Contaminant Levels (MCLs).

Beneficial use levels

Levels determined on a site-specific basis dependent on the actual usage of the groundwater and the necessary water quality level needed to maintain those uses.

- When recoverable mobile LNAPL is present (see [Light non-aqueous phase liquid management strategy](#)).
- When an emergency condition exists (see [Petroleum remediation program general policy](#)).

B. Additional investigation or monitoring

The extent and magnitude of soil and groundwater contamination, as well as the extent of mobile LNAPL if present, must be determined prior to submitting the [Investigation report](#). Additional investigation or monitoring, however, is often necessary after the [Investigation report](#) is completed to refine the CSM.

In the case of groundwater monitoring, the goal is to demonstrate plume stability, a condition for site closure. If plume stability is not apparent after six quarters of monitoring, MPCA staff will consider the need for a corrective action, continued groundwater monitoring, or other risk reduction or elimination methods.

Recommending additional investigation or monitoring in the [Investigation report](#) or a subsequent [Monitoring report](#) may be appropriate in, but not limited to, the following circumstances.

Additional investigation:

- When further assessment is required for a sensitive groundwater condition
- When an expanding groundwater plume exists
- When water line construction data are unknown and permeation risk is a concern
- When field-detectable vapor impacts require further investigation
- When further assessment beyond a preliminary soil gas assessment is required to evaluate the vapor intrusion exposure pathway
- When further delineation of surface soil contamination is required prior to corrective action approval
- When site conditions change or new information indicates a need to update the CSM with further investigation

Additional monitoring:

- When groundwater plume stability has not been established
- When water supply wells are at risk or have been impacted
- When surface water risk requires additional monitoring to establish discharge concentrations and trends
- When further assessment of field-detectable vapor impacts to subsurface structures is needed
- When further assessment of contaminant concentrations in permanent soil gas or sub-slab soil gas monitoring points is needed
- When monitoring of site conditions during or following corrective action implementation is needed to determine corrective action effectiveness

C. Site closure

A recommendation for site closure is appropriate when all the following conditions are met:

- Proper treatment of excavated soil is completed and documented
- Mobile LNAPL is recovered to the maximum extent practicable
- The groundwater plume is demonstrably stable (see [Soil and groundwater assessments performed during site investigations](#))
- The corrective action goals are achieved

VII. 2008 Petroleum release notification bill

Effective August 1, 2008, all tank owners will be responsible for providing information to all residents contacted as part of the receptor survey. This information will include notification of the release, results of the receptor survey, and any corrective actions taken on behalf of the release. The complete bill language is provided below:

Sec. 11. [116.482] Petroleum Release Notification

(a) When a potential receptor survey is conducted for a petroleum tank release as provided in agency guidance documents, the tank owner must provide information on the results of the survey, reports of all releases, and any corrective actions, as defined in section 115C.02, that are related to the petroleum tank release in an understandable manner to residents contacted in the survey. The information may be provided through personal contact, mail, or e-mail. (b) An owner may delegate the owner's responsibility under paragraph (a) to the owner's consultant or contractor, as those terms are defined in section 115C.02, or to the operator of the tank.

To assist the tank owner in complying with this law, the MPCA has developed a guidance document that contains a letter template to facilitate communication to all contacted residents. See [Petroleum tank release follow-up notification](#). Following completion of a potential receptor survey as defined in this guidance document, submit a notification letter to all residents contacted as part of the survey. The example template is an illustration of language that should satisfy the law's requirements. Tank owners and their consultants may use the template as is or modify it to suit their site-specific situation.

Soil sample collection and analysis procedures

Petroleum Remediation Program

This document describes the procedures for field screening of petroleum-contaminated soil and collection of soil samples for laboratory analysis.

The Minnesota Pollution Control Agency (MPCA) Petroleum Remediation Program (PRP) conducts random on-site audits of fieldwork. Give the PRP at least 48 hours' notice prior to conducting fieldwork at sites under program oversight. Find information on the fieldwork notification process at <https://www.pca.state.mn.us/waste/field-work-notifications>. Prior notification of fieldwork is mandatory and will be verified upon submittal of the results.

To assure data quality, the U.S. Environmental Protection Agency (EPA) has required the MPCA to develop a [Quality Assurance Program Plan \(QAPP\)](#) for the PRP. The objective of the QAPP is to define the Quality Assurance/Quality Control (QA/QC) procedures to be followed for the collection and analysis of environmental samples. This ensures sufficient precision and accuracy of samples used in the PRP.

I. Field screening procedures

A. Soil headspace screening

Use the polyethylene bag headspace method described below to characterize soil contamination at petroleum release sites.

1. Use photoionization detectors (PIDs) with a 10.2 eV (+/-) or greater lamp source. Perform PID instrument calibration on site and at least daily to yield "total organic vapors" in parts per million by volume of a benzene equivalent. Follow the manufacturer's instructions for operation, maintenance, and calibration of the instrument. Keep calibration records in a bound book. MPCA staff reserve the right to request these records.
2. Use a resealable one-quart polyethylene freezer bag. Half-fill the bag with sample (the volume ratio of soil to air is equal), then immediately seal it. Manually break up the soil clumps within the bag. Note: Immediately after opening the split spoon sampler or soil sample liner, transfer soil to field screening bags. Collect soil samples from excavations or soil stockpiles from freshly exposed surfaces.
3. Allow headspace development for at least 10 minutes at approximate room temperature. Vigorously shake bags for 15 seconds at the beginning and end of the headspace development period. Headspace development decreases with temperature. When temperatures are below the operating range of the instrument, perform headspace development and screening in a heated vehicle or building. Record the ambient temperature during headspace screening. Complete headspace screening within approximately 20 minutes of sample collection.
4. After headspace development, introduce the instrument sampling probe through a small opening in the bag to a point about one-half of the headspace depth. Keep the probe free of water droplets and soil particles.
5. Record the highest meter response on a sampling form. Maximum response usually occurs within about two seconds. Erratic meter response may occur if high organic vapor concentrations or moisture is present. Note any erratic headspace data in the sampling form. Do not collect analytical samples from the polyethylene bag.

B. Petroleum sheen test

The petroleum sheen test is a quick and easy field method used to determine if a soil sample is considered petroleum saturated. A soil is defined as petroleum-saturated when pore spaces contain some petroleum light non-aqueous phase liquid (LNAPL), with the remainder occupied by air and/or water. Detection of sheen or droplets of product when conducting this test is direct evidence that LNAPL is present and the soil sample is petroleum saturated.

1. Place a small quantity of petroleum-contaminated soil in a jar or on a large spoon. Alternatively, use the soil in the polyethylene bag after measuring the soil headspace described above.
2. Add enough water to break apart and submerge the soil particles. Add water directly to the polyethylene bag if using soil from headspace screening. Let the sample rest for a minimum of 10 minutes prior to examining for sheen or droplets of product.
3. If droplets of product or sheen are present on the water surface, the test result is positive and the soil is considered petroleum saturated.

II. Soil sampling procedures

A. Soil sampling - site characterization for investigation purposes

1. Minimize the possibility of cross-contamination by using disposable sampling equipment that is certified as clean for each sample collected. If disposable sampling tools are not available, specify the cleaning procedures used. Wear clean sampling gloves at each sampling point. When using a split-spoon or similar sampler, wash it with a detergent solution (e.g., Liquinox or equivalent), and rinse before each use.
2. When sampling excavation sidewalls or floors, remove at least one foot of exposed soil prior to collecting the sample to ensure collection of a fresh sample. See [Excavation of petroleum contaminated soil](#) for sampling requirements.
3. Collect samples from split-spoon samplers or soil sample liners using a procedure that will minimize losses due to volatilization. Collect samples as soon as possible after the surface of the soil has been exposed to the atmosphere. Do not collect analytical samples from soil cores that have been exposed for more than a few minutes. In order to allow for sample selection based on field screening results, immediately transfer an undisturbed portion of the soil core to a resealable one-quart polyethylene freezer bag, sealed with no headspace, and placed on ice in a cooler. After the sampling interval has been determined, collect the analytical sample from the undisturbed bagged core sample. Complete sample containerization and preservation within two hours of retrieving the core from the subsurface. Document the procedure in the [Investigation report](#). See [Soil and groundwater assessments performed during site investigations](#) for sampling requirements.
4. EPA Method 5035 is required when sampling soil for volatile contaminants per EPA SW-846. Collect soil samples using coring devices (e.g., cut syringe, EnCore™, or US Analytical's Eazydraw Syringe™ sampler, or other approved coring device) and either put the "cored" soil directly into containers provided by the analytical laboratory (verify that the laboratory has pre-weighed these containers) or place the sealed coring device (for an EnCore™ type sampler) containing the soil in a cooler containing ice. The correct volume of soil to use in the coring device is established by weighing a similar soil sample before coring the analytical sample. Do not weigh analytical sample into the sample container because doing so can undesirably aerate the soil sample. The holding time is 14 days for soil samples preserved by methanol or frozen in an approved coring device. Samples in a coring device that are not frozen must be extracted within 48 hours. **Do not retain soil previously used for field screening or soil classification for analytical samples.**
 - a) Gasoline range organics (GRO) and volatile organic compound (VOC) sampling: Collect GRO and VOC samples according to the Wisconsin Department of Natural Resources Modified GRO method and EPA Method 5035, respectively. These methods require the use of methanol as a preservative for most

sampling. When methanol is used as the preservative, GRO and VOC results can be obtained from the same sample. Preserve approximately 25 grams of soil with 25 ml of methanol in a tared 60-ml vial. A maximum of 35 grams of soil is recommended to enable a 1:1 ratio of soil to extraction solvent in the sample container. Other sample sizes, such as 5 grams of soil and 5 mL of methanol in a 40-mL VOC vial, can be utilized if the 1:1 ratio is maintained. An approved sampler (e.g., EnCore™ or similar certified sampler) can also be used to hold the samples for 48 hours from the time of collection when held at 4 ± 2 degrees Celsius, or 14 days from the collection date when frozen below -12 degrees Celsius, before methanol preservation. A dry weight vial without methanol preservation is also required for every sample. Clean the vial threads to assure a good seal with the cap provided.

