Minnesota Pollution Control Agency

# Ground Water Sample Collection and Analysis Procedures

**Guidance Document 4-05**

Petroleum Remediation Program

## 1.0 Introduction

This guidance document describes the procedures for collecting ground water samples at leaking petroleum storage tank sites and applies to temporary and permanent monitoring wells. Unforeseen circumstances during sampling may necessitate modifying these procedures. When Minnesota Pollution Control Agency (MPCA) staff approval cannot be obtained in advance, contact the MPCA as soon as possible to evaluate needs for re-sampling. 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 specific sampling procedures; if sampling a monitoring well for multiple programs, follow the most restrictive procedure.

The MPCA Petroleum Remediation Program (PRP) conducts random on-site audits of field work. The PRP must be given at least 48 hours notice prior to conducting field work at sites under program oversight. Information on the field work notification process can be found at http://www.pca.state.mn.us/programs/prp-fieldwork.html. This prior notification of field work is mandatory and will be verified upon submittal of the results.

To assure data quality, the United States Environmental Protection Agency (EPA) has required MPCA to develop a Quality Assurance Program Plan (QAPP) for the PRP. The objective of the QAPP is to define the Quality Assurance and 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. The PRP QAPP can be found at http://www.pca.state.mn.us/publications/p-eao2-04.pdf.

## 2.0 Analytical Parameters and Methods

Analytical parameters and methods required to fulfill PRP ground water sampling requirements are outlined in Section 9 and Appendices A to C. **The MPCA requires (see http://www.pca.state.mn.us/programs/qa_p.html) Minnesota Department of Health (MDH) certification of fixed based and mobile laboratories reporting data to MPCA programs. Laboratories reporting data will be required to include the MDH certification number on analytical reports.**

Laboratories must report all quality assurance as required by the method used (e.g., spike and surrogate recoveries, duplicate relative percent differences, and blanks). If a non-certified mobile laboratory is used for screening, split ten percent of the samples with a certified fixed base laboratory. Data supporting site closure must be generated by a Minnesota certified laboratory. In appendices and tables, clearly label data generated by mobile laboratories and fixed base laboratories. Laboratories will submit chromatograms in support of Gasoline Range Organics/Diesel Range Organics (GRO/DRO) analyses indicating contamination is present. For all sample analyses, unless otherwise noted in this document, use an EPA-approved method or equivalent.

## 3.0 Field Procedures

Exercise care to avoid cross contamination of ground water 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.



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### 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 ground water, 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 Free product measurements

If free product is suspected or if strong petroleum odors are present in a well, attempt to measure free product 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 free product are not normally sampled. Notify the MPCA immediately of all new free product discoveries (see Guidance Document 2-02 *Free Product: Evaluation and Recovery*).

## 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 ground water 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 comes in contact with 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 ground water sampling

Several studies indicate that in most situations unpurged ground water sampling (samples collected **without** prior purging of the well) produce data adequate for PRP needs. The Minnesota Petroleum Remediation Program allows unpurged ground water sampling when all the following are true:

- Wells are screened across the water table in unconsolidated and unconfined aquifers.
- Wells are screened in reasonably permeable formations ($T \geq 50$ $ft^2$/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 BTEX, MTBE, and/or GRO.
- Non-aqueous phase liquids (NAPL) are not present.

Contact the MPCA project hydrologist if you have questions about the need for unpurged ground water sampling at your site.

## 5.0 Field Parameters

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. MPCA staff reserve 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 ground water 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. If the meter can hold the slope well over time, routine calibration later in the day can be conducted with only one buffer. The single buffer calibration should normally be conducted using a pH = 7 buffer for natural waters. At a minimum, verify the pH meter calibration every 2 hours by a single-point calibration 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. 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.

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 ground water 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, polytetrafluoroethylene 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 ground water 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. 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 so as 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 which has moved through the pumping mechanism cannot be used for Volatile Organic Compounds (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-milliliter (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 in the sampling form.

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

- One trip blank and one temperature blank for each cooler of VOC, BTEX/MTBE, GRO, or DRO samples
- 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. If more than ten wells are being sampled, it is required that one duplicate be taken per every ten 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 ten samples.

Parameters required are:

- trip blank (only for volatile organic analyses to include VOCs, BTEX/MTBE, and GRO)
- equipment blank, reusable equipment only (VOCs, BTEX/MTBE, GRO/DRO)
- duplicates (all project parameters)

These parameters are required for analyses performed for a site. See the table in Section 9 for further information.

