

# 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, and 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 them 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 field work. Give the PRP at least 48 hours' notice prior to conducting field work at sites under program oversight by submitting a field work notification via the [MPCA Online services portal](#). **Prior notification of field work is mandatory** and will be verified upon submittal of the results.

To assure data quality, the U.S. Environmental Protection Agency (EPA) requires the MPCA to maintain a [Quality Assurance Program Plan \(QAPP\)](#) for the PRP. The QAPP defines 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 Science and data 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. Use an EPA-approved method or equivalent for all sample analyses, unless otherwise noted in this document. Provide chromatograms for positive gasoline range organics (GRO) and diesel range organics (DRO) analyses. Properly scale these chromatograms 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; do not set 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 may 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.

Immediately notify the Minnesota duty officer of all new LNAPL discoveries. For additional instruction, 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 the quantity of water purged on the sampling form. Prior to sampling temporary monitoring wells, purge a smaller volume to reduce sample turbidity, to 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 permanent wells when other equipment is not available or has failed. The sampling of groundwater using bailers is not recommended, and should only be done in special circumstances and with approval from the MPCA. See Section 6.2 for more details about the use of bailers. Pumps, except gas lift pumps and inertial pumps/tubing and check valve, can be used to purge and sample any permanent or temporary well and are the preferred method for groundwater sampling. Field crews should install wells with a diameter no less than 2 inches to allow for the use of a sampling pump. Allowable pump types include:

- Submersible low flow, electric centrifugal pumps, such as Grundfos® Redi-Flo2, etc
- Peristaltic suction lift pumps, with a maximum working depth of 20-25 feet
- Submersible, positive displacement bladder pumps
- Conventional submersible, electric centrifugal pumps, but only if permanently installed in the well
- Piston pumps

**Do not attempt to sample groundwater with an inertial pump/tubing and check valve method.** The “check valve” method is known to produce poor quality groundwater samples due to removal of volatiles from the water column through agitation.

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 used on the sampling form as well as the amount of 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:

- Clean inside and out with a laboratory-grade detergent (Liquinox or equivalent)/clean-water solution, applied with a scrub brush where practical.
- Rinse with tap water followed by a final rinse with distilled or deionized water.
- Inspect for remaining particles or surface film, and repeat cleaning and rinse procedures if necessary.
- 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 completely flush out contaminants, 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) produces 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, with a transmissivity of  $\geq 50 \text{ ft}^2/\text{day}$ .
- 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 (PVOs) 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 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 pump

**Pumps are the preferred sampling method.** 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 must not 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.
- Do not allow water that has entered the pump to re-enter the well during purging or sampling.

## 6.2 Sampling wells using a bailer

**Using bailers as a groundwater sampling method is discouraged.**

However, bailers may be used during special circumstances with MPCA approval. Special circumstances include but are not limited to:

- Equipment/pump breakdown during sampling.
- A petroleum sheen is observed on water (LNAPL).
- Slow recovery wells

A well is considered to be fast-recovering if it recovers to 80 percent or more of its static conditions within 2 hours.

A well is considered to be slow-recovering if it takes longer than 2 hours to recover to 80 percent of its static water level.

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.

## 6.3 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, collect unpreserved samples and note the lack of preservation on the chain-of-custody form. Analyze unpreserved samples 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.

Analysis parameters required for each type of QA/QC sample 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 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 ambient field 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 the ambient field 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, carefully evaluate the water supply system, including the well, water line, water treatment units, such as water softeners or filters, and other appurtenances, such as water heaters or pressure tanks. Identify a sampling location and determine how much water to purge prior to sampling. 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.

- Identify potential sampling points located ahead of water treatment and other appurtenances and select the one located closest to the well. This will often be at or near the pressure tank. Identify the sampling point and any appurtenances between the sampling point and well on sampling forms. If water samples must be collected after the pressure tank, denote whether the tank is a captive air (i.e., bladder) tank or a conventional (i.e., non-bladder) tank.
- 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:

- 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.
- 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.
- 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, such as 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.

- 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:**

- Collect water samples after the water has sat in the supply line for at least 8 hours.
- Identify potential sampling points located prior to water treatment units, such as water softeners or filters, and other appurtenances, such as water heaters or pressure tanks. After identifying potential sampling points, select the one that is located closest to the potentially impacted section of water line.
- 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, denote whether the tank is a captive air (i.e., bladder) tank or a conventional (i.e., non-bladder) tank.
- 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:**

- 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 ahead of water treatment units, such as water filters or dechlorinators, and other appurtenances, such as water heaters.
- Ideally, collect water samples after water has sat in the water line for at least 8 hours. In some scenarios, such as water mains or high usage service laterals, this may not be possible. In those instances, collect water samples during low flow times if it is feasible to do so.