- b) Diesel range organics (DRO) sampling: Collect DRO samples according to the Wisconsin Department of Natural Resources Modified DRO method. Place approximately 25 grams of soil in a tared 60-ml vial without preservative. A maximum of 35 grams of soil is recommended to enable a 1:1 ratio of soil to extraction solvent in the sample container. An approved sampler can also be used to hold the sample until it is extracted following the Wisconsin DRO protocols. Collect another vial for dry weight determination on the sample. Clean the vial threads to assure a good seal with the cap provided. Add methylene chloride to the DRO samples within 10 days. The laboratory must complete the extraction process and sample analysis within 47 days of collection.
5. Label all vials, place in a covered cooler with ice, and transport to the laboratory for analysis. Samples should be kept at a stable temperature of 4 ± 2 degrees Celsius. Include a container of water for sample temperature verification (temperature blank). The labels should indicate:
 - a) Type of analysis
 - b) Name of facility
 - c) Monitoring point identification
 - d) Name of person collecting sample
 - e) Time and date the sample was collected
 - f) Name of preservative added, if applicable
 6. Collect, transport, and deliver samples under chain of custody.
 7. Samples not transported or analyzed within the accepted holding time are invalid.

B. Soil sampling – characterization for off-site treatment/disposal

1. Analysis for VOCs, GRO, and DRO requires collection of grab samples from representative portions of the stockpile or from soil borings conducted in locations that are representative of soil contaminated by the release. Use the sampling procedures described in subsection A above. Base the number of soil samples on Table A.

Table A. Number of grab samples required from contaminated soil stockpiles.

Cubic yards of soil in pile	Number of grab samples
Less than 50	1
51-500	2
501-1,000	3
1,001-2,000	4
2,001-4,000	5
Each additional 2,000	One additional sample

Analysis of soil samples is not normally necessary if less than 10 cubic yards of contaminated soil will be land treated, unless the soil could potentially be considered a hazardous waste.

2. Analysis for metals (arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver) and polychlorinated biphenyls (PCBs) requires collection of a separate composite sample. To take a composite sample from a stockpile, collect 15 samples from randomly selected locations within the stockpile, place samples in a clean container, mix thoroughly, and remove a single subsample. To take a composite sample from soil borings, collect 15 samples from randomly selected locations in borings that represent soil that will be excavated. Place samples in a clean container, mix thoroughly, and remove a single subsample. In each case, send the single subsample to the laboratory for analysis.

III. Soil analysis

The MPCA requires laboratory certification. See the [MPCA quality system webpage](#) and [Methods and analytes requiring laboratory certification](#). Laboratories reporting data are required to include the name of the certifying organization on analytical reports. Certification is currently required for fixed-base and mobile laboratories analyzing VOCs. Certification for mobile labs must meet the same requirements established for fixed-base laboratories.

If a noncertified mobile laboratory is used for sample screening, split ten percent of samples with a certified fixed-base laboratory. An MPCA-recognized certified laboratory must generate data supporting site closure. In appendices and tables, clearly label data generated by mobile laboratories and fixed-base laboratories. For all sample analyses, unless otherwise noted in this document, use an EPA-approved method or equivalent. Provide chromatograms for positive GRO and DRO analyses. These chromatograms must be properly scaled in order to show enough detail to allow for interpretation and identification.

Table B lists the analyses for the different types of petroleum products.

Table B. Required analyses and laboratory procedures.

Petroleum product	Parameters
Leaded gasoline, aviation gasoline	A, B, D
Unleaded gasoline, ethanol-blended fuel	A, B
Unused petroleum products: fuel Oil, motor Oil, diesel Fuel, kerosene, jet fuels	A, C, G
Used oil (e.g., motor oil, other used petroleum products). See notes 1, 2, and the section on used oil special considerations below.	A, C, E, F, G
Unknown petroleum or hydrocarbons mixture	A, B, C, E, F, G
Other petroleum products	Site specific
Hydraulic fluids	A, C, F, G

- A. Volatile organic compounds (VOCs) by the most recent version of EPA Method 8260 (see Note 6). Find the VOC target analyte list in Appendix A.
If groundwater at the site will be analyzed for VOCs, then analyze soil for only petroleum VOCs (PVOCs) by the most recent version of EPA Method 8260 or Method 8021. PVOC analysis QA/QC procedures are in Section IV. The PVOC target analyte list is in Appendix B.
- B. Wisconsin Department of Natural Resources Modified Gasoline Range Organics (GRO) Method (see Note 3)
- C. Wisconsin Department of Natural Resources Modified Diesel Range Organics (DRO) Method (see Notes 4 and 5)
- D. Lead (see Note 7)
- E. Resource Conservation and Recovery Act (RCRA) metals - arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver (see Note 2)
- F. Polychlorinated biphenyls (PCBs) using the most recent version of EPA Method 8082 by the Aroclors method (see Note 2). See Appendix C for specific Aroclors. Complete analysis for PCBs for hydraulic fluids used in elevators and other hydraulic fluids subject to high heat prior to the 1980s.

- G. Polycyclic aromatic hydrocarbons (PAHs) by the most recent version of EPA Method 8270. PAH analysis QA/QC procedures are found in Section IV. The PAH target analyte list is found in Appendix D.

Note that the MPCA project manager will determine the need for PAH analysis. If a drinking water aquifer is impacted by fuel oil or higher boiling point petroleum product contact the project manager.

Notes:

1. Do not confuse used oil with waste oil. **Used oil** means any oil that (because of use) is contaminated by physical or chemical impurities. Examples of used oil include, but are not limited to, motor oils, metal cutting oils, and hydraulic fluids. **Waste oil** means oil that is discarded or spilled before use.
2. During investigation at used oil sites, collect samples for all of the parameters listed (VOCs, DRO, RCRA metals, and PCBs), but direct your laboratory to analyze only the VOC and DRO samples initially. If any of these compounds are detected, proceed with analysis of the metals and PCB samples. Note: If you are sampling to fulfill soil disposal requirements, analyze samples for all required parameters (VOCs, DRO, metals, and PCBs). See below for special considerations for soil contaminated with used oil.
3. This is a purge-and-trap, gas chromatography (GC) procedure that uses a 10-component blend of gasoline compounds for the quantification standard. Collect approximately 25 grams of soil using a zero headspace method and placed into a tared 60-mL vial containing 25 mL of methanol followed by measuring the total weight in the laboratory. The sample must be cooled to 4 ± 2 degrees Celsius and must be received by the laboratory within four days (EnCore™ samplers can be held for 48 hours) and analyzed within 21 days of collection. To ensure the extraction of the volatiles, the soil must be sonicated for 20 minutes (ensure the temperature does not exceed room temperature) before samples are analyzed. Use a methanol trip blank when using methanol as a preservative as this ensures no contamination is present in the methanol. The method quantitation limit shall be no more than 10 mg/kg dry weight, assuming 100% solids.
4. This is a solvent extraction, direct injection, GC procedure that uses a ten-component blend of typical diesel oil components for a quantification standard. Collect approximately 25 grams of soil using a zero headspace method and placed into a tared 60-mL vial followed by measuring the total weight in the laboratory. The samples must be cooled to 4 ± 2 degrees Celsius, received by the laboratory and preserved in solvent within 10 days, and analyzed within 47 days of collection. The method quantitation limit shall be no more than 10 mg/kg dry weight, assuming 100% solids. Separate samples are required for GRO and DRO analyses.
5. The DRO analysis method can have false positives that lead to elevated results, which are not from petroleum compounds. The DRO analysis method is a very useful screening method, but may not provide an accurate determination of petroleum compounds for making site decisions. When false positives are suspected, cleanup of extracts to remove non-petroleum compounds may be necessary. See Section IV for laboratory QA/QC procedures for DRO cleanup.
6. This is a purge-and-trap, gas chromatography method. Sampling is similar to GRO (see Note 3). Base the reporting limits and quality assurance for all parameters on the most recent version of EPA Method 8260. Note that PVOC holding time is 14 days and must be sampled using EPA Method 5035. If a mobile laboratory is being used for the analysis of soil samples, the mobile laboratory must follow the method specified calibration and quality control procedures required by the referenced method.
7. Sampling for lead is required for fulfilling soil disposal requirements. Specifically, soil that will be treated after its removal that is actually or potentially contaminated with leaded gasoline must be analyzed to determine if it exhibits the toxicity characteristic for lead. If a total lead analysis indicates a level equal to or greater than 100 mg/kg, perform a Toxicity Characteristic Leaching Procedure (TCLP). If the TCLP level exceeds 5 mg/L, manage the soil as a hazardous waste in accordance with [Minn. R. ch. 7045](#).

Special considerations for soil contaminated with used oil:

This section outlines additional procedures for testing used oil contaminated soil to determine if the soil is considered a hazardous waste. If the soil is considered a hazardous waste, manage the soil in accordance with [Minn. R. ch. 7045](#).

1. Soil with a PCB concentration above 50 mg/kg is considered a hazardous waste.
2. Soil is considered a hazardous waste if it is contaminated with any hazardous waste listed in [Minn. R. 7045.0135](#). If the generator of the soil can certify to the satisfaction of MPCA staff, by previous knowledge or chemical analysis, that the soil is not contaminated with waste listed in Minn. R. 7045.0135 the soil need not be managed as a hazardous waste.
3. If the concentration of total halogenated compounds determined by VOC analysis is greater than 1,000 mg/kg, the soil is presumed to be hazardous waste unless the generator can rebut this presumption to the satisfaction of MPCA staff, through previous knowledge or chemical analysis.
4. Soil is considered hazardous if it exhibits the toxicity characteristic of any of the following contaminants: arsenic, barium, cadmium, chromium, lead, mercury, selenium, silver, endrin, lindane, methoxychlor, toxaphene, 2,4-dichlorophenoxyacetic acid, and 2,4,5-trichlorophenoxypropionic acid. Do not test for contaminants known not to be present, such as pesticides and herbicides, if the generator certifies to the satisfaction of the MPCA that the contaminants are not present. Contaminants exceeding levels in Table C are considered to potentially exhibit the toxicity characteristic and a complete TCLP must be performed:

Table C. Levels at which TCLP will be required

Contaminant	Soil concentration (mg/kg)
Arsenic	100
Barium	2,000
Cadmium	20
Chromium	100
Lead	100
Mercury	4.0
Selenium	20
Silver	100
Endrin	0.40
Lindane	8.0
Methoxychlor	200
Toxaphene	10
2,4-Dichlorophenoxyacetic Acid	200
2,4,5-Trichlorophenoxypropionic Acid	20

If soil exhibits the toxicity characteristic, it is considered a hazardous waste.