**B. Trip blank samples:** Trip blanks for VOCs and BTEX/MTBE are filled and sealed by the analytical laboratory with organic-free water. Trip blanks consist of a set of pre-filled 40-ml purge-and-trap vials and are to accompany each cooler containing VOC or BTEX/MTBE 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 or BTEX/MTBE samples they have accompanied.

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 for each sampling event

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 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.**

## 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 ground water 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 Form* 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 ground water 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

Thermally 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.

## 9.0 Analytical Parameters and Laboratory Methods

This table specifies analytical parameters for ground water samples at petroleum release sites in the PRP. For all sample analysis, unless otherwise noted, use an EPA-approved method or equivalent.

| Petroleum Product | Parameters |
|---|---|
| Regular Gasoline, Aviation Gasoline | A, (B), C, E |
| Unleaded Gasoline | A, (B), C |
| Unused Petroleum Products: Fuel Oil, Motor Oil, Diesel Fuel, Kerosene, Jet Fuels, Mineral Oil/Spirits, Crude Oil, Stoddard Solvents | A, D, H** |
| Used Oil: Used Motor Oil, Other Used Oils (see Notes 1 & 2) | A, D, F, G*, H** |
| Unknown Petroleum or Hydrocarbons Mixture | A, C, D, F, G*, H** |
| Other Petroleum Products | Site Specific |
| Hydraulic Fluids | A, D, G*, H** |

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

**A.** VOCs listed in Appendix A by the most recent MDH-certified version of EPA method 8260 (see Note 3)

**B.** BTEX/MTBE (see Note 3)

**C.** Wisconsin Department of Natural Resources Modified GRO Method (see Notes 4 and 6)

**D.** Wisconsin DNR Modified DRO Method (see Notes 5 and 6)

**E.** Lead, Total (Only at point of use for ground water. Contact the MPCA project manager when dealing with surface water.)

**F.** RCRA Metals - Arsenic, Barium, Cadmium, Chromium, Lead, Mercury, Selenium, and Silver (see Note 2)

**G.** Polychlorinated Biphenyls (PCBs) using the most recent MDH-certified version of EPA method 8082 by the Arochlor method. See Appendix B for specific Arochlors.

*Analyses for PCBs should be completed for hydraulic fluids used in elevators and other hydraulic fluids subject to high heat prior to the 1980s.

**H.** Polyaromatic Hydrocarbons (PAHs) by the most recent MDH-certified version of EPA method 8270 or 8270 SIM, modified to include the list of target analytes in Appendix C. The table used to calculate BaP equivalents is found in on the Drinking Water Criteria spreadsheet at http://www.pca.state.mn.us/publications/risk-drinkingwatercriteria.xls on the MPCA Web site. The existing Health Based Values for ground water BaP equivalents are listed on this Web page.

**Note that the MPCA Project Manager (PM) will determine the need for PAH analysis. Contact the PM if a drinking water aquifer is impacted by fuel oil or heavy petroleum.

**Notes:**

1. Do not confuse used oil with waste oil. **Used oil** means any oil that (as a result 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 before use.

2. During investigation at used oil sites, collect samples for **all** of the parameters listed (VOCs, DRO, RCRA metals, 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 components may be required. All samples must be extracted and analyzed within holding times.

3. VOC analysis by the most recent MDH-certified version of EPA method 8260 is required for all drinking water supply samples, all temporary monitoring well samples, and during the first two sampling events at permanent monitoring wells. If VOCs other than BTEX/MTBE are present, MPCA staff may require continued sampling for VOCs (however, if the contaminants present did not originate from a release from a permanent petroleum storage tank, 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 BTEX/MTBE are present, then reduce the analyte list to BTEX/MTBE beginning with the third sampling event. The laboratory procedure should be purge-and-trap GC. Store all samples at approximately 4 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 reporting limits (RLs) for all parameters should be equal to or better than the program-required RLs listed in Appendix A, with quality control procedures specified in the most recent MDH-certified version of EPA method 8260.

4. This is a purge-and-trap, GC procedure that utilizes a ten-component blend of gasoline compounds for the quantification standard. The samples must be kept at about 4 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 0.1 ppm for water.