- 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.
- 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 may develop their own forms providing 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 several key steps in the groundwater sampling event. The sampling form must 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, such as odor, color, and sheen. Attach a copy of the sampling form(s) in the appendices 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. Take measures to prevent water damage to paper work and sample labels. 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  $4 \pm 2$  degrees Celsius temperature specification. In

this situation it must be demonstrated that samples are in the in the process of cooling as evidenced by the temperature blanks being at  $4 \pm 2$  degrees Celsius.

## 9.0 Analytical parameters and laboratory methods

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

Petroleum product	Parameter
Leaded 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 3 and 4)	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 5). The VOC target analyte list is found in Appendix A. EPA Method 8260 SIM may be required for groundwater sample results to achieve lower RLs. 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 6).
- B. Petroleum VOCs (PVOCs) by the most recent version of EPA Method 8260 or Method 8021 (see Note 5). 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 7 and 9)
- D. Wisconsin Department of Natural Resources Modified Diesel Range Organics DRO method (see Notes 8, 9, and 10)
- 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 4)
- 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.
  - a. Note: 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 (see Note 2).
  - a. Note: 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. For leaded fuel release sites, see [Investigation requirements for fuel releases containing lead scavengers](#).
3. 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.
4. During investigation at used oil sites, collect samples for all 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. Extract and analyze all samples within holding times.
5. 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). If lower RLs are needed for sites with DCA or EDB, EPA Method 8260 SIM can be used. 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  $4 \pm 2$  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.
6. 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.
7. 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  $4 \pm 2$  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.
8. 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  $4 \pm 2$  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.
9. Separate samples are required for GRO and DRO analyses.
10. The DRO analysis method can have false positives that lead to elevated results caused by interference of naturally occurring non-petroleum matter, such as plant detritus and peat in the form of polar organic compounds. However, some petroleum products and petroleum degradation byproducts are also known to have significant levels of polar organic 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. One of the most widely used DRO cleanup methods is the DRO silica gel cleanup method (SGC).

SGC works by attaching to and eliminating polar organics, which are typically associated with natural organic matter. However, some precautions should be taken when using the SGC method in groundwater investigations, as groundwater does not contain notable levels of naturally occurring organic matter; therefore the SGC method may remove petroleum products from that sample. The following steps should be followed if and when the DRO SGC method is used at a site investigation:

- Groundwater samples must always be split; one analyzed for DRO with SGC, and one without SGC. Analytical results must be paired in this way to provide meaningful data.
- Collect groundwater samples from upgradient wells and/or areas where contamination is known to not be present, to document background DRO levels.
- Include chromatograms for both pre- and post-cleanup samples. See Section 10 for laboratory QA/QC procedures for DRO cleanup.
- Samples transported incorrectly or analyzed beyond the required holding times are considered invalid.

## 10.0 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, as well as the QC procedures listed below.
- **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.
  - **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%.
  - **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%.
  - **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.
  - **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.

- **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.
- **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%.
- **Holding time:** The samples must be analyzed within 14 days of sample collection.
- **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:

$$RPD = \frac{ABS(R_1 - R_2)}{(R_1 + R_2) * 2} * 100$$

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 the 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, as well as the QC procedures listed below.

- **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.
- **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%.
- **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%.
- **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.

- **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.
- **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.
- **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%.
- **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%.
- **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:

- 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).
- 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.
- 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:** Analyze water samples for these target analytes using the most recent version of EPA Method 8011. All QC elements defined in the method must be followed. Laboratories must also incorporate the quality control procedures listed below.

- **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.

- **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%.
- **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%.
- **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.
- **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.
- **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.
- **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 65% and 135% with a RPD of less than or equal to 30%.
- **Holding time:** The samples should be extracted and analyzed within 14 days of sample collection.
- **Confirmation analysis:** Confirmation analysis using a column of different polarity must be performed.



## Appendix A: Target analyte 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
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

<b>Chemical name</b>	<b>CAS #</b>	<b>Report level (µg/L)</b>
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 tertiary-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

Chemical name	CAS #	Report level (µg/L)
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.