IV. Required laboratory quality assurance/quality control

A. PVOC analysis: Analyze samples for the target analytes listed in Appendix B using the most recent version of EPA Method 8260 or Method 8021. Follow all quality control (QC) elements defined in the method. Laboratories should also incorporate the QC procedures listed below.

1. **Initial calibration:** The initial calibration curve must contain at least five calibration points. For Methods 8260 and 8021, the r^2 for each curve must be greater than or equal to 0.990, or the r must be greater than or equal to 0.995. If the ratio of response to concentration is constant (<15% relative standard deviation for Method 8260 and <20% relative standard deviation for Method 8021), linearity can be assumed and the average response factor can be used in place of a calibration curve. The recovery (accuracy) for each point in

the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, dilute the sample into the calibration range and re-analyzed.

2. **Continuing calibration verification:** Analyze one low-level standard at the report level (RL) and one mid-level calibration verification standard prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12-hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for the target analytes in the low-level standard should be between 60% and 140% of the true value. The %R for the target analytes in the mid-level standards should be between 70% and 130% of the true value (with a %D of less than or equal to 30%).
3. **Initial demonstration of capability:** Analyze 4-7 replicate mid-level check standards. Percent recovery (%R) must be equal to 70-130%. The percent relative standard deviation (%RSD) must be less than 20%.
4. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven standards. The RL should be approximately three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met.
5. **Batch quality control:** A batch is defined as up to 20 environmental samples analyzed in a 12-hour analytical sequence. At a minimum, each batch must contain a method blank, a laboratory control sample (LCS), and a matrix spike/matrix spike duplicate (MS/MSD) pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a laboratory control sample duplicate (LCSD) is prepared and analyzed.
6. **Method blanks:** Analyze one method blank per QC batch of 20 samples or less. The concentration of PVOs in the method blank must be less than the associated report level. If the method blank is contaminated, take measures to eliminate the problem. Re-extract and re-analyze affected samples. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.
7. **Accuracy/precision:** One LCS is required per batch. The %R must be between 70% and 130%. One MS and MSD is required per batch. The %R for each analyte in the MS/MSD must be between 70% and 130% with a relative percent difference (RPD) of less than or equal to 30%.
8. **Holding time:** Analyze the samples within 14 days of sample collection.
9. **Confirmation analysis:** For Method 8021, confirmation analysis using a dissimilar detector or a column of different polarity must be performed, or by GC/mass spectrometry analysis. Evaluate the agreement between the quantitative results by calculating the relative percent difference (RPD) between the two results. The formula is:

$$RPD = (ABS(R1 - R2)/((R1 + R2)/2)) * 100$$

The RPD should be ≤40%. If one result is significantly higher, check the chromatograms to see if an obviously overlapping peak is causing the high result. If no overlapping peaks are noted, examine the baseline to determine if there were any data system problems during peak integration.

If no anomalies are noted, report the higher result and add a flag that alerts the data user of the disparity between the results on the two detectors or columns.

- B. **PAH analysis:** Analyze samples for these target analytes in Appendix D using the most recent version of EPA Method 8270. 1-Methylnaphthalene and 2-methylnaphthalene are included in the list of PAH target analytes for the PRP. Follow all QC elements defined in the method. Laboratories should also incorporate the QC procedures listed below.

1. **Initial calibration:** The initial calibration curve should contain at least five calibration points. The *r* for each curve must be greater than or equal to 0.995. If the ratio of response to concentration is constant (<20% relative standard deviation), linearity can be assumed and the average response factor can be used in place of a calibration curve. The recovery (accuracy) for each point in the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, dilute the sample into the calibration range and re-analyze.
2. **Continuing calibration verification:** Analyze one low-level standard at the report level (RL) and one mid-level calibration verification standard prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12-hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for the target analytes in the low-level standard should be between 60% and 140% of the true value. The %R for the target analytes in the mid-level standards should be between 80% and 120% of the true value (with a %D of less than or equal to 20%).
3. **Initial demonstration of capability:** Analyze 4-7 replicate mid-level check standards. Percent recovery (%R) must be equal to 70-130%. The percent relative standard deviation (%RSD) must be less than 20%.
4. **Method detection limit/Report level:** Method detection limits (MDLs) and Ls are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven standards. The RL should be approximately three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met.
5. **Batch QC:** A batch is defined as up to 20 environmental samples prepared in the same 24-hour period. At a minimum, each batch must contain a method blank, a LCS, and a MS/MSD pair. If there is not enough sample to prepare and analyze a MS/MSD pair, prepare and analyze an LCSD.
6. **Method blanks:** Analyze one method blank per QC batch of 20 samples or less. The concentration of PAHs in the method blank must be less than the associated report level. If the method blank is contaminated, take measures to eliminate the problem. Re-extract and re-analyze affected samples. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above 10 times the blank contamination will not need to be qualified.
7. **Accuracy/precision:** One LCS is required per batch. The laboratory should generate in-house limits for accuracy. The % recoveries should be between 50% and 150%. One MS and MSD is required per batch. The laboratory should generate in-house limits for accuracy and precision. The % recoveries for each analyte in the MS/MSD should be between 50% and 150% with a RPD of less than or equal to 30%.
8. **Surrogates:** Surrogates are added to all environmental and QC samples. The laboratory should generate in-house limits for surrogate recoveries. The % recoveries should be between 50% and 150%.
9. **Holding time:** The samples should be extracted within 7 days of collection and analyzed within 40 days of extraction.
 - C. **DRO cleanup:** Clean up soil extracts prior to DRO analysis using three methods, either separately or in combination. The methods include: 1) EPA Method 3630C, silica gel cleanup, 2) EPA Method 3650B, acid/base partitioning, and 3) EPA Method 3611B, alumina column cleanup. When DRO cleanup is requested, pre-cleanup analysis should be completed prior to conducting the cleanup. If there are no detections in the pre-cleanup analysis, the laboratory should not conduct the cleanup and post-cleanup analysis.

DRO clean-up results are accepted only if quality assurance documentation shows results that meet acceptance criteria, i.e. no significant loss of petroleum compounds. The quality control acceptance criteria for the clean-up results will be as follows:

1. At least one method blank, one laboratory duplicate, one matrix spike, and one laboratory control sample must be run through the complete clean-up and analysis process for up to 20 samples (1/20).
2. The laboratory must provide a narrative of the entire clean up and analysis process. They must also provide pre- and post-cleanup results and compare the pre-cleanup chromatogram with that of the post-cleanup chromatogram for every sample when cleanup is completed.
3. The RPD between sample duplicates, matrix spike pairs, or laboratory control sample pairs must be less than or equal to 20%. However, use the difference between duplicates to measure precision if the concentration of the target analyte in the sample/sample duplicate is less than five times the report level. The difference must then be less than or equal to the report level.

Appendix A: Target analyte list for volatile organic compounds

Chemical name	CAS #	Report level (mg/kg dry weight)*
1,1,1,2-Tetrachloroethane	630-20-6	1.0
1,1,1-Trichloroethane	71-55-6	1.0
1,1,2,2-Tetrachloroethane	79-34-5	1.0
1,1,2-Trichloroethane	79-00-5	1.0
1,1,2-Trichlorotrifluoroethane	76-13-1	1.0
1,1-Dichloroethane	75-34-3	1.0
1,1-Dichloroethene	75-35-4	1.0
1,1-Dichloropropene	563-58-6	1.0
1,2,3-Trichlorobenzene	87-61-6	1.0
1,2,3-Trichloropropane	96-18-4	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
1,2,4-Trimethylbenzene	95-63-6	1.0
1,2-Dibromo-3-chloropropane	96-12-8	5.0
1,2-Dibromoethane	106-93-4	1.0
1,2-Dichlorobenzene	95-50-1	1.0
1,2-Dichloroethane	107-06-2	1.0
1,2-Dichloropropane	78-87-5	1.0
1,3,5-Trimethylbenzene	108-67-8	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,3-Dichloropropane	142-28-9	1.0
1,4-Dichlorobenzene	106-46-7	1.0
2,2-Dichloropropane	594-20-7	1.0
2-Chlorotoluene	95-49-8	1.0
4-Chlorotoluene	106-43-4	1.0
Acetone	67-64-1	20
Allyl chloride	107-05-1	1.0
Benzene	71-43-2	1.0
Bromobenzene	108-86-1	1.0
Bromochloromethane	74-97-5	1.0
Bromodichloromethane	75-27-4	1.0
Bromoform	75-25-2	1.0

Chemical name	CAS #	Report level (mg/kg dry weight)*
Bromomethane	74-83-9	2.0
n-Butylbenzene	104-51-8	1.0
sec-Butylbenzene	135-98-8	1.0
tert-Butylbenzene	98-06-6	1.0
Carbon tetrachloride	56-23-5	1.0
Chlorobenzene	108-90-7	1.0
Chlorodibromomethane	124-48-1	1.0
Chloroethane	75-00-3	1.0
Chloroform	67-66-3	1.0
Chloromethane	74-87-3	1.0
cis-1,2-Dichloroethene	156-59-2	1.0
cis-1,3-Dichloropropene	10061-01-5	1.0
Dibromomethane	74-95-3	1.0
Dichlorodifluoromethane	75-71-8	1.0
Dichlorofluoromethane	75-43-4	1.0
Ethylbenzene	100-41-4	1.0
Ethyl ether	60-29-7	1.0
Hexachlorobutadiene	87-68-3	1.0
Isopropylbenzene	98-82-8	1.0
p-Isopropyltoluene	99-87-6	1.0
Methyl ethyl ketone (2-butanone)	78-93-3	10
Methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1	5.0
Methyl <i>tertiary</i> -butyl ether	1634-04-4	2.0
Methylene chloride	75-09-2	2.0
Naphthalene	91-20-3	1.0
n-Propylbenzene	103-65-1	1.0
Styrene	100-42-5	1.0
Tetrachloroethene	127-18-4	1.0
Tetrahydrofuran	109-99-9	10
Toluene	108-88-3	1.0
trans-1,2-Dichloroethene	156-60-5	1.0
trans-1,3-Dichloropropene	10061-02-6	1.0
Trichloroethene	79-01-6	1.0
Trichlorofluoromethane	75-69-4	1.0
Vinyl chloride	75-01-4	1.0
m&p-Xylene	179601-23-1	1.0
o-Xylene	95-47-6	1.0