5. This is a solvent extraction, direct injection, GC procedure that utilizes a ten-component blend of typical diesel oil components for the quantification standard. Collect water samples in one- (1) liter amber bottles. The samples must be kept at about 4 degrees Celsius, received by the laboratory within 4 days from collection, and analyzed within 47 days of the collection date. The reporting limit shall be no more than 0.1 ppm for water.

6. Separate samples are required for GRO and DRO analyses.

7. Samples transported incorrectly or analyzed beyond the required holding times are considered invalid.

## Appendix A: Target analyte list for volatile organic compounds (VOCs)

| Chemical Name | CAS # | Report Level (ug/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 |

| Chemical Name | CAS # | Report Level (ug/L) |
|---|---|---|
| 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 *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 polychlorinated biphenyls (PCBs)

| Chemical Name | CAS # | Report Level (ug/L) |
|---|---|---|
| Arochlor 1016 | 12674-11-2 | 0.25 |
| Arochlor 1221 | 11104-28-2 | 0.50 |
| Arochlor 1232 | 11141-16-5 | 0.25 |
| Arochlor 1242 | 53469-21-9 | 0.25 |
| Arochlor 1248 | 12672-29-6 | 0.25 |
| Arochlors 1254 | 11097-69-1 | 0.25 |
| Arochlor 1260 | 11096-82-5 | 0.25 |

## Appendix C: Target analyte list for polycyclic aromatic hydrocarbons (PAHs)

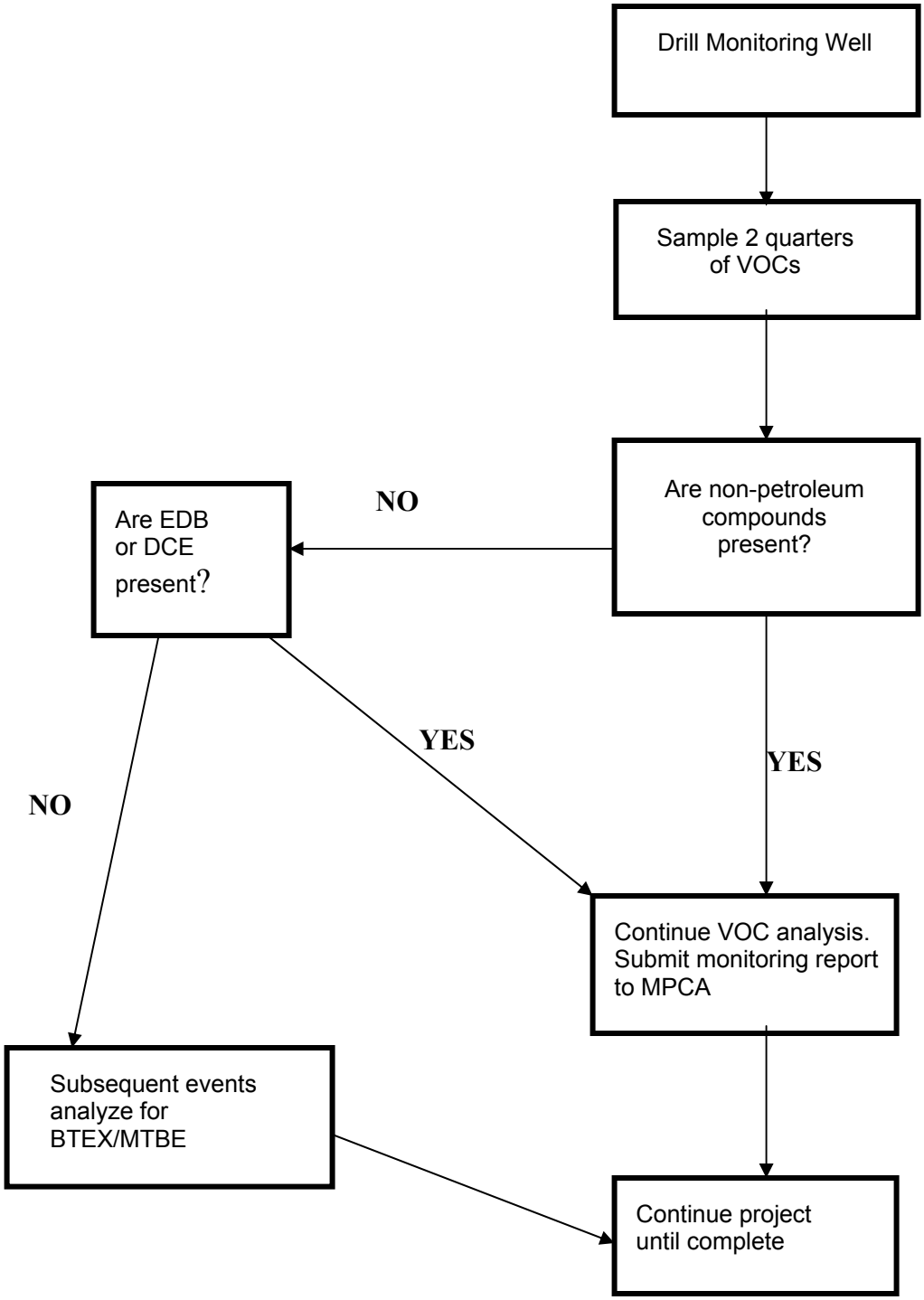
| Chemical Name | CAS # | Report Level (ng/L) |
|---|---|---|
| Acenaphthene | 83-32-9 | 10 |
| Acenaphthylene | 208-96-8 | 10 |
| Anthracene | 120-12-7 | 10 |
| Benzo(a)anthracene | 56-55-3 | 10 |
| Benzo(b)fluoranthene | 205-99-2 | 10 |
| Benzo(j)fluoranthene | 205-82-3 | 10 |
| Benzo(k)fluoranthene | 207-08-9 | 10 |
| Benzo(g,h,i)perylene | 191-24-2 | 10 |
| Benzo(a)pyrene | 50-32-8 | 10 |
| Chrysene | 218-01-9 | 10 |
| Dibenz(a,h)acridine | 226-36-8 | 10 |
| Dibenz(a,j)acridine | 224-42-0 | 10 |
| Dibenz(a,h)anthracene | 53-70-3 | 10 |
| 7H-Dibenzo(c,g)carbazole | 194-59-2 | 10 |
| Dibenzo(a,e)pyrene | 192-65-4 | 50 |
| Dibenzo(a,h)pyrene | 189-64-0 | 50 |
| Dibenzo(a,i)pyrene | 189-55-9 | 50 |
| Dibenzo(a,l)pyrene | 191-30-0 | 50 |
| 7,12-Dimethylbenz(a)anthreacene | 57-97-6 | 10 |
| 1,6-Dinitropyrene | 42397-64-8 | 1000 |
| 1,8-Dinitropyrene | 42397-65-9 | 1000 |
| Fluoranthene | 206-44-0 | 10 |
| Fluorene | 86-73-7 | 10 |