*Assuming 100% solids

Appendix B: Target analyte list for petroleum volatile organic compounds

Chemical name	CAS #	Report level (mg/kg dry weight)*
1,2,4-Trimethylbenzene	95-63-6	1.0
1,3,5-Trimethylbenzene	108-67-8	1.0
Benzene	71-43-2	1.0
Ethylbenzene	100-41-4	1.0
Methyl <i>tertiary</i> -butyl ether	1634-04-4	2.0

Chemical name	CAS #	Report level (mg/kg dry weight)*
Naphthalene	91-20-3	1.0
Toluene	108-88-3	1.0
m&p-Xylene	179601-23-1	1.0
o-Xylene	95-47-6	1.0

*Assuming 100% solids

Appendix C: Target analyte list for polychlorinated biphenyls

Chemical name	CAS #	Report level (mg/kg dry weight)*
Aroclor 1016	12674-11-2	0.050
Aroclor 1221	11104-28-2	0.100
Aroclor 1232	11141-16-5	0.050
Aroclor 1242	53469-21-9	0.050
Aroclor 1248	12672-29-6	0.050
Aroclor 1254	11097-69-1	0.050
Aroclor 1260	11096-82-5	0.050

*Assuming 100% solids

Appendix D: Target analyte list for polycyclic aromatic hydrocarbons

Chemical name	CAS #	Report level (mg/kg dry weight)*
Acenaphthene	83-32-9	0.17
Acenaphthylene	208-96-8	0.17
Anthracene	120-12-7	0.17
Benzo(a)anthracene	56-55-3	0.17
Benzo(b)fluoranthene	205-99-2	0.17
Benzo(k)fluoranthene	207-08-9	0.17
Benzo(g,h,i)perylene	191-24-2	0.17
Benzo(a)pyrene	50-32-8	0.17
Chrysene	218-01-9	0.17
Dibenz(a,h)anthracene	53-70-3	0.17
Fluoranthene	206-44-0	0.17
Fluorene	86-73-7	0.17
Indeno(1,2,3-cd)pyrene	193-39-5	0.17

Chemical name	CAS #	Report level (mg/kg dry weight)*
2-Methylnaphthalene	91-57-6	0.17
Naphthalene	91-20-3	0.17
Phenanthrene	85-01-8	0.17
Pyrene	129-00-0	0.17
1-Methylnaphthalene	90-12-0	0.17

*Assuming 100% solids

Groundwater sample collection and analysis procedures

Petroleum Remediation Program

1.0 Introduction

This document describes the procedures for collecting groundwater samples at Minnesota Pollution Control Agency (MPCA) Petroleum Remediation Program (PRP) sites. It applies to temporary and permanent monitoring wells, as well as water supply wells. Unforeseen circumstances during sampling may necessitate modifying these procedures. When approval to modify procedures cannot be obtained in advance, contact the MPCA as soon as possible to evaluate the need for resampling. Clearly note all deviations from the specified procedures on the sampling information form used for each well and document in the monitoring report. Other MPCA programs may have different sampling procedures; if sampling a monitoring well for multiple programs, follow the most restrictive procedure.

The PRP conducts random on-site audits of fieldwork. The PRP must be given at least 48 hours notice prior to conducting fieldwork at sites under program oversight. Information on the fieldwork notification process can be found at <https://www.pca.state.mn.us/waste/field-work-notifications>. Prior notification of fieldwork is mandatory and will be verified upon submittal of the results.

To assure data quality, the United States Environmental Protection Agency (EPA) has required the MPCA to develop a [Quality Assurance Program Plan \(QAPP\)](#) for the PRP. The objective of the QAPP is to define the quality assurance/quality control (QA/QC) procedures to be followed for the collection and analysis of environmental samples. This ensures sufficient precision and accuracy of samples used in the PRP.

2.0 Analytical parameters and methods

Analytical parameters and methods required to fulfill PRP groundwater-sampling requirements are outlined in Section 9 and Appendices A to E.

The MPCA requires laboratory certification. See the [MPCA quality system](#) webpage and [Methods and analytes requiring laboratory certification](#). Laboratories reporting data are required to include the name of the certifying organization on analytical reports. Certification is currently required for fixed-base and mobile laboratories analyzing volatile organic compounds (VOCs). Certification for mobile labs must meet the same requirements established for fixed-base laboratories.

If a noncertified mobile laboratory is used for sample screening, split 10% of the samples with a certified fixed-base laboratory. Data supporting site closure must be generated by an MPCA-recognized certified laboratory. In appendices and tables, clearly label data generated by mobile laboratories and fixed-base laboratories. For all sample analyses, unless otherwise noted in this document, use an EPA-approved method or equivalent. Chromatograms for positive gasoline range organics (GRO) and diesel range organics (DRO) analyses must be provided. These chromatograms must be properly scaled in order to show enough detail to allow for interpretation and identification.

3.0 Field procedures

Exercise care to avoid cross-contamination of groundwater samples by adhering to these guidelines:

- Follow procedures for proper storage and transportation of equipment.
- Avoid contaminating equipment or sample bottles on site by setting them on or near potential contamination sources such as uncovered ground, contaminated vehicle, vehicle exhaust, etc.
- Avoid handling bottles or equipment with contaminated hands or gloves. All field crew personnel must wear clean gloves made of appropriately inert material. Replace gloves when soiled and between sampling locations.
- Carefully clean all non-disposable well purging or sampling devices.

3.1 Sampling order

When previous water quality data is available, begin with the least contaminated wells, and proceed to increasingly contaminated wells. When contaminant distribution is unknown, begin with wells upgradient of likely contaminant source(s), continue with downgradient wells, and finish with wells in or closest to suspected contaminant source(s).

3.2 Water level measurements

Decontaminate water level probes between each sampling point by wiping or scrubbing off soil or other foreign material, washing with a laboratory grade detergent (Liquinox or equivalent)/clean-water solution, and rinsing with tap water followed by a final rinse with distilled or deionized water. If the probe comes in contact with free product or highly contaminated groundwater, wash equipment using a desorbing agent (dilute solution of water and isopropanol or methanol) followed by a thorough tap water rinse and a final distilled or deionized water rinse.

Prior to well purging or sampling, measure and record initial static water levels for all wells. Determine water levels to the nearest 0.01-foot as measured from the surveyed reference point. Take water level measurements at all applicable site monitoring wells and piezometers within the shortest practical time interval (the same day).

Reference the depth to water from the measuring point marked at the top of the innermost well casing. If the well casing is unevenly trimmed, mark and survey the highest point on the casing for use as the measuring point. Convert the water level measurement to water level elevation using the surveyed elevation of the top of each well casing.

Record the well depth during each sampling event on the sampling form. The well depth can be measured with the same instrument used to measure the water level. Record the well depth to the nearest 0.1 feet. In addition, record the general physical condition of the well on the sampling form.

3.3 Light non-aqueous phase liquid measurements

If petroleum light non-aqueous phase liquid (LNAPL) is suspected or if strong petroleum odors are present in a well, attempt to measure LNAPL thickness using an interface probe or bailer lowered slowly into the well. A tape measure and water finding paste can also be used. Wells containing LNAPL are not normally sampled. Notify the MPCA immediately of all new LNAPL discoveries (see [Light non-aqueous phase liquid management strategy](#)).

4.0 Well development and purging

4.1 Well development

Develop new permanent wells prior to sampling to ensure adequate hydraulic connection with the aquifer and to remove any drilling fluids. Develop wells by pumping and surging until relatively clear water is produced. Document development procedures, including the amount of water removed.

4.2 Well purging (standard purge and sample method)

This section discusses the standard purge method to be used when unpurged sampling (Section 4.4 below) is not allowed.

For permanent monitoring wells, purge a minimum of three well-casing water column volumes before collecting samples for laboratory analysis. Record on the sampling form the quantity of water purged. Prior to sampling temporary monitoring wells, purge a smaller volume to reduce sample turbidity, generate effluent for measurement of field parameters in a flow cell if used, and to remove water that has leaked into the sampling point through probe rod or auger flight joints during installation.

Purging equipment includes bailers or pumps. Bailers are only acceptable for purging and sampling permanent wells where the water level in the well is 30 feet or less from grade, or in extremely slow recharging wells. In temporary wells where the well casing diameter is less than two inches and the water level is beyond the reach of a peristaltic pump (25 feet), attempt sampling with tubing and a check valve or, as a last resort, with a mini bailer. Pumps (except gas lift pumps) can be used to purge and sample any permanent or temporary well, but are necessary in permanent wells where the water level is greater than 30 feet below grade. Allowable pump types include:

- Submersible low flow, electric centrifugal pumps (e.g., Grundfos ® Redi-Flo2, etc)
- Peristaltic suction lift pumps (maximum working depths are 20-25 feet)
- Submersible, positive displacement bladder pumps
- Conventional submersible, electric centrifugal pumps (only if permanently installed in the well)
- Tubing and check valve
- Piston pumps

Do not allow water that has entered the pump to re-enter the well during purging or sampling. This can occur if using a pump without a check valve or in wells with slow recharge rates when the well is pumped dry and is allowed to recover prior to sampling.

Wells with extremely slow recharge rates may require other purge methods. If normal purging is clearly impractical, evacuate the well to near dryness and allow partial recovery twice. Following the second well evacuation, sample the well when sufficient recovery has occurred. Clearly note the conditions and procedures actually used on the sampling form as well as the amount water purged in well volumes.

Purging should remove all the stagnant water in the well so it is replaced by fresh groundwater from outside the borehole. Purge wells that do not have extremely slow recharge rates by withdrawing water from the top two feet of the water column. Repeated vertical adjustment of the purging equipment intake may be necessary if the water level drops. Set the pump rate at the lowest practical rate to avoid excessive drawdown and turbidity in the well. Measure the field parameters immediately after or during well purging.

4.3 Equipment decontamination

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. 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. Bailers must be laboratory cleaned or disposable. Decontaminate

equipment between each sampling point. After cleaning, inspect for residues or other substances that may survive normal cleaning. If inspection reveals that decontamination was insufficient, implement additional measures as needed and document. Decontaminate equipment in the following manner:

- A. Clean inside and out with a laboratory-grade detergent (Liquinox or equivalent)/clean-water solution, applied with a scrub brush where practical.
- B. Rinse with tap water followed by a final rinse with distilled or deionized water.
- C. Inspect for remaining particles or surface film, and repeat cleaning and rinse procedures if necessary.
- D. Sampling equipment that contacts free product or heavily contaminated areas requires use of a desorbing agent (dilute solution of water and isopropanol or methanol) followed by a thorough tap water rinse and a final distilled or deionized water rinse.

Clean the internal surfaces of pumps and tubing by circulating decontamination fluids through them. Ensure that a sufficient quantity of rinse water is circulated to flush out contaminants completely, detergents, and desorbing agents if used. When transporting or storing decontaminated equipment, protect it in a manner that minimizes the potential for contamination.

4.4 Unpurged groundwater sampling

Several studies indicate that in most situations unpurged groundwater sampling (samples collected without prior purging of the well) produce data adequate for PRP needs. The PRP allows unpurged groundwater sampling when all the following conditions are true:

- Wells are screened across the water table in unconsolidated and unconfined aquifers.
- Wells are screened in reasonably permeable formations (transmissivity $\geq 50 \text{ ft}^2/\text{day}$).
- Wells are redeveloped yearly to ensure a good hydraulic connection to the aquifer (the method assumes adequate cross flow of water through the saturated interval of screen).
- Contaminants monitored are limited to petroleum volatile organic compounds (PVOCs) and/or GRO.
- LNAPL is not present.

Contact the MPCA if you have questions about the need for unpurged groundwater sampling at your site.

5.0 Field parameters

Field parameter measurement is required. The recommended method is to measure specific conductance, temperature, pH, dissolved oxygen, and redox potential in the field utilizing a flow cell just prior to sampling or individual field tests immediately thereafter. Record calibration information and all measurements on the sampling form. Equipment calibration and maintenance logs must be maintained for the equipment used during sampling events. The MPCA reserves the right to request these records.

5.1 Specific conductance

Soak the conductivity cell in distilled or deionized water for at least one hour before use and calibrate each day. While making field measurements, record the true electrical conductivity (EC). Specific conductance (EC corrected to 25 degrees Celsius) is calculated from the EC and the water temperature. Record both the EC and specific conductance (SC) measurements on the sampling form.

5.2 Temperature

Inspect the temperature probe to ensure it is in good operating condition. Record groundwater temperature to the nearest 0.1 degrees Celsius.

5.3 pH

Measure pH using a direct reading probe following the instrument's instruction manual. Keep the electrode tip moist.

Before sampling each day, calibrate the pH meter by following at least a two-point calibration method and verify with a third buffer. The reading should be within 0.1 unit for the pH of the third buffer. If the meter can hold the slope well over time, routine calibration later in the day can be conducted with only one buffer. At a minimum, verify the pH meter calibration every two hours by a single-point calibration at pH 7, for natural waters, before taking measurements. Report pH readings to the nearest 0.1 unit.

After calibrating, allow the pH probe to equilibrate with fresh aquifer water for a minimum of five minutes before the first pH measurement.

5.4 Dissolved oxygen

The recommended method for measuring dissolved oxygen is using a membrane electrode probe in a flow cell or a luminescence-based sensor. Modified Winkler and Colorimetric ampoule methods can also be used under proper field conditions. When measuring dissolved oxygen, take care to avoid turbulence and sample aeration.

When using a membrane electrode probe, follow the instrument's instruction manual. Calibrate before taking measurements at each new sampling point or every two hours. Replace the membrane every two to four weeks.

Follow the instrument's instruction manual when using a luminescence-based sensor. Calibrate every eight hours. Replace the probe cap every 365 days or more often if the cap becomes damaged or fouled.

Only stable meter readings are considered valid. If non-stable readings are observed, note and record the non-stable measurements on the sampling form and in the monitoring report. Report dissolved oxygen readings to the nearest 0.1 mg/L.

5.5 Redox potential

Measure redox potential in the field using a direct reading probe (preferably using a flow cell). Take care to avoid turbulence and sample aeration.

6.0 Sample collection

Use only laboratory supplied sampling containers and preservative for groundwater samples. Following the addition of chemical preservative (if used), observe sample containers for a reaction between the sample and the chemical preservative. If a reaction is observed, collect unpreserved samples in new containers and note on the chain-of-custody form.

6.1 Sampling wells using a bailer

Bailers are only acceptable for purging and sampling wells where the static water level in the well is 30 feet or less from grade, or in extremely slow recharging wells. Record the type of bailer used to sample each well on the sampling form. Use bailers in the following manner:

- Use only new, disposable, certified-clean high-density polyethylene or polytetrafluoroethylene bailers or laboratory-cleaned stainless steel bailers for sampling. Reusable PVC bailers can be used for purging only.
- Use a new retrieval line for each sampling point.
- Do not allow the bailer or line to touch the ground, a dirty ground cloth, or any other potentially contaminated surface.
- Do not allow the bailer to free fall into the water column. The bailer should enter the water column as gently as possible. A knot in the line referencing the groundwater level is useful.

- Try not to submerge the bailer much below the top to prevent mixing and to ensure water removal from the top of the water column.
- Withdraw the bailer gently from the water column and bring it to the surface quickly.
- Keep the check valve on the bottom clear of sediment and in proper working order to minimize the amount of water that drips back into the well.
- If the same bailer is not used for purging and sampling, discard the first two sample bailer volumes as rinse water.
- Transfer the sample from the bailer to the sample container quickly while minimizing turbulence and exposure to the atmosphere. The MPCA recommends the use of a bottom-emptying device.

6.2 Sampling wells using a pump

Pumps can be used to sample any well with sufficient recovery. If recovery is so slow that a satisfactory water column height (for normal pump operation) is not reached in a reasonable amount of time, a bailer can be used for sample collection. Record the type of pump used to sample each well on the sampling form. Use pumps in the following manner:

- Adjust the flow rate to the lowest practical setting, and maintain a continuous pumping rate. Slow recharging wells or wells with a small water column height may require cycling of the pump. Pumping should be continuous and sampling conducted immediately following purging. The pump must be equipped with a check valve or operate to prevent water in the discharge line from flowing back into the well.
- Completely purge any final rinse water remaining in the sampling pump or discharge line by pumping at least two tubing volumes through the pump before sample collection begins.
- Peristaltic pumps can be used for sampling; however, water that has moved through the pumping mechanism cannot be used for VOC/GRO samples. The following procedure is the only acceptable use of peristaltic pumps for VOC/GRO samples: run the pump until the suction line is filled with clean water, shut the pump off and remove the suction line from the well, reverse the flow direction of the pump discharging water from the suction line into the sample vial. Samples other than VOC/GRO can be collected from the discharge line.
- Water that has entered the pump should not be allowed to re-enter the well during purging or sampling.

6.3 Filling sample containers

Do not open sample bottles until they are ready to be filled. Follow these procedures:

- Keep the area surrounding the wellhead as clean as practical to minimize the potential for contamination of samples.
- Minimize the potential for airborne contamination during sample collection. If vehicles or generators are running during sample collection, fill containers upwind from engine exhaust sources. If conditions are dusty, shield the sample collection area from wind-borne contamination.
- Use a clean pair of gloves at each new sampling point.

When sampling with a pump, hold the discharge tube as close as possible to the sample container without allowing the sample tubing to contact the container. For VOCs, fill 40-mL purge-and-trap vials in a manner that minimizes turbulence, air entrapment, and overfilling. Fill the bottle completely leaving a positive meniscus at the top of the vial. After capping, invert the vial and tap with a finger to check for air bubbles. If bubbles are present, discard the vial and fill a replacement. If the sample water effervesces (produces bubbles) when added to an HCl-preserved vial, unpreserved samples should be collected and the lack of preservation must be noted on the chain-of-custody form. Analysis of unpreserved samples must be within a seven-day holding time.

Collect multiple bottles to guard against loss by breakage and to allow for laboratory quality assurance.

6.4 Trip blanks, equipment blanks, duplicate samples, and field blanks

Collect sample blanks to detect background or method contamination and duplicate samples to evaluate variability in analytical methods. Collect duplicate samples at wells suspected to have moderate or high levels of contamination and in the same type of container as the corresponding primary samples. Assign duplicate samples identification aliases on the sample bottle label and on the chain-of-custody form to avoid alerting laboratories that the sample is a duplicate. Record the true identity of the samples on the sampling form.

A. When sampling temporary wells and during each permanent well sampling event, collect QA/QC samples as follows:

- One trip blank for each cooler of VOCs, petroleum VOCs (PVOCs), low-level 1,2-dibromoethane (EDB), and GRO.
- One temperature blank for each cooler of samples, except for lead or Resource Conservation and Recovery Act (RCRA) metals if they are shipped in their own cooler.
- One equipment blank each day, by each field sampling crew, if re-useable sampling equipment is used.
- At least one duplicate set per sampling event per analysis. If more than 10 wells are being sampled, it is required that one duplicate be taken per every 10 samples.
- Two additional volumes of a sample are required for DRO water analysis. The laboratory will use these for spike and spike duplicate samples. The rate of spike and spike duplicates is one per 10 samples.

Parameters required are:

- Trip blank (only for volatile organic analyses to include VOCs, PVOCs, low-level EDB, and GRO)
- Equipment blank, reusable equipment only (VOCs, PVOCs, GRO/DRO)
- Duplicates (all project parameters)

See the table in Section 9 for further information.

- B. **Trip blank samples:** Trip blanks for VOCs, PVOCs, low-level EDB, and GRO are filled and sealed by the analytical laboratory with organic-free water. Trip blanks consist of a set(s) of pre-filled 40-mL purge-and-trap vials and are to accompany each cooler containing VOC, PVOC, low-level EDB, or GRO samples. These sample vials travel with the actual sample vials to and from the field in the cooler, to the well head, etc., so the blanks are exposed to the same conditions as the actual samples. Fresh VOC vials and a trip blank should be obtained from the laboratory for each sampling event. The vials are not opened until analyzed in the laboratory along with the actual VOC, PVOC, low-level EDB, or GRO samples they have accompanied. Note: more than one set of trip blanks may be needed depending on the specific combination of analyses.
- C. **Equipment blank samples:** Equipment blanks are used to determine the adequacy of the decontamination procedures applied to reusable sampling equipment. Equipment blanks should be collected using the same lot of sample containers, the same sampling equipment, and the same sampling methods that are used to collect the other samples. Deionized blank water should contact all of the interfaces that the sample water will contact. These may include the sampling mechanism, ambient air, sample container and, when applicable, pumps, tubing and filtration membranes.