## Appendix C: Target analyte list for PAHs, *Continued*

| Chemical Name | CAS # | Report Level (ng/L) |
|---|---|---|
| Indeno(1,2,3-cd)pyrene | 193-39-5 | 10 |
| 3-Methylcholanthrene | 56-49-5 | 10 |
| 5-Methylchrysene | 3351-31-3 | 10 |
| 2-Methylnaphthalene | 91-57-6 | 50 |
| Naphthalene | 91-20-3 | 50 |
| 5-Nitroacenaphthene | 602-87-9 | 100 |
| 6-Nitrochrysene | 2/8/7496 | 200 |
| 2-Nitrofluorene | 607-57-8 | 100 |
| 1-Nitropyrene | 5522-43-0 | 100 |
| 4-Nitropyrene | 57835-92-4 | 100 |
| Phenanthrene | 85-01-8 | 10 |
| Pyrene | 129-00-0 | 10 |
| Quinoline | 91-22-5 | 10 |

## Web pages and phone numbers:

| | |
|---|---|
| MPCA staff: | http://data.pca.state.mn.us/pca/emplsearch.html |
| MPCA toll free: | **1-800-657-3864** |
| Petroleum Remediation Program Web page: | http://www.pca.state.mn.us/programs/lust_p.html |
| MPCA Info. Request: | http://www.pca.state.mn.us/about/inforequest.html |
| Petrofund Web page: | http://www.state.mn.us/cgi-bin/portal/mn/jsp/content.do?id=-536881377&agency=Commerce |
| Petrofund phone: | **651-215-1775 or 1-800-638-0418** |
| **State Duty Officer:** | **651-649-5451 or 1-800-638-0418** |


Drill Monitoring Well
Sample 2 quarters of VOCs
Are non-petroleum compounds present?
NO
Are EDB or DCE present?
YES
YES
NO
Continue VOC analysis. Submit monitoring report to MPCA
Subsequent events analyze for BTEX/MTBE
Continue project until complete