Place pumps and tubing that have been decontaminated or decontaminated pumps and new tubing from the same lot as used in the well sampling into a short mock up section of well casing (assuming there is not a permanent sampling pump installation), fill with clean water, and fill sample vials for the equipment blank. When using bailers, collect the equipment blank by pouring clean water into the freshly decontaminated bailer and then filling the sample vials.

- D. **Duplicate samples:** Collect duplicate samples by sequentially filling all containers as close together in time as practical. Collect at least one field duplicate sample per sampling event per analysis.
- E. **Field blank samples:** Field blanks are used to evaluate possible cross-contamination of samples from the field (ambient) conditions that are present at the sampling location. Deionized water is poured into the appropriate sample vials and shipped to the laboratory with the other samples. Field blanks are not required at every site and are typically collected when cross-contamination from field (ambient) conditions is suspected.

6.5 Sampling submerged water table wells

Detection of both free and dissolved phase products requires proper placement of monitoring well screens. Water table monitoring well screens, including temporary wells, must intersect the water table. However, there are sites where there are significant fluctuations in the water table, or where low permeability soils make it difficult to properly place the well screen. In these situations, follow the guidance below.

- Do not collect analytical samples from permanent water table wells where the screen top is submerged more than two feet below the water table, as measured from the top of the well screen, not the sand pack.
- If a permanent water table well screen is submerged less than two feet, try to lower the water table during well purging. If well purging lowers the water level to intersect the well screen, sample the well as before. Samples collected in this manner are sufficient for routine monitoring, but may not be considered valid for site closure requirements.
- If a permanent water table well screen is submerged for more than three sampling quarters, a new well may be necessary.
- Unpurged sampling of submerged screens is not allowed (see Section 4.4).

Note: These sampling requirements do not apply to monitoring wells deliberately screened below the water table to detect vertical contaminant migration.

6.6 Water supply well sampling

The goal of water supply well sampling is to collect a representative sample of the groundwater supplying a well. To ensure a representative sample, careful evaluation of the water supply system is necessary, including the well, water line, water treatment units (e.g., water softeners, filters, etc.), and other appurtenances (e.g., water heaters, pressure tanks, etc.). The evaluation includes identifying a sampling location and determining how much water to purge prior to sampling. In addition, sample collection procedures must minimize sample disturbance and potential cross contamination. Follow the protocols listed below when sampling a water supply well and document site-specific procedures on the sampling form.

1. Identify potential sampling points located prior to water treatment and other appurtenances and select the one located closest to the well. This will often be at or near the pressure tank. The sampling point and any appurtenances between the sampling point and well should be identified on sampling forms. If water samples have to be collected after the pressure tank, it should be noted whether the tank is a captive air (i.e., bladder) tank or a conventional (i.e., non-bladder) tank.
2. Follow the steps below to determine the purge water volume:
 - Step 1. Calculate the volume of standing water in the water line and any appurtenances between the well and the sampling point.
 - Step 2. Determine the volume of well water to purge based on the available well information using one of the three options listed below in order of preference.
 - a. If a Minnesota Department of Health well record or reliable well construction information is available, calculate three well casing water column volumes. Add this volume to the volume from Step 1 and purge the total volume before sampling.

- b. If well construction is unknown, measure field parameters (pH, temperature, and specific conductance) during purging until readings are stable after purging the volume calculated in Step 1.
- c. If well construction is unknown and a meter to measure field parameters is not available, purge the well for a minimum of 10 minutes at full discharge rate after purging the volume calculated in Step 1.

The preferred sampling point is often located in a basement or utility area. If a drain is present, it may be possible to purge directly from the sampling point. If a drain is not available near the sampling point, purge the water system from another location with a drain (e.g., kitchen sink, bathroom sink, and bathtub) or outside tap. Carefully monitor the discharge point during purging to avoid flooding or water damage. Record the volume of water purged on the sampling form.

3. Open the sampling point tap and collect the sample immediately after purging. The water flow rate during sampling should be the minimum required to maintain a continuous flow while minimizing aeration. Observe the following precautions while filling sample containers:
 - Remove the aerator from the tap, if present.
 - Do not sample through a garden hose or any other attachments or filters on the tap.
 - Do not allow sampling containers to contact the tap during filling.
 - If sampling from a tap with hot and cold water, purge and fill containers with only cold water.

6.7 Sampling for water line permeation assessment

The purpose of the sampling is to obtain a worst-case sample from the section of water line that passes through the contaminated area of concern. Use the following sampling protocol at petroleum release sites where water line permeation is a potential exposure pathway.

For water supply systems served by an on-site well:

1. Water samples should be collected after the water has sat in the supply line for at least 8 hours.
2. Identify potential sampling points located prior to water treatment units (e.g., water softeners, filters, etc.) and other appurtenances (e.g., water heaters, pressure tanks, etc.). After identifying potential sampling points, select the one that is located closest to the potentially impacted section of water line.
3. Calculate the volume of water standing in the supply system between the sampling point and the potentially impacted water line section. This calculation should include the water in the lines and any appurtenances (if samples cannot be collected prior to the appurtenances). Note: if water samples have to be collected after the pressure tank, it should be noted whether the tank is a captive air (i.e., bladder) tank or a conventional (i.e., non-bladder) tank.
4. Open the sampling tap and collect the water samples immediately after the volume of water determined in Step #3 has been purged from the system.

For water supply systems served by a municipal or community water supply system:

1. Identify potential sampling points located as close as possible down gradient to the potentially impacted section of water line (note: potentially impacted sections of water lines can include both water mains and individual service laterals). If possible, sampling points should be located prior to water treatment units (e.g., water filters, dechlorinators, etc.) and other appurtenances (e.g., water heaters, etc.).
2. Ideally, collect water samples after water has sat in the water line for at least 8 hours. In some scenarios, this may not be possible (e.g., water mains, high usage service laterals, etc.). In those instances, collect water samples during low flow times if it is feasible to do so.

3. Calculate the volume of water standing in the supply system between the sampling point and the potentially impacted section of water line. This calculation should include the water in the lines and any appurtenances (if samples cannot be collected prior to the appurtenances).
4. Open the sampling tap and collect the water samples immediately after the volume of water determined in Step #3 has been purged from the system.

7.0 Documentation of sampling event

Record all data and document procedures used on a sampling form. Consultants and responsible parties are free to develop their own forms as long as they are specifically designed for documentation of field activities and collection of field data. The sampling form provides a means to verify whether correct procedures were followed during a number of key steps in the groundwater sampling event. The sampling form should include at a minimum: sampling point ID, sampling personnel, field conditions, type of well, well depth, water level, calculation of purge volume, purging method, sampling order, field parameters, and other relevant observations (e.g., odor, color, sheen). Submit a copy of the sampling form in the appendices section of the [Investigation report](#) or [Monitoring report](#).

7.1 Chain of custody

Initiate a chain-of-custody form in the field at the time of sampling and include a copy in the monitoring report.

7.2 Exceptions to sampling procedures

Note any exceptions to routine groundwater sampling procedures on the sampling form and in the monitoring report. Also, include the following details in the monitoring report:

- The reason for the exception.
- The identification of all samples and individual parameters that may have been impacted either in terms of the quantitative or legal integrity of their reported values.
- The significance of the potential impacts to the integrity of each sample.
- Footnote any potentially significant impact on sample integrity when reporting or referring to the results.

7.3 Field conditions

Record field conditions during the sampling event on the sampling form. Include a statement in the monitoring report regarding the likelihood that any unusual field conditions had a significant impact on the sampling results. Report the following field conditions:

- Air temperature
- Wind speed
- Precipitation/moisture
- Ambient odors
- Airborne dust

8.0 Sample preservation handling, and transport

Preserve all samples in the field immediately after sample collection by placing the samples in an insulated cooler containing ice. Ensure enough samples are collected to allow for possible breakage and quality assurance needs. Assure that paper work and sample labels are not damaged by water. Include a container of water for the temperature blank and record the temperature just before transporting samples and upon receipt at the laboratory to verify that samples were kept refrigerated. Samples that are hand delivered directly to the laboratory on the day they were collected may not meet the 4 ± 2 degrees Celsius temperature specification. In this situation it must be demonstrated that samples are in the process of cooling as evidenced by the temperature blanks being at 4 ± 2 degrees Celsius.

9.0 Analytical parameters and laboratory methods

This table specifies analytical parameters for groundwater samples at PRP sites. For all sample analyses, unless otherwise noted, use an EPA-approved method or equivalent.

Petroleum product	Parameters
Leaded gasoline, aviation gasoline	A/B, C, E, I
Unleaded gasoline, ethanol-blended fuel (see Note 1)	A/B, C
Unused petroleum products: fuel oil, motor oil, diesel fuel, kerosene, jet fuels	A, D, H
Used oil: used motor oil, other used oils (see Notes 2 and 3)	A, D, F, G, H
Unknown petroleum or hydrocarbons mixture	A, C, D, F, G, H, I
Other petroleum products	Site Specific
Hydraulic fluids	A, D, G, H

Note: Drinking water supply samples must be analyzed for VOCs every event.

- A. Volatile organic compounds (VOCs) by the most recent version of EPA Method 8260 (see Note 4). The VOC target analyte list is found in Appendix A. For some chemicals, the drinking water standard is lower than the required Method 8260 report level (RL) listed in Appendix A. EPA Method 524 may be required for drinking water supply samples to achieve lower RLs (see Note 5).
- B. Petroleum VOCs (PVOCs) by the most recent version of EPA Method 8260 or Method 8021 (see Note 4). PVOC analysis QA/QC procedures are found in Section 10. The PVOC target analyte list is found in Appendix B.
- C. Wisconsin Department of Natural Resources Modified Gasoline Range Organics GRO Method (see Notes 6 and 8)
- D. Wisconsin Department of Natural Resources Modified Diesel Range Organics DRO Method (see Notes 7, 8, and 9)
- E. Lead, total (Only at point of use for groundwater. Contact the MPCA when dealing with surface water.)
- F. Resource Conservation and Recovery Act (RCRA) metals - arsenic, barium, cadmium, chromium, lead, mercury, selenium, and silver (see Note 3)
- G. Polychlorinated biphenyls (PCBs) using the most recent version of EPA Method 8082 by the Aroclor method. See Appendix C for specific Aroclors. Analysis for PCBs should be completed for hydraulic fluids used in elevators and other hydraulic fluids subject to high heat prior to the 1980s.
- H. Polycyclic aromatic hydrocarbons (PAHs) by the most recent version of EPA Method 8270. PAH analysis QA/QC procedures are found in Section 10. The PAH target analyte list is found in Appendix D.
Note that the MPCA will determine the need for PAH analysis. Contact the MPCA if a drinking water aquifer is impacted by fuel oil or heavy petroleum.
- I. Low-level analysis for 1,2-dibromoethane (EDB) and 1,2-dibromo-3-chloropropane (DBCP) by EPA Method 8011. EDB/DBCP analysis QA/QC procedures are found in Section 10. The EDB/DBCP target analyte list is found in Appendix E. Standard operating procedures outlining laboratory QA/QC limits should be provided to the MPCA for review prior to completing this analysis.

Note that the MPCA will determine the need for low-level EDB/DBCP analysis. Contact the MPCA to discuss the need for this analysis if a drinking water aquifer is impacted by leaded gasoline or an unknown petroleum mixture.

Notes:

1. For ethanol-blended fuel releases, see [Investigation requirements for ethanol-blended fuel releases](#) for additional sampling requirements.
2. Do not confuse used oil with waste oil. Used oil means any oil that (because of use) has become contaminated by physical or chemical impurities. Examples of used oil include, but are not limited to,

motor oils, quench oils, metal cutting oils and hydraulic fluids. Waste oil means virgin oil that is discarded or spilled before use.

3. During investigation at used oil sites, collect samples for all of the parameters listed (VOCs, DRO, RCRA metals, and PCBs), but direct your laboratory to analyze only the VOC and DRO samples initially. If any of these compounds are detected, proceed with analysis of the RCRA metals and PCB samples. RCRA metals analysis for water samples should be a total analysis. Subsequent analysis for the dissolved metals may be required. All samples must be extracted and analyzed within holding times.
4. VOC analysis by the most recent version of EPA Method 8260 is required for all temporary monitoring well samples and during the first two sampling events at permanent monitoring wells. If VOCs other than PVOCs are present, the MPCA may require continued sampling for VOCs. Note that if EDB or 1,2-dichloroethane (DCA) are present, continued VOC sampling is required (see Figure 1). However, if the contaminants present did not originate from a petroleum tank release, the costs for continued VOC sampling may not be reimbursable through Petrofund. When gas chromatography/mass spectrometry (GC/MS) is not completed based on the instructions stated above, or holding times are not met, additional sampling will be necessary for confirmation purposes. In permanent monitoring wells, if only petroleum hydrocarbons are present (with the exception of EDB or DCA) reduce the analyte list to PVOCs beginning with the third sampling event. The laboratory procedure should be purge-and-trap GC or GC/MS. Store all samples at 4 ± 2 degrees Celsius and deliver them to the laboratory within 4 days from collection. Sample analysis occurs within 14 days of the collection date if preserved, otherwise analyzed within 7 days. The RLs for all parameters should be equal to or better than the program-required RLs listed in Appendices A and B, with quality control procedures specified in the most recent version of EPA Method 8260.
5. Drinking water supply samples may be analyzed using EPA Method 8260; however, the RLs may not be low enough to quantify certain chemicals at or below their health-based standard. Analyze drinking water samples using the most recent version of EPA Method 524 if lower RLs are needed. If residual chlorine may be present in the sample, preserve the samples with ascorbic acid instead of hydrochloric acid.
6. This is a purge-and-trap, GC procedure that uses a ten-component blend of gasoline compounds for the quantification standard. The samples must be cooled to 4 ± 2 degrees Celsius, received by the laboratory within 4 days from collection, and analyzed within 14 days of the collection date. The method detection limit shall be no more than 100 µg/L for water.
7. This is a solvent extraction, direct injection, GC procedure that uses a ten-component blend of typical diesel oil components for the quantification standard. Collect water samples in 1-liter amber bottles. The samples must be kept at 4 ± 2 degrees Celsius, extracted by the laboratory within 7 days from collection, and analyzed within 47 days of the collection date. The reporting limit shall be no more than 100 µg/L for water.
8. Separate samples are required for GRO and DRO analyses.
9. The DRO analysis method can have false positives that lead to elevated results that are not from petroleum compounds. The DRO analysis method is a very useful screening method, but may not provide an accurate determination of petroleum compounds for making site decisions. When false positives are suspected, cleanup of extracts to remove non-petroleum compounds may be necessary. See Section 10 for laboratory QA/QC procedures for DRO cleanup.
10. Samples transported incorrectly or analyzed beyond the required holding times are considered invalid.

10.0 Required laboratory quality assurance/quality control

- A. PVOC analysis:** Samples should be analyzed for the target analytes listed in Appendix B using the most recent version of EPA Method 8260 or Method 8021. All quality control (QC) elements defined in the method must be followed. Laboratories should also incorporate the QC procedures listed below.
- 1. Initial calibration:** The initial calibration curve must contain at least five calibration points. For Methods 8260 and 8021, the r^2 for each curve must be greater than or equal to 0.990, or the r for each curve must be greater than or equal to 0.995. If the ratio of response to concentration is constant (<15% relative standard deviation for Method 8260 and <20% relative standard deviation for Method 8021), linearity can be assumed and the average response factor can be used in place of a calibration curve. The recovery (accuracy) for each point in the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and re-analyzed.
 - 2. Continuing calibration verification:** Analyze one low-level standard at the RL and one mid-level calibration verification standard prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12-hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for the target analytes in the low-level standard should be between 60% and 140% of the true value. The %R for the target analytes in the mid-level standards should be between 70% and 130% of the true value (with a %D of less than or equal to 30%).
 - 3. Initial demonstration of capability:** Analyze 4-7 replicate mid-level check standards. Percent recovery (%R) must be equal to 70-130%. The percent relative standard deviation (%RSD) must be less than 20%.
 - 4. Method detection limit/report level:** Method detection limits (MDLs) and report levels (RLs) are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven standards. The RL should be approximately three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met.
 - 5. Batch quality control:** A batch is defined as up to 20 environmental samples analyzed in a 12-hour sequence. At a minimum, each batch must contain a method blank, a laboratory control sample (LCS), and a MS/MSD pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a laboratory control sample duplicate (LCSD) is prepared and analyzed.
 - 6. Method blanks:** Analyze one method blank per QC batch of 20 samples or less. The concentration of PVOCs in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be re-extracted and re-analyzed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.
 - 7. Accuracy/precision:** One LCS is required per batch. The %R must be between 70% and 130%. One MS and MSD is required per batch. The %R for each analyte in the MS/MSD must be between 70% and 130% with a relative percent difference (RPD) of less than or equal to 30%.
 - 8. Holding time:** The samples must be analyzed within 14 days of sample collection.

9. **Confirmation analysis:** For Method 8021, confirmation analysis using a dissimilar detector or a column of different polarity must be performed, or by GC/MS analysis. The agreement between the quantitative results is evaluated by calculating the RPD between the two results. The formula is:

$$RPD = (ABS(R1 - R2)/((R1 + R2)*2))*100$$

The RPD should be $\leq 40\%$. If one result is significantly higher, check the chromatograms to see if an obviously overlapping peak is causing the high result. If no overlapping peaks are noted, examine the baseline to determine if there were any data system problems during peak integration.

If no anomalies are noted, report the higher result and add a flag that alerts the data user of the disparity between the results on the two detectors or columns.

- B. **PAH analysis:** Samples should be analyzed for these target analytes in Appendix D using the most recent version of EPA Method 8270. 1-Methylnaphthalene and 2-methylnaphthalene are included in the list of PAH target analytes for the PRP. All QC elements defined in the method must be followed. Laboratories should also incorporate the QC procedures listed below.

1. **Initial calibration:** The initial calibration curve should contain at least five calibration points. The r^2 for each curve must be greater than or equal to 0.995. If the ratio of response to concentration is constant ($<20\%$ relative standard deviation), linearity can be assumed and the average response factor can be used in place of a calibration curve. The recovery (accuracy) for each point in the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and re-analyzed.
2. **Continuing calibration verification:** Analyze one low-level standard at the report level (RL) and one mid-level calibration verification standard prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12-hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for the target analytes in the low-level standard should be between 60% and 140% of the true value. The %R for the target analytes in the mid-level standards should be between 80% and 120% of the true value (with a %D of less than or equal to 20%).
3. **Initial demonstration of capability:** Analyze 4-7 replicate mid-level check standards. Percent recovery (%R) must be equal to 70-130%. The percent relative standard deviation (%RSD) must be less than 20%.
4. **Method detection limit/report level:** MDLs and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven standards. The RL should be approximately three to five times the MDL. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met.
5. **Batch quality control:** A batch is defined as up to 20 environmental samples extracted in the same 24-hour period. At a minimum, each batch must contain a method blank, a LCS, and a MS/MSD pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a LCSD is prepared and analyzed.
6. **Method blanks:** Analyze one method blank per QC batch of 20 samples or less. The concentration of PAHs in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be re-extracted and re-analyzed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above 10 times the blank contamination will not need to be qualified.

7. **Accuracy/precision:** One LCS is required per batch. The laboratory should generate in-house limits for accuracy. The % recoveries should be between 50% and 150%. One MS and MSD is required per batch. The laboratory should generate in-house limits for accuracy and precision. The % recoveries for each analyte in the MS/MSD should be between 50% and 150% with a RPD of less than or equal to 30%.
 8. **Surrogates:** Surrogates are added to all environmental and QC samples. The laboratory should generate in-house limits for surrogate recoveries. The % recoveries should be between 50% and 150%.
 9. **Holding time:** The samples should be extracted within 7 days of collection and analyzed within 40 days of extraction.
- C. DRO cleanup:** Groundwater extracts may be cleaned up prior to DRO analysis using three methods, either separately or in combination. The methods include: 1) EPA Method 3630C, silica gel cleanup, 2) EPA Method 3650B, acid/base partitioning, and 3) EPA Method 3611B, alumina column cleanup. When DRO cleanup is requested, pre-cleanup analysis should be completed prior to conducting the cleanup. If there are no detections in the pre-cleanup analysis, the laboratory should not conduct the cleanup and post-cleanup analysis.
- DRO clean-up results will be accepted only if quality assurance documentation shows results that meet acceptance criteria, i.e. no significant loss of petroleum compounds. The quality control acceptance criteria for the clean-up results will be as follows:
1. At least one method blank, one laboratory duplicate, one matrix spike, and one laboratory control sample must be run through the complete clean-up and analysis process for up to 20 samples (1/20).
 2. The laboratory must provide a narrative of the entire clean up and analysis process. They must also provide pre- and post-cleanup results and compare the pre-cleanup chromatogram with that of the post-cleanup chromatogram for every sample when cleanup is completed.
 3. The relative percent difference (RPD) between sample duplicates, matrix spike pairs, or laboratory control sample pairs must be less than or equal to 20%. However, if the concentration of the target analyte in the sample/sample duplicate is less than five times the report level, the difference between duplicates is used to measure precision. The difference must then be less than or equal to the RL.
- D. 1,2-Dibromoethane (EDB) and 1,2-Dibromo-3-chloropropane (DBCP) in groundwater:** Water samples should be analyzed for these target analytes using the most recent version of EPA Method 8011. All QC elements defined in the method must be followed. Laboratories should also incorporate the quality control procedures listed below.
1. **Initial calibration:** The initial calibration curve must contain at least five calibration points. The r^2 for each curve must be greater than or equal to 0.990, or the r for each curve must be greater than or equal to 0.995. If the ratio of response to concentration is constant (<20% relative standard deviation), linearity can be assumed and the average response factor can be used in place of a calibration curve. The recovery (accuracy) for each point in the curve must be 70% to 130% except for the lowest point in the curve, which must be 60% to 140%. The lowest calibration point in the curves shall be at or below the analyte report level. If a sample concentration exceeds the highest calibration standard from the initial calibration, the sample must be diluted into the calibration range and re-analyzed.
 2. **Continuing calibration verification:** Analyze one low-level standard at the RL and one mid-level calibration verification standard prior to the samples. Bracket the batch of samples with a second mid-level calibration verification standard (in each 12-hour period, up to 20 environmental samples can be analyzed between standards). The percent recovery (%R) for the target analytes in the low-level standard should be between 60% and 140% of the true value. The %R for the target analytes in the mid-level standards should be between 70% and 130% of the true value (with a %D of less than or equal to 30%).

3. **Initial demonstration of capability:** Analyze 4-7 replicate mid-level check standards. Percent recovery (%R) must be equal to 70-130%. The percent relative standard deviation (%RSD) must be less than 20%.
4. **Method detection limit/report level:** Method detection limits (MDLs) and RLs are determined annually or after a major change to the instrument conditions. The MDLs are determined per the procedure defined in 40 CFR 136, Appendix B. Analyze a minimum of seven standards. The RL should be approximately three to five times the MDL. Report results to the MDL and flag estimated concentrations. The lowest calibration point in the curves shall be at or below the analyte report level. If the accuracy of the RL standard does not meet the 60% to 140% criteria, a new RL standard is chosen and analyzed until the accuracy criteria are met.
5. **Batch quality control:** A batch is defined as up to 20 environmental samples extracted in the same 24-hour period. At a minimum, each batch must contain a method blank, a LCS, and a MS/MSD pair. If there is not enough sample to prepare and analyze a MS/MSD pair, a LCSD is prepared and analyzed.
6. **Method blanks:** Analyze one method blank per QC batch of 20 samples or less. The concentration of EDB or DBCP in the method blank must be less than the associated report level. If the method blank is contaminated, measures must be taken to eliminate the problem. Affected samples must then be re-extracted and re-analyzed. If the contamination cannot be eliminated, the results must be qualified to indicate the problem. All concentration levels for the affected target analyte that are less than ten times the concentration in the blank should be qualified with a "B" to indicate that the sample results may contain a bias related to the blank contamination. Concentrations of the affected analyte that are above ten times the blank contamination will not need to be qualified.
7. **Accuracy/precision:** One LCS is required per batch. The %R must be between 70% and 130%. One M) and MSD is required per batch. The %R for each analyte in the MS/MSD must be between 65% and 135% with a RPD of less than or equal to 30%.
8. **Holding time:** The samples should be extracted and analyzed within 14 days of sample collection.
9. **Confirmation analysis:** Confirmation analysis using a column of different polarity must be performed.

Appendix A: Target analyte list for volatile organic compounds

Chemical name	CAS #	Report level (µg/L)
1,1,1,2-Tetrachloroethane	630-20-6	1.0
1,1,1-Trichloroethane	71-55-6	1.0
1,1,2,2-Tetrachloroethane	79-34-5	1.0
1,1,2-Trichloroethane	79-00-5	1.0
1,1,2-Trichlorotrifluoroethane	76-13-1	1.0
1,1-Dichloroethane	75-34-3	1.0
1,1-Dichloroethene	75-35-4	1.0
1,1-Dichloropropene	563-58-6	1.0
1,2,3-Trichlorobenzene	87-61-6	1.0
1,2,3-Trichloropropane	96-18-4	1.0
1,2,4-Trichlorobenzene	120-82-1	1.0
1,2,4-Trimethylbenzene	95-63-6	1.0
1,2-Dibromo-3-chloropropane	96-12-8	5.0
1,2-Dibromoethane	106-93-4	1.0
1,2-Dichlorobenzene	95-50-1	1.0
1,2-Dichloroethane	107-06-2	1.0
1,2-Dichloropropane	78-87-5	1.0
1,3,5-Trimethylbenzene	108-67-8	1.0
1,3-Dichlorobenzene	541-73-1	1.0
1,3-Dichloropropane	142-28-9	1.0
1,4-Dichlorobenzene	106-46-7	1.0
2,2-Dichloropropane	594-20-7	1.0
2-Chlorotoluene	95-49-8	1.0
4-Chlorotoluene	106-43-4	1.0
Acetone	67-64-1	20
Allyl chloride	107-05-1	1.0
Benzene	71-43-2	1.0
Bromobenzene	108-86-1	1.0
Bromochloromethane	74-97-5	1.0
Bromodichloromethane	75-27-4	1.0
Bromoform	75-25-2	1.0
Bromomethane	74-83-9	2.0
n-Butylbenzene	104-51-8	1.0
sec-Butylbenzene	135-98-8	1.0

Chemical name	CAS #	Report level (µg/L)
tert-Butylbenzene	98-06-6	1.0
Carbon tetrachloride	56-23-5	1.0
Chlorobenzene	108-90-7	1.0
Chlorodibromomethane	124-48-1	1.0
Chloroethane	75-00-3	1.0
Chloroform	67-66-3	1.0
Chloromethane	74-87-3	1.0
cis-1,2-Dichloroethene	156-59-2	1.0
cis-1,3-Dichloropropene	10061-01-5	1.0
Dibromomethane	74-95-3	1.0
Dichlorodifluoromethane	75-71-8	1.0
Dichlorofluoromethane	75-43-4	1.0
Ethylbenzene	100-41-4	1.0
Ethyl ether	60-29-7	1.0
Hexachlorobutadiene	87-68-3	1.0
Isopropylbenzene	98-82-8	1.0
p-Isopropyltoluene	99-87-6	1.0
Methyl ethyl ketone (2-butanone)	78-93-3	10
Methyl isobutyl ketone (4-methyl-2-pentanone)	108-10-1	5.0
Methyl <i>tertiary</i> -butyl ether	1634-04-4	2.0
Methylene chloride	75-09-2	2.0
Naphthalene	91-20-3	1.0
n-Propylbenzene	103-65-1	1.0
Styrene	100-42-5	1.0
Tetrachloroethene	127-18-4	1.0
Tetrahydrofuran	109-99-9	10
Toluene	108-88-3	1.0
trans-1,2-Dichloroethene	156-60-5	1.0
trans-1,3-Dichloropropene	10061-02-6	1.0
Trichloroethene	79-01-6	1.0
Trichlorofluoromethane	75-69-4	1.0
Vinyl chloride	75-01-4	1.0
m&p-Xylene	179601-23-1	1.0
o-Xylene	95-47-6	1.0

Appendix B: Target analyte list for petroleum volatile organic compounds

Chemical name	CAS #	Report level (µg/L)
1,2,4-Trimethylbenzene	95-63-6	1.0
1,3,5-Trimethylbenzene	108-67-8	1.0
Benzene	71-43-2	1.0
Ethylbenzene	100-41-4	1.0
Methyl <i>tertiary</i> -butyl ether	1634-04-4	2.0
Naphthalene	91-20-3	1.0
Toluene	108-88-3	1.0
m&p-Xylene	179601-23-1	1.0
o-Xylene	95-47-6	1.0

Appendix C: Target analyte list for polychlorinated biphenyls

Chemical name	CAS #	Report level (µg/L)
Aroclor 1016	12674-11-2	0.25
Aroclor 1221	11104-28-2	0.50
Aroclor 1232	11141-16-5	0.25
Aroclor 1242	53469-21-9	0.25
Aroclor 1248	12672-29-6	0.25
Aroclor 1254	11097-69-1	0.25
Aroclor 1260	11096-82-5	0.25

Appendix D: Target analyte list for polycyclic aromatic hydrocarbons

Chemical name	CAS #	Report level (µg/L)
Acenaphthene	83-32-9	5
Acenaphthylene	208-96-8	5
Anthracene	120-12-7	5
Benzo(a)anthracene	56-55-3	5
Benzo(b)fluoranthene	205-99-2	5
Benzo(k)fluoranthene	207-08-9	5
Benzo(g,h,i)perylene	191-24-2	5
Benzo(a)pyrene	50-32-8	5
Chrysene	218-01-9	5
Dibenz(a,h)anthracene	53-70-3	5
Fluoranthene	206-44-0	5
Fluorene	86-73-7	5
Indeno(1,2,3-cd)pyrene	193-39-5	5
2-Methylnaphthalene	91-57-6	5
Naphthalene	91-20-3	5
Phenanthrene	85-01-8	5
Pyrene	129-00-0	5
1-Methylnaphthalene	90-12-0	5

Appendix E: Target analyte list for 1,2-dibromoethane and 1,2-dibromo-3-chloropropane

Chemical name	CAS #	Report level (µg/L)
1,2-Dibromo-3-chloropropane	96-12-8	0.05
1,2-Dibromoethane	106-93-4	0.05

Figure 1. Monitoring well VOC sampling requirements.